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Plasma Immersion Ion Implantation on Polymers

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COMMON ABBREVIATIONS

PIII: Plasma immersion ion implantation

PIIID: Plasma immersion ion implantation and deposition

FCVA: Filtered Cathodic Vacuum Arc

UHMWPE: Ultra-high Molecular Weight Polyethylene

PTFE: Polytetrafluoroethylene

PET: Polyethylene terephthalate

XPS: X-ray photoelectron spectroscopy

XRD: X-ray diffraction

SEM: Scanning Electron Microscopy

CAFM: Conductive Atomic Force Microscopy

Abstract

The focus of this thesis is to achieve plasma based surface modification of polymers. Highly ionized carbon plasma was generated from a filtered cathodic arc source in a vacuum chamber. The use of a highly negative pulse voltage applied on the substrate holder formed a plasma sheath around the substrate holder during the on-pulse. Ions were accelerated in the plasma sheath towards the polymer, thus creating the process: plasma immersion ion implantation (PIII). In this process, ions were implanted up to a depth of about 50 nm and with pulse voltages of between 3 kV and 12 kV. Ion-solids interactions provided both physical and chemical modifications to the modified layer.

Carbon plasma immersion ion implantation was carried out on *ultra-high molecular weight polyethylene* (UHMWPE), a polymer that is commonly used in biomedical total joint replacements. Characterization of the carbon ion modified UHMWPE was carried out using Raman spectroscopy and X-ray photoelectron spectroscopy to study the modification of their chemical properties. From the results, there was formation of mainly C-C bonds in the modified layer. Mechanical characterization of their wear rates and nano-hardness showed improvements over virgin UHMWPE. Scanning electron microscopy images were taken at relatively low voltages of 6 kV to show the roughening and significant damage to the surfaces at higher pulse voltages.

In the next section, nickel plasma immersion ion implantation was used to modify the electrical properties of *polyethylene terephthalate* (PET). PET is a common and flexible polymer that has been used in several electronic applications. The electrical

resistivity of Ni ion modified PET dropped by about $10^9 \Omega/sq$. Using conductive atomic force microscopy, topography and current images were obtained simultaneously at low temperatures. From the current images, it was found that Ni ion modified PET with higher electrical conductivity resulted in the formation of well-defined conducting regions.

Formation of thermal spikes during ion implantation of polymers was proposed and discussed as a mechanism for the formation of Ni nanoparticles. Heat diffusion equation was used to simulate the quenching of the thermal spike into its surrounding polymer. The quenching time was found to be significant.

Chapter 1:

Introduction

In this chapter, a background in the surface modification of polymers is first presented to gain a thorough understanding in the technology of surface modification of polymers. Several important aspects will be covered: the commercial advantages of using polymers, the wide range of polymers being used today by the electronic and biomedical industries, the ideal surface properties required in different applications, the processing techniques and the challenges involved.

The background shows that there are inevitably a vast number of possibilities in the surface modification of polymers. The scope of the PhD project has to be limited by processing technique, types of polymers and applications of interest. The motivation and objectives of this project were then identified and presented in this chapter.

The organization of this thesis is summarized in the last section to provide an overview of the seven chapters.

1.1 Background

In today's age of consumerism, plastics, fibers, rubber, nylons and acrylic are common items that have been taken for granted because of their relatively low-cost. All these items fall under the scientific term "polymer" and it is often their trade names; Mylar, Kapton or Teflon that precedes their lengthy scientific names such as polyethylene terephthalate, polyimide or polytetrafluoroethylene respectively. They offer many advantages over other common materials such as metal alloys, semiconductors and ceramics. They are light-weight and can be easily fabricated into different shapes [1-3]. Their applications include milk bottles (polyethylene); artificial hearts (polyurethane); automobile tyres (rubber) and electrical insulators (polyvinylchloride). Besides their bulk properties, researchers have become more interested in their surface properties and their surface interactions with other materials. Their surface properties are considered essential in mechanical, electronics and biomedical applications as they often affects device reliability [3-7]. Thus, modifying the surface properties of polymers to produce desirable surface properties is identified as an intense research interest in the field of polymer engineering.

Ion implantation is seen as an effective surface modification technique, which uses energetic ions to alter the outermost surfaces of polymers without affecting their bulk properties [8-11] and enhance their surface properties for various applications. Recently, plasma immersion ion implantation (PIII) has been implemented to treat three-dimensional and complex shapes to enable conformal modification of the materials. When combined with condensable plasma, deposition occurs and the process becomes plasma immersion ion implantation and deposition (PIIID). For both

types of processes, the surface properties such as wear resistance [4, 12], nano-hardness [4, 12, 13] and bio-compatibility were reported to show good improvements.

1.2 Motivation

There is a wide range of polymers to select from and two polymers are chosen for surface modification because of their usage in their respective fields. The first is *ultra-high molecular weight polyethylene* (UHMWPE), which is used in biomedical total joint implants [14, 15] as a suitable material for the socket (Figure 1.1). However, this material is not recommended for long-term applications due to the large amount of wear debris generated during the articulation of orthopaedic devices and this is found to be the most common cause of the failure [1, 2, 8]. Hence, better mechanical properties are desirable.

Figure 1.1 A total joint replacement implant with UHMWPE as socket

The second type of polymer chosen is *polyethylene terephthalate* (PET). As PET is a choice material used in recyclable plastic bottles, it is familiar to most people. Other lesser known usage of this material is in artificial heart valve sewing rings [16] and flexible circuit boards [17]. Plasma based modification of PET has seen several improvements of its surfaces such as good gas-barrier properties [18] and better blood compatibility [19].

For both types of polymers, plasma immersion ion implantation and deposition (PIIID) is utilized to modify their surface properties. PIIID has been seen as an effective surface modification technique, which uses energetic ions to alter the outermost surfaces of polymers without affecting their bulk properties [8-11]. PIIID is also capable of treating three-dimensional and complex shapes. Surface properties of polymers such as wear resistance [4, 12], nano-hardness [4, 12, 13], and adhesion to metal films [8, 20, 21] were reported to show positive improvements. In recent years, this technique was also applied to tailor the surface properties of biomedical devices and biomaterials to improve biocompatibility [3, 22, 23], reduce bacteria adhesion [24] and even prevent complications in short term devices [25].

Despite the possible applications for PIIID, it has remained challenging to researchers in working with polymers. Besides their relatively complex chemistry, most polymers are also good insulators and have low melting temperatures. These factors prove to be limiting during application of high pulse voltages and conventional characterization techniques. To overcome these challenges, there is a need to understand the interaction of ions with polymers.

Plasma immersion ion implantation using varying types of ions have shown to produce different surface modifications in polymers. In this project, two types of ions were investigated.

(a) Carbon plasma immersion ion implantation

Carbon ion modification was chosen due to its potential in modifying the surface properties to a large extent without introducing a new element in the polymers which is made up mostly of C, O and H. It is expected to have good bio-compatibility as DLC films on polymers have shown to have good cell adhesion and bio-compatibility [1, 3, 22, 26]. Furthermore, investigations over the years have shown that improvements in wear resistance by ion-implanted polymer are largely due to the cross-linking layer formed during ion implantation [7, 27, 28]. The use of highly ionized carbon plasma during ion implantation may promote the formation of a cross-linking layer and this has been investigated with UHMWPE. The experimental results are shown in Chapter 4.

(b) Nickel plasma immersion ion implantation

Metal plasma ion implantation have been shown to have their niche of applications [29-34] such as in depositing thin metal films with good adhesion on polymers. Metal ions are able to lower the resistivity of polymers further for use in electronic applications when compared to non-metallic ions [35]. Metal ions are significantly different in terms of their mass as compared with gaseous or carbon ions and this

physical property results in ion-polymer interactions in a smaller confined volume (shallow implantation depth). Another process that may occur with metal ions is the agglomeration of implants as metal is insoluble in the polymer matrix and is less likely to bond with the free radicals caused by ion bombardment. The presence of implants at sufficiently high doses also contributes to electrical conductivity due to hopping mechanism between precipitates of the implanted species [36]. Metal plasma immersion ion implantation (nickel) and experiments have been done to study some of these surface modification effects on polymers. These results are presented in Chapter 5.

1.3 Objectives

1. To use a combined technique of filtered cathodic vacuum arc (FCVA) with substrate pulse biasing (by a high voltage pulser) to modify the surfaces of polymers.
2. To study related issues on the technique, PIIID on polymers.
3. To investigate effects of carbon and nickel PIIID on surface modification of polymers and the characterization of ion modified polymers.

1.4 Major Contributions

- (i) The surface modification of UHMWPE and PET using PIIID at different pulse voltages and implantation time and their modified properties have been studied systematically using various characterization methods.

(ii) Topography and current imaging of Ni implanted PET was performed simultaneously using CAFM. Using the CAFM at low temperatures was necessary as the inherent property of the polymer is soft. The successful current images of Ni implanted PET revealed a well-defined granular structure which exhibits higher conductivity than surrounding regions.

(iii) An analysis was done by comparing the current profiles of Ni ion modified PET, a C ion modified PET and a Ni film deposited on PET sample. The results showed that Ni ion modified PET have better defined conducting regions.

(iv) CAFM measurements at low temperatures provided current values at a fixed bias voltage. From these values, the conducting mechanisms of ion modified polymers of different electrical resistivities were differentiated.

(v) Theoretical estimation of the thermal spike and its quenching time in the ion implantation of PET were provided. The thermal spike concept was introduced to explain the thermal contribution by ion implantation to the surface modification of polymers on a micro-scale level. In addition, a thermal induced diffusion mechanism was proposed to explain the formation of conducting well defined structures as shown in CAFM images.

1.5 Organization of Thesis

Chapter 1 provides the background in the area of surface modification of polymers and then introduces the motivation and objectives of this thesis. It is then followed by the major contributions by the author.

Chapter 1 Introduction

Chapter 2 first discusses the theoretical aspect of this thesis that includes the irradiation effects of ion implantation on polymers and ion-polymer interactions. Thermal contribution to the surface of polymer during ion bombardment is understood through the formation of thermal spikes. The chapter is followed by an overview of the two main modification equipment used to achieve PIIID on polymers: the cathodic vacuum arc deposition and high voltage pulser. The PIIID experimental parameters and challenges of using PIIID technique in the modification of polymers will be discussed.

Chapter 3 outlines the use of various characterization techniques for determining the chemical and physical changes to the modified surfaces of polymers before and after ion implantation.

Chapter 4 discusses the experimental details and data analysis of carbon ion implantation into *ultra-high molecular weight polyethylene* (UHMWPE), a polymer used in the application of orthopedic applications.

Chapter 5 discusses the experimental details and data analysis of nickel ion implantation into *polyethylene terephthalate* (PET), a polymer used in many applications including flexible electronic circuits.

Chapter 6 discusses the experiments and data obtained from the use of conductive atomic force microscope (CAFM) measurements at low temperatures and the conducting mechanism concluded from the CAFM measurements. Formation of

Chapter 1 Introduction

thermal spikes during ion implantation in polymers is proposed as a mechanism for the formation of nanoparticles. The quenching time of a thermal spike is estimated by the liquid quench technique.

Chapter 7 provides the conclusion of the thesis and recommendations for future work.

Chapter 2:

Theory and Experimental Techniques

In Chapter 2, a background of plasma immersion ion implantation and its surface modification characteristics are presented. This section covers ion-polymer interactions, irradiation effects of ion implantation on polymer surfaces and the surface composition of PIII modified insulators. Some theories which are used to explain experimental results are explained here. They are thermal spikes in ion implantation of polymers and the electronic transport mechanism of ion implanted polymers. Ion-polymer interactions are explained with the aid of the TRIM software.

The focus is on the PIIID technology and there are several theoretical and experimental parameters discussed. The choice of the experimental parameters is explained. The problem of charging effects by applying a high substrate bias by PIIID on polymers are explained and are, to some extent, overcome by use of the conducting grid.

The filtered cathodic vacuum arc source is introduced. Carbon and nickel cathodes have been used in the surface modification process and the different shielding requirements of the two cathodes are discussed.

2.1 Modification of polymers by PIIID

In this project, the surface modifications of polymers by PIIID were carried out using carbon and nickel plasma with negative pulse voltages of between 3 kV and 12 kV applied at the substrate. There are three main modifications that arise from this process in polymers that are discussed. The ways in which the polymers' surfaces are modified are:

- (a) Formation of a modified layer;
- (b) Formation of chemical bonds between ion and polymer;
- (c) Sputtering which may leads to erosion at high dose;

PIIID modification of polymers results in surface modification differently from ion implantation because of the formation of a modified layer, rather than a buried layer with Gaussian depth profile. The surface composition of this modified layer is further discussed in Section 2.2. With the use of condensable plasma in PIIID, there are greater ion-polymer interactions occurring at the surfaces which lead to formation of chemical bonds between ions and polymers. Ion-polymer interactions are discussed in greater details in Section 2.3 with the help of simulation software, Transport and Range of Ions in Matter (TRIM) code (SRIM 2003 software version 2003.20) [37, 38]. Using relatively low pulse voltage results in low ion energies may lead to sputtering at high doses. This is discussed in the later section on PIIID of insulating materials in Section 2.6.

2.1.1 Polymer structure

A polymer is a long-chain molecule composed of a large number of identical units bonded together. These units may consist of all carbon chains (homochain) or contain more than one atom type (heterochain) such as those decorated with H, O, N, or other atoms. All polymers can be classified into two major groups based on their thermal processing behaviour. Polymers that can be heat-softened in order to process into a desirable form are called thermoplastics [39]. The two types of polymers, UHMWPE and PET, belong to this group. The other group, thermosets are polymers whose individual chains have been chemically linked by covalent bonds during polymerization. Once formed, these cross-linked networks resist heat softening, creep and solvent attack, but cannot be thermally processed [39]. These thermosets are more suitable for coatings and adhesive applications.

The polymers used in this work are semi-crystalline materials. Regular crystalline units are linked together by random-conformation chains that constitute amorphous regions. The crystalline and amorphous regions have their distinct properties, which give the semi-crystalline polymer a range of physical, thermal and mechanical properties. Crystalline structure refers to the state where polymer molecules are oriented, or aligned, in a regular array and amorphous structure refers to a state of almost complete lack of order among the molecules [40].

2.2 Surface composition of ion modified polymers

The surface compositions affect the surface energy, electrical resistivity or wear mechanism of the surfaces of ion modified polymers and are used in explaining these changes in properties for ion modified polymers. The surface composition is also important in understanding the first interactions of the ion modified polymer with their application environment. For ion modified polymers by PIII, the depth profiles suggest that the peak concentration of implants is located very near the surfaces. This was observed in the depth profiles for nitrogen PIII modified insulators [41] and metal ions modified PIIID polymers [42] as shown in figure 2.1 (a) and (b), respectively. This contrasts with the depth profile of ion implanted polymer and the theoretical depth profile calculated by means of TRIM code as seen in figure 2.2 [43]. Even in figure 2.2, it is observed that due to the insulating nature of polymer, there is a slight shift of the peak concentration towards the surface which differs from TRIM calculation. It suggests that there may be effects arising the backscattering of implanted ions, charge accumulation at the ion bombarded surface or thermal diffusion along the latent tracks to the surface of the polymer target [43]. For PIII modified polymers, the peak concentration was shifted further towards the surface of the polymer, resulting in a modified layer rather than a buried layer of implants. A smooth transition of elemental compositions from surface to substrate regions and formation of an ion mixing layer was also observed [42]. The shift in peak concentration was likely due to a combination of several factors such as the insulating nature of the polymer, the finite rise and fall time of the pulse voltage of the applied substrate bias [44], thermal diffusion and surface reactions of the polymer immersed

in plasma. Surface reactions of the polymer immersed in plasma are likely to result in chemical bonding between the polymer and gaseous ions (in non-condensable plasma) or deposited atoms (in condensable plasma). These factors affect the surface composition of ion modified polymers.

Figure 2.1 (a) Nitrogen depth profiles from fused quartz treated at 40 kV [41] (b) XPS depth profile of a Kapton sample biased to 7 kV in Al magnetized plasma

[42]

Figure 2.2 (a) Sb depth profile for polyethylene film implanted with $5 \times 10^{16} \text{ Sb}^+ / \text{cm}^2$ at 100 keV. (b) Boron depth profile for polyethylene (PE), polyamide (PA) and cellulose (CE) films implanted with $5 \times 10^{16} \text{ B}^+ / \text{cm}^2$ at 100 keV.

2.3 Ion-polymer interactions

The ion beam irradiation effects on materials have been widely covered by researchers [45-49] since conventional ion beam implantation was implemented in the modification of materials. The effects of radiation of ions on the structure and properties of solids do not differ much between conventional ion implantation and plasma immersion ion implantation (PIII). In conventional ion implantation, the study of radiation effects on solids is often simplified due to three reasons: the ion energy is mono-energetic, the ion beam is not affected by unstable plasma conditions and there are established theories and programs that simulate an ion beam interaction with single element or complex targets. Thus, when discussing ion-polymer interactions, it is still worth discussing the mechanisms behind the modifications of polymers from a “conventional” point of view.

Several characteristic parameters appeared to be crucial in affecting ion-polymer interactions: (a) ion mass, (b) ion energy, (c) ion dose and (d) the composition of the target. These parameters determine the amount of deposited energy and the penetration range of the impinging ions or the thickness of the modified layer [50]. These parameters are taken into account when using TRIM. Simulation of Ni ions with ion energies of 20 keV was done using TRIM to illustrate the ion-polymer interactions in the modified layer. TRIM uses the Ziegler, Biersack and Littmark (ZBL) model developed in 1984 and has become a standard code for the prediction of charged particle stopping in matter. It is commonly cited for range and damage

distributions in amorphous materials [51] and recently has been used in several PIII related work [9, 52, 53].

In Figure 2.1, Ni ions of ion energies 20 keV undergo a series of energy-loss collisions with both target atoms (nuclear collisions) and electrons (electronic collisions), finally coming to rest some hundreds of atom layers below the surface [54]. The red dots are collisions between the ion (Ni) and target atoms (i.e. O, C and H), in which the target atoms are knocked from their lattice sites. The green dots are collisions between the recoiling target atoms and other target atoms. The dot is only plotted if the transferred energy is large enough to displace the atom hit from its lattice site, thus the plot shows the number of displacements which have occurred.

Figure 2.3 TRIM simulation of Ni ions with energy 20 keV implanted into PET. The red dots indicate collisions between Ni ions implanted into the target from the left and target atoms. The green dots indicate collision between recoiling target atoms and other target atoms.

During the path traveled by implanted ions, the ions deposit energies and induce significant and damaging effects in the substrate within a process time of 10^{-13} second [54]. Energetic ions are slowed down in materials by momentum transfer to target atoms (“nuclear stopping”) and by exciting the electronic system of the target (“electronic stopping”). The resultant process is atomic mixing, which may involve simple collisional mixing or more complicated beam-induced diffusional processes. TRIM will be used again in Chapter 6 to calculate the nuclear and electronic stopping powers of Ni ion in PET.

An important effect of ion-polymer interactions on carbon-based polymers is the breaking of bonds and through this process, it is possible to drive out volatile species (H, O, N) thereby giving rise to major changes in stoichiometry and in structure [36]. With increasing dose, the material shrinks and becomes increasingly carbon rich. Thus after intense ion-bombardment, the resulting material is similar to highly amorphous carbons. Early interest in the ion modification of carbon-based polymer was triggered by the realization that an ion beam could cause either scission of polymer chains or cross-linking between them, thereby either dramatically decreasing or increasing their molecular weight [48, 55, 56].

The displacement of target atoms by energetic collisions can cause permanent damage in a polymer mainly in the form of chain scission by displacing atoms from polymer chains. If a bond that makes up part of the backbone of the molecules breaks, this main scission results in degradation, with products of a lower average molecular weight. Alternatively, the electronic excitation or removal of valence electrons

(ionization) can result in the formation of free radicals that may readily cross-link the polymer chains, thereby increasing the molecular weight, hardness and wear resistance. Continued cross-linking causes the surface region to become a three-dimensional network, which becomes an infusible and insoluble gel. It is worth noting, however, that incomplete reaction of free radicals may drastically increase chemical reactivity and thus promote oxidation.

2.4 Thermal spikes in ion implantation of polymers

There have been several attempts by researchers to identify the thermal contributions or provide thermal considerations in the process of PIID of materials [57-59]. Experimental measurements of actual change in temperature remains difficult due to extremely high voltage applied during PIID and for polymers, their insulating property makes it inaccurate to use thermocouples that can only measure the temperature of the conducting substrate holder. Most estimation has been based on simplifying assumptions and theoretical estimates [60]. One recent discussion by Oates [57] identifies the dramatic implications for the distribution of the implanted ions if diffusion occurs when temperature increases sufficiently for the surface region to become fluid. He concludes his discussion by stating, “that the issue of temperature is relevant for ion implantation of polymers and should be discussed in any discussion of modification mechanisms”. This section is a general introduction of the experimental and simulation examples of thermal spike effects in ion implantation. The concept of thermal spikes in ion implantation of polymers is applied in Chapter

6 where the calculation of the thermal spike radius and its quench time using a cylindrical-shape model are presented.

Experimental and simulation examples of thermal spike effects

Atomic collision cascades initiated by energetic ions or recoil atoms are widely established as the origin of many radiation effects in solids. On the other hand, thermal spike effects may help to explain observations beyond these collision cascades such as interface mixing [61], local melting [62] and latent track formation [63]. Early papers describes a spike as a limited volume with the majority of atoms temporarily in motion[64].

The history of thermal spikes concept has been covered adequately in “Ion Implantation and Beam Processing” by J. A. Davies [54]. The anomaly large damage levels observed in many semiconductor implantations are consistent with the formation (and subsequent rapid quenching) of a pseudo-liquid region around each heavy ion track. Simple collisional theories have been employed to predict damage distributions and the level of ion damage. These theories include the linear cascade theory (Sigmund, 1969; Winterbon et al., 1970), which generates the expected spatial distribution of displaced atoms from knowledge of the energy deposited into nuclear collision processes. However, it was found that linear cascade theory does not account for the discrepancy between experimentally determined damage cross-section and predicted number of displaced atoms. Hence, the effects of energy spikes were considered.

Thermal spikes are known to give rise to excess damage by a process where the local “hot spot” surrounding the ion track extends out considerably beyond the high-density collisions [65]. Kinetic energy loss by elastic nuclear collision with target atoms becomes so large that the energy density around the end of each ion track can reach several eV per atom and some sort of collective “hot spot” occurs for at least a few picoseconds after the ion comes to rest [54]. Thus a thermal spike is also associated with localized melting. Thermal spikes in ion implantation also lead to two effects. The first effect is the dynamic annealing of the surface of the material during ion implantation. The second effect stems from the first effect in which a high dose rate results in thermal or bulk annealing of damaged layers due to a rise in target temperature during implantation. Studies of dose rate illustrate the differences between the two cases. Higher dose rate for Ar^+ implants at room temperature gives rise to more damage for the same implanted dose. No dose-rate effect is evident for liquid N_2 implantations, where all bombardment-induced damage is “frozen in” [66].

Other evidence of temperature related consequences of thermal spikes can be seen in the longer stopping range in experiments using depth profiling characterization techniques. These techniques include Rutherford backscattering (RBS) [67, 68] secondary ion mass spectrometry (SIMS) [69] and the post-diffusion of dopants (or sometimes called radiation-enhanced diffusion) in implanted polymers [70-74]. The conclusion, especially for heavy ions in light substrates, shows that the experimental range parameters exceed significantly the ones proposed by the ZBL theory (estimated by the software TRIM). Some experiments have been related to electron microscopy study; Howe and Rainville [75] have found that at sufficiently high mean

deposited energy (i.e. > 0.5 eV/atom), each implanted ion produces an observable amorphous blob which strongly suggests that each high density cascade is initially a molten zone which is subsequently quenched rapidly enough to remain amorphous.

Thermal spikes and rapid quenching process that follows thermal spikes have also been applied to ion-assisted deposition where it can modify thin film properties [76] and is related to stress relaxation mechanism in the deposition of thin films [77]. In these analytical works, the thermal spikes in ion implantation of thin films have been approximated as a hemispherical region with radius, r (r is proportional to $\sqrt[3]{E}$) around the impact site (Figure 2.2).

Figure 2.4 Schematic diagram of the thermal spike produced surrounding the site of an energetic ion impact [77, 78]

The thermal effects in the formation of tetrahedral amorphous carbon have been analytically studied using the assumption of an isotropic medium by Marks [78]. Marks found that the time taken for the energy in a thermal spike to be quenched is proportional to the square of the initial spike radius. If the thermal spike endures long

enough, there will be sufficient time for significant atomic movements and relaxation corresponding to local annealing.

In analytical studies of thermal spikes, there are two significant parameters; the thermal spike radius and the time taken for the region to quench to the surrounding temperature. The quench time depends on the size of the thermal spike radius and the thermal conductivity of the target.

Experimental studies of thermal spikes associated spikes with melting and formation of amorphous regions [61, 62, 78]. Thermal spikes create a larger modified volume where the melt region will eventually quench into an amorphous state. There are several studies determining the thermal spike radius experimentally. The formation of “latent” ion tracks in polymers have been related to thermal spikes [63, 79, 80]. However, the quench time due to single ion implantation cannot be easily determined experimentally. Thus, the quench time of a thermal spike is of interest, given that the thermal conductivity (κ) of polymer is significantly lower than in other well-studied materials like metals, graphite and tetrahedral amorphous carbon (ta-C). Thermal spikes allow the excited region created by incident ions to transform to local surface melting and lower κ results in longer quench time. A longer quench time in a time scale of 10^{-9} to 10^{-6} sec would allow transition comparable to pulsed lasers in creating amorphous-to-polycrystalline transition in the outer regions of the amorphous layer of implanted Si [54]. Moreover, the melting temperature is low for polymers and thermal spike volume is expected to be large for these low melting point materials [81].

Thus, the formation of thermal spikes is further discussed in Chapter 6 and the quench time of a thermal spike resulting from a heavy ion with keV energies is obtained in by solving an analytic model of a thermal spike in PET. The aim is to provide evidence of a longer quench time and larger damage region than it is normally predicted in other materials or by TRIM. This phenomenon may help to explain thermal related effects such as the formation of clusters of implanted atoms.

2.5 Electronic transport mechanism of ion modified polymers

Insulating polymers modified by the PIID have shown a change in their electronic properties which includes a large increase in their room temperature conductivity from 10^{-13} to more than 10^2 S/cm after ion implantation [6, 82, 83]. The change in conductivity of ion-implanted polymers also depends primarily on implantation dosage level [35, 84]. The models used in examining the conduction mechanism includes the quasi-one-dimensional variable range hopping [85] or tunneling between metallic particles embedded in an insulating medium. Both the models predict identical expression for the dc electrical conductivity. The temperature dependent of the observed conductivity usually follows the equation [83] :

$$\sigma_T = \sigma_0 \exp[-(T_0 / T)^\gamma] \quad (2.1)$$

where $\sigma_0 = \sigma(T \rightarrow 0)$, T_0 is the characteristic temperature obtained from the slope of $\sigma(T)$ plot and γ is a fitting parameter.

Experiments have shown that the temperature dependent behavior of increased dosage levels differs from the insulating conductivity described above [83, 84]. Semi-metallic

behavior is seen at higher dosage levels for carbonized ion-implanted polymers and these polymers indicate weaker temperature dependence. The conductivity data better fit a semi-metallic model $\sigma(T) = \sigma_D + \Delta\sigma(T)$, where the temperature dependent correction term $\Delta\sigma(T)$ is due to the electron-electron interaction and weak localization effects [86]. The model developed by Du [83] for ion-implanted PBO with semi-metallic behavior includes this temperature dependent correction term:

$$\sigma(T) = \sigma_D + mT^{1/2} + B \ln[\sinh(T/c)^{3/2}] \quad (2.2)$$

where the first term σ_D is a constant current, arising from the Drude conductivity, the second term $mT^{1/2}$ arises from localization (L) effects and the third term $B \ln[\sinh(T/c)^{3/2}]$ arises from interaction (I) effects. The additional terms c , m , and B are fitting parameters.

Conducting AFM was used in this work to examine the conducting mechanism and distribution of conducting regions by localized current measurement and nanoscale current imaging. Drift during temperature variation prevents the measurement of current for a defined Ni nanoparticle site, so the temperature dependence of the maximum current, i_T , was considered and evaluated for each current image. The insulating and semi-metallic models based on equation 2.1 and 2.2 were adopted for i_T sampled from Ni implanted PET, assuming the proportionality between conductivity and current. These results are presented in Chapter 6.

2.6 Plasma immersion ion implantation (PIII)

PIII was initially developed by Conrad [87, 88] in 1987 as an alternative to overcome some limitations of conventional ion implantation. It is able to reduce processing times for a larger area and at a lower cost than conventional ion implanters. It has been mostly applied to conducting or semi-conducting materials. However, in the past decade, research has been expanding into obtaining polymers with desirable surface properties [1, 2, 6, 9, 31, 89-91]. In addition, ion implantation can combine with other methods such as etching, deposition of thin films and deposition of additional polymer layers [18, 68, 92]. Combined processes can result in the creation of novel microstructures and nanostructures on polymer surfaces. This highlights the exciting prospect of developing PIII for surface modification of polymers.

When combined with condensable plasmas such as in the cathodic arc source used in this thesis, modification by the PIII technique results in deposition during the “off” pulse. Therefore, this form of process will be referred to as *plasma immersion ion implantation and deposition* (PIIID) in later chapters to describe the situation in condensing plasma. This technique has been exploited in thin film deposition to reduce intrinsic stress in thin films in order to grow thicker or multilayered amorphous carbon films with exceptional adhesion to the substrates [77, 93]. However, when examining the ion interaction with the polymeric surface, deposition may reduce the modified depth and cover the modified layer. In order to reduce film deposition, there are several methods to employ, among which is the use of a pulsed cathodic arc where the pulse of the plasma formation can be controlled to synchronize with the pulsed

substrate bias so that the deposition is minimized. Another method which has been employed here is to place the substrate holder away so that it is not in direct line of sight with the cathode [94]. During the “on” pulse, an ion sheath will still be formed around the substrate holder to accelerate ions into the substrate, but during the “off” pulse, there is a significant reduction in deposition rate.

In Table 2.1, some published work on ion modification of polymers by conventional ion implanters and PIII and their applications are shown. Both techniques uses similar types of ions such as N, O, C, Ar, Al, Ti and show similar surface modified properties such as electrical resistivity, wear resistance, hardness, adhesion and surface energy. However, ion implanters tend to be very directional and it can be a slow technique to modify a three dimensional object using manipulation. This is where advances in PIII technology would be important as its non line-of-sight plasma processing indicates it is able to process complex and three dimensional objects. Some problems and issues such as arcing, non-uniform dose distribution remains to be resolved for insulators and conductors. Despite of these problems, potential applications have been demonstrated in biomedical materials [95-97] where the structures can often be complex such as in cylinders and on curved surfaces. Other advantages include its relatively small size and lower equipment costs. Using low to medium substrate voltage bias (10 - 20 kV) has also proven to be sufficient for modifying the surface properties such as mechanical hardness or surface energy [2, 10, 27].

Chapter 2 Experimental Techniques and Theory

Table 2.1 Some published work on ion implantation of polymers

Year	Researchers	Substrate material	Type of ion	Energy/ Bias	Fluence (ions cm ⁻²)	Surface property modification	Ref
Conventional ion implanters							
1984	Kaplan	Organic thin films	Ar ⁺ ion beam irradiation	2000 keV	10 ¹⁷	Optical, electrical	[82]
1996	Allen	UHMWPE				Wear behaviour	[11]
1998	Du	PBO, PBT, BBL	⁸⁴ Kr ⁺ ion implanter	200 keV	4 x 10 ¹⁶	Electronic behaviour	[83]
1998	Guzman	PC	N ⁺ implanter	160 keV	4 x 10 ¹⁶ – 4 x 10 ¹⁷	Nano-hardness, abrasion and chemical resistance	[98]
1998	Bhattacharya	PC	O ⁻	2500 keV	5 x 10 ¹³ – 3 x 10 ¹⁴	Abrasion resistance (for eyewear)	[99]
2000	Saha	PP	12C ⁺ , 3MV Pelletron	3600, 5400 keV	5 x 10 ¹³ – 5 x 10 ¹⁴	Physico-chemical	[100]
2000	Dworecki	PET membranes	O ⁵⁺ , N ⁴⁺ , Kr ⁹⁺ , ECR ion source	10 keV	10 ¹⁵	Electrical	[101]
2002	San	Nylon 6	Al, Ti, Fe, Ni, MEVVA	55 kV	2 x 10 ¹⁵ – 1 x 10 ¹⁷	Nano-hardness, tribology	[4]
2002	Guzman	PTFE	N ⁺ implanter	160 keV	1 x 10 ¹⁴ – 1 x 10 ¹⁷	Adhesion	[8]
2002	Rodriguez	PC	Si ⁺ , N ⁺ , D ⁺ , D ₂ ⁺ , H ⁺ , H ₂ ⁺ , ion implanter	100 – 150 keV	1 x 10 ¹⁵ – 1 x 10 ¹⁶	Mechanical	[12]
2003	Zhang	UHMWPE	N ₂ ⁺ , C ₃ H ₈ ⁺ , ion implantator	80 keV	1 x 10 ¹⁴ – 5 x 10 ¹⁵	Surface energy and chemical	[102]
2004	Valenza	UHMWPE	H ⁺ , He ⁺ , Ar ⁺ , Xe ⁺	300 keV	10 ¹⁴ - 10 ¹⁷	Nano-hardness, wear resistance	[7]
Plasma immersion ion implantation							
1997	Han	PET, PS, PE, PVC, PC	O ⁺ rf plasma, PIII	10 kV	1 mTorr of working gas	Wetting	[10]
2000	Dong	UHMWPE	N rf plasma, PIII	15 kV	0.5 – 1 x 10 ¹⁷	Wear resistance	[2]
2002	Yoshida	PET	rf C ₂ H ₂ , PIII	15 kV		Oxygen barrier	[103]
2001	Shi	UHMWPE	N ⁺ - PIII	20 kV	1 - 4 x 10 ¹⁷	Wear resistance	[27]
2002	Lim	PS/PD, PET, PI	Ar ⁺ rf plasma, PIII	50 kV	1 x 10 ¹⁶ – 5 x 10 ¹⁷	Resistivity	[6]
2004	Wang	PET	C ₂ H ₂ , PIIID	5 kV	30 sccm	Anticoagulation behaviour	[22]

2.6.1 Description of the PIII system

The PIII (HV Pulser) system used in this thesis was developed by the Australian Nuclear Science and Technology Organization (ANSTO). It has a power supply which is capable of delivering negative voltage pulses up to 30 kV with varying frequencies and pulse duration. A computer provides feedback and estimates several important parameters such as incident dose rate and time-averaged ion current density, j_{ion-av} . The parameters such as pulse voltage, pulse frequency and pulse duration can be varied in experiments, enabling a wide range of material properties to be obtained. The pulse voltage affects the substrate bias that can be applied to increase the ion energies, thus increasing implantation depth. For thin film deposition with substrate bias, the pulse frequency and pulse duration are varied with effects to the stress and mechanical properties in the films and the deposition rate of the films [104-107].

Figure 2.5 Picture of a PIII system with computer control

2.6.2 Plasma immersion ion implantation for insulating materials

The processes involved during PIII will be discussed in this section in the following areas: sputtering effects which limits the final retained dose (Section 2.6.2.2), charging effects in insulators which reduces the actual voltage (Section 2.6.2.4), and design of experimental setup for insulators (Section 2.6.2.5). In addition, the important parameters are discussed in the following sections: the ion energy range (Section 2.6.2.1), incident ion dose (Section 2.6.2.3) and duty cycle which controls the actual implantation time (Section 2.6.2.6).

2.6.2.1 Rise time and ion energy range in PIII

One of the important differences between conventional ion implantation and PIII is the energy range of the implanted ions. As mentioned in Section 2.2, in conventional ion implantation, there are mostly mono-energetic ions. The effects of the finite rise and fall time in PIII has been covered in greater detail by other research groups [44]. Due to the finite rise and fall times of the voltage pulses, it has been found that the ions implanted during the rise and fall times have ion energies less than the applied pulse voltage. This means that the ion energy distribution is broader in PIII and will affect the implanted ions' profile. In the PIII modification of polymers, the modified layer has a different distributed profile with the surface receiving a higher incident dose [41] as compared to a Gaussian profile distribution calculated by TRIM [43].

2.6.2.2 Sputtering process

During ion bombardment, sputtering of implanted atoms or substrate atoms are part of the process of using highly energetic ions. Sputtering may occur with increasing dose rate. This may lead to reduced retained dose and surface roughening of the modified layer. A thin layer of material deposited during the PIID process can be beneficial as the deposited layer gets sputtered away instead of the actual implanted layer. This reduces the rate of sputtering on the polymeric surface [51].

Sputtering of the target atoms from the surface also occurs during ion bombardment. This process can lead to appreciable surface erosion and ultimately, the removal of already implanted atoms. It may also leads to surface roughening of the modified surfaces as well as accounts for dose limitation of the implanted ions [71].

2.6.2.3 Determination of ion energies and incident ion dose rate

Similar to the ion implantation process, the ion energies and incident dose are often cited as important variables which affect the surface properties. The importance of a high ion dose is that latent tracks (formed mainly by nuclear collisions of the incoming ion) overlaps at high fluence [108], providing highly “damaged” region and giving rise to a high concentration of defects [109]. The method in which the incident ion energy and ion dose are estimated are described here. This allows a comparison between PIII and conventional ion beam implantation process. However, this incident ion dose cannot account for the final retained dose in the substrate. There are several

characterization techniques employed to measure the retained ion dose and they are electron-based characterization techniques such as TOF-SIMS and RBS [51].

Ion energy

The ion energy in PIID modification of polymer with a cathodic arc source will have two components. The first component is the ion energy of the plasma. The second component is any additional energy provided by the high negative voltage pulses that accelerates ions towards the substrate. The ion energy of the plasma is between 80 and 100 eV [93, 110]. The ion energy of the second component is variable depending on the ion charges produced by the cathodic arc source and the applied pulse voltage. The mean ion energy will be the mean ion charge multiplied by the applied voltage. In a carbon cathode, the mean ion charge is taken to be 1^+ and in Ni cathode, the mean ion charge is taken to be 1.76^+ [111, 112].

In actual experiments, the actual ion energies will be lower than the applied voltages [44, 89, 113]. The factors which contribute to this situation will be elaborated in the later sections.

Incident ion dose rate

The estimation of the incident dose rate was based on the monitoring program supplied with ANSTO PIII high voltage pulser. This estimation took into account several important factors such as secondary electrons emission and effective charge of an ion.

Firstly, a signal provides a pulse every 0.52 mC of the integrated current. The time-averaged pulse current I_{av} (mA) is calculated from the period T_p of these pulses

$$I_{av} = 52 / T_p \quad (2.4)$$

However this current I_{av} contains a significant contribution from secondary electrons ejected from the surface of the target by impinging ions and must be divided by a factor of $\gamma + 1$ to give the real ion current to the target. γ is the ion-impact secondary electron yield and is defined as the average number of electrons emitted per incident ion. The value $\gamma = 3.12$, measured for N_2 ions for a silicon surface was used in this estimation [114].

If A is the exposed area of the target, the time-averaged ion current density,

$j_{ion-av} (\mu A.cm^{-2})$ is given by:

$$j_{ion-av} = I_{av} / A.(\gamma + 1) \quad (2.5)$$

The time-averaged dose rate is given by $j_{ion-av} / e.Z$ where e is the charge of the electron and Z is the mean charge state of the ion. The area of the substrate holder is taken as the exposed area and is about 50 cm^2 . $Z = 1$ and 2 is taken as the mean charge state for C and Ni ions, respectively.

However, the use of integrated current measured by the pulse power supply unit will include displacement current due to the growth of the equilibrium sheath and other transients in the circuit. In order to detect the effect of the displacement current, the

integrated current values can be recorded for a range of pulse lengths (range for the power supply: 10 to 50 μs). The current component which is associated with the ion implantation through the equilibrium sheath should scale linearly with the pulse length. The constant current component which is due to the rise time transient and the current due to the ions collected in the matrix sheath which was implanted with reduced energy can then be derived. Thus, before the displacement current is determined, the calculated dose rate presents an upper bound of the actual values. The time-average dose rate calculated from the lower integrated current will give a lower bound for the actual dose rates.

In the experiments carried out in this thesis, the upper bound dose rate was found to be about $2.4 \times 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$. The lower bound dose rate was found to be about $10^{13} \text{ cm}^{-2} \cdot \text{s}^{-1}$ by observing the displacement current when no high pulse voltage has been applied. The incident ion dose is according calculated according to the modification time:

$$\text{Incident ion dose} = \text{Dose rate} \times \text{Time} \quad (2.6)$$

2.6.2.4 Charging effects on an insulator's surface

In the PIII technique, substrates are immersed directly in the plasma and biased negatively with high voltage pulses. This produces an expanding sheath which accelerates ions into the target. In the case of an insulator with bias applied to a substrate holder, the dielectric property causes a voltage drop to occur across the insulator and the insulator acts as a capacitor.

This capacitor is charged by the three effects:

- (a) positive surface charge accumulating from the ions implanted,
- (b) neutrals being sputtered from the surface of the polymer, and
- (c) secondary electrons emission from the insulator under ion bombardment.

C⁺ implantation into polymer

Figure 2.6 Causes of charging effects due to a negative pulse voltage

There are several consequences of this process. Firstly, the dielectric polarization indicates that the surface voltage is lower than the applied voltage which means a reduction in accelerating bias for the ion. Emmert [115] estimates that the reductions in implantation energies and dose in polymer sheets typically range between 10 and 40 %, depending on polymer's thickness and plasma parameters. Secondly, the positive surface charge and secondary electron emissions contributes to the surface charging of the insulator to the extent when voltage is too high, arcing will inevitably occur between the two extremes of the capacitor, resulting in breakdown of the polymer [89]. The use of pulsed voltage is necessary when bias voltage is high (in range of 3 kV and above) to reduce any heating effects caused by the incident ions.

2.6.2.5 Design of experimental setup for insulators

One of the ways to overcome the limitations caused by polymers' insulating nature is to place a conducting grid several millimeters above the surface of the polymer. The conducting grid will neutralize the positive charge effect as it emits electrons when ions bombard it. The conducting grid helps in reducing the surface charge accumulated on the insulating substrates by reflecting secondary electrons back and this method has been shown useful [10, 41, 113, 116].

The placement of the grid has several considerations which are sufficiently covered by Matossian [117]:

- (a) The grid is preferably made of a mesh of thin wires about 0.010 inches thick and arranged such that at least 70 percent of the area of the grid piece is open. This is because ion losses occur to the grid, thus high transmission of ions is needed.
- (b) It is preferably placed at least about 1/2 inch above the surface of the object in order to avoid a "shadow" effect of the grid wires on the surface of the object being plasma modified. The grid may also be moved relative to the surface of the object in a manner that eliminates the shadowing effect of the grid.
- (c) The grid is shaped to make the electric potential field more uniform near the surface of the object, effectively "smoothing" the electric potential field while still achieving uniform processing of the surface. The arcing that prevents plasma processing of surfaces having sharp features is thereby avoided, so that

both electrically conducting objects and electrically non-conducting objects having sharp surface features may be plasma processed.

The grid used in the experiments described in Chapter 4, was designed and implemented to fulfil some of the requirements as outlined by Matossian. A 0.5 mm thick stainless steel grid (60 x 60 mm in size) was machined with a laser to achieve 1 x 1 mm square holes which gives an open space of 65%. The grid covers the substrate (average size of 30 x 30 mm) sufficiently even at the edges. However, the grid was placed 5 mm above the substrate as this distance was found to be sufficient in reducing shadowing effects on the substrate.

Figure 2.7 Position of the substrate holder placed parallel to the incoming plasma

In the case of using thinner substrates in Chapter 5, it is likely that charge does not build up as significantly as in the thicker UHMWPE substrates used in Chapter 4, thus the mesh was not used during Ni ion modification of PET. This is due to charge dissipation mechanisms as thinner insulators have lower breakdown strength and will

therefore conduct charge to the substrate holder through dielectric breakdowns through the polymer. A breakdown will discharge the surface as soon as the potential difference across the polymer exceeds its breakdown strength. The dielectric strengths of PET and UHMWPE are 17 kV.mm^{-1} and 28 kV.mm^{-1} , respectively [118]. This translated into breakdown strengths of 1.7 kV for PET (0.1 mm substrate) and 140 kV for UHMWPE (5 mm substrate). This implies that at applied pulse voltages between 8 kV and 12 kV, the PET substrates is likely to face regular surface charge dissipation during PIIID modification.

2.6.2.6 Pulse frequency and duration

The selection of pulse frequency and pulse duration depended on the substrates. In this case, the polymers are insulators and therefore steps were taken to minimise the possible charging effects and heating effects as discussed in Section 2.5.2.4.

The pulse duration of $10 \mu\text{s}$ was chosen as it was the lower limit of the pulser. An arc current of 60 A was used in the experiments. In order to compensate for the reduction in dose rate, a relatively high pulse frequency of 900 Hz was chosen.

Figure 2.8 Pulse frequency and pulse duration in an ideal pulse cycle

The duty cycle, η , varies with the pulse frequency and pulse duration. The duty cycle is calculated as:

$$\eta = \frac{t_{on}}{t_{on} + t_{off}} \quad (2.7)$$

, where t_{on} is the pulse duration of the “on” pulse, and t_{off} is the duration of the “off” pulse.

In the experiments carried out in this thesis, t_{on} is fixed at $10 \mu s$ and $t_{on} + t_{off}$ is fixed at $T = \frac{1}{900} s$, which gives $\eta = 0.9\%$. This value indicates that, for about 1 % of the total implantation time, the substrate is subject to energetic ion bombardment. While this is expected to reduce heating effects on the polymer, this value has its implications for PIID modification. It can be interpreted as 99 % of the time, the substrate is subjected to plasma deposition when placed in condensing plasma and a layer of amorphous carbon will very quickly reduce the implantation dose into the substrate. Hence there is the need to place the substrate in a position parallel to the incoming plasma as described in Figure 2.7.

2.7 Cathodic Arc Sources

Cathodic arc sources as a source of plasma was first implemented together with substrate biasing by PIID by Brown et al [26, 119]. Besides cathodic arc sources, gaseous plasma (N_2^+ , $C_3H_8^+$, O^+ , H^+ , He^+ , Ar^+ , Xe^+) is another main source of ions to modify the hardness, wear resistance, surface energy and electrical conductivity of polymer surfaces [7, 82, 98, 99, 101, 102, 120]. In contrast to most gaseous plasmas

sources, the use of cathodic arc sources has several advantages. The cathodic arc plasma source is nearly fully ionized with a mean ion charge state greater than 1^+ [51]. This highly ionized plasma complements well with PIII as the technique does not involve ion-mass separation and all the ions in the plasma (monoatomic and molecular) are implanted [89]. The high ionizing efficiency of ions in the plasma increases the number of ions (incident ion flux) and hence, aids in the process of chemical reactivity with polymer surfaces. Furthermore, the use of solid cathodes can also avoid the use of environment-hazardous gas such as acetylene gases.

2.7.1 Filtered cathodic vacuum arc system

In this study, an off-plane double bend (OPDB) filtered cathodic vacuum arc (FCVA) system [110, 121] is used to produce highly ionized carbon or nickel plasma. Metal cathodic arc source is further discussed in the next section. In this section, the filtered bend and cathodic arc source for carbon will be discussed.

Figure 2.9 shows the schematic representation of the FCVA deposition system that is used to generate carbon plasma. The FCVA system consists of three main sections: the cathodic arc source, plasma filtering duct and a vacuum chamber.

(a) Cathodic arc source

A pure graphite disk (60 mm diameter) of 99.999% purity was used as a cathode. The cathode is mounted onto stainless steel cavity and cooled by a high flow rate water chiller. An electrical welding machine (Prestopac 120) with a tunable

current of 10 to 120 A is used as the power supply. The anode of the power supply is connected to the ground (deposition chamber) and the cathode of the power supply is connected to the cathode. An arc trigger (or a striker) connected to the ground is used to initiate an arc. The magnetic field generated by the anode/cathode coils is used to control the cathode arc spot movement.

A cathodic arc plasma results when an arc discharge is initiated between two metal electrodes in vacuum. It is characterized by relatively high current and a relatively low voltage between the anode and cathode. The highly ionized plasma, produced by vaporized moving arc spots on the graphite cathode, works as the conducting media to sustain the high current discharge at low voltage. The cathode material suffers a complicated transition from solid phase to an expanding, non-equilibrium plasma via liquid and dense, equilibrium non-ideal plasma phase [51]. The ions in the plasma have energies in the range 80 - 100 eV, depending on the source material. This makes the cathodic arc an excellent source for carrying out processes which involve moderate energetic bombardment during film growth [122] and deposition of tetrahedral amorphous carbon (ta-C) films [123]. In the experiments, the arc voltage ranges from 18 to 20 V and arc current is typically set at a value of 60 A.

(b) Plasma filtering duct

The plasma generated from the arc spot on the cathode passes through a patented Off-Plane-Double-Bend (OPDB) filter that consists of a toroidal solenoid with the copper coil wound on the outside [124, 125]. It effectively prevents macro-

particles in the plasma from reaching the substrate. A set of baffles is also installed inside the torus to further improve macroparticle-filtering efficiency.

(c) Vacuum chamber

Prior to implantation, the base pressure in the chamber was 5×10^{-6} Torr and the pressure increased to 5×10^{-5} Torr during the process. The deposition chamber, which is grounded, is placed at the exit of the plasma-filtering duct. The vacuum system consists of rotary pump and cryo-pump.

Figure 2.9 Filtered cathodic vacuum arc deposition system

2.7.2 Metal cathodic arc source

The main difference in a metal cathodic arc source is the shield for the magnetic cathode and has been discussed previously [126, 127]. It will be briefly described here. Generally, for non-ferromagnetic metal and carbon cathodes, the arc remains in a stable state after ignition. However, for the ferromagnetic metal cathode, the arc is unstable because the high permeability of the metal changes the distribution of the magnetic field around the cathode. When a ferromagnetic metal is used as the cathode, the magnetic flux concentration at the edge of the target is higher which results in the centre of the arc remaining at the edge of the target during the process. This extinguishes the arc after a short time. To solve this problem, a shield is designed as shown in Figure 2.10. The shield for the cathode consists of three main parts: the aluminium cylinder, the pure iron O-ring, and the BN O-ring. The shield is in a floating potential that separates the electrical field between the cathode and the anode into two parts. The configuration prevents the plasma from being formed in this area. The ring of pure iron provides a larger virtual target surface, which results in a stable arc spot. The BN O-ring is set on top of the aluminium cylinder. The inner diameter of the BN O-ring is 60 mm, which can shield the target well and stop the arc from being extinguished.

Figure 2.10 Schematic illustration of the modified cathode [126]

2.8 Summary

In this chapter, some theory related to polymers, surface composition of modified polymers, ion-polymer interactions, thermal spikes in ion implantation of materials and electronic transport mechanism of modified polymer were discussed as an introduction to these concepts which would be used in the later chapters. In ion-polymer interactions, TRIM was used to illustrate the ion implantation processes for nickel ion implantation in PET. PIII and cathodic arc sources which are used in the surface modification of the polymers were presented. The issues related to using PIII on polymers were discussed. The PIII parameters that determines the duty cycle are the pulse frequency and duration. The charging effects on insulators and the method of using a conducting grid to minimise charging effects were presented. The difference in shielding requirements for the carbon and metal cathodic arc sources used in the experiments was explained.

Chapter 3:

Characterization Techniques

Characterization data and analysis forms a crucial part in the modification of materials. It provides qualitative and quantitative feedback to the experiments. Chapter 3 elaborates the use of various characterization equipments for determining the physical, chemical and resistivity changes to polymer structures after surface modification. Many characterization techniques require careful consideration when applied to polymers and these aspects are highlighted in this chapter as well.

In characterizing the chemical microstructure of ion implanted polymer, visible Raman spectroscopy has been carried out. The X-ray photoelectron spectroscopy (XPS) provides important information on the chemical bonds and atomic element concentration in the modified layers. Scanning electron microscopy (SEM) is able to provide surface structural images of the modified surfaces. The surface profiler gives the surface roughness and thickness of deposited films. The mechanical properties are characterized by the tribometer and Triboscope[®] (nano-hardness). Conductive atomic force microscope (CAFM) is utilized to obtained topography and current images simultaneously at low temperatures.

3.1 Visible Raman spectroscopy

Raman spectroscopy (Renishaw Raman Imaging Microscope with argon green laser light of wavelength $\lambda = 514.5$ nm) is used to characterize microstructure changes in materials. The monochromatic laser beam provides a light quantum $h\nu_0$ that hits a molecule in the sample and causes an elastic scattering process, i.e., Rayleigh scattering. The inelastic process, during which vibrational energy is exchanged, is called Raman scattering [36, 128]. An optical system directs the laser light onto a sample, then collects and analyses the returning light which is contained within the spectrometer. A microscope is attached to the left-hand side of the spectrometer. It provides a convenient means of mounting the sample, focusing the laser beam onto it, and passing the returning beam into the spectrometer for analysis and detection.

The large differences in the Raman spectra of various forms of carbon make this technique useful in distinguishing one form of carbon from another. Thus, this non-destructive method was used to characterize the microstructure of the carbon implanted UHMWPE samples in the region between 400 cm^{-1} and 2000 cm^{-1} (Section 4.3). It was also used in the characterization of carbon implanted fused silica (Section 7.2). After ion implantation, a distinct broad peak around 1560 cm^{-1} was observed for the samples.

The broadening of this peak can be understood by firstly considering the Raman allowed mode for an ideal single graphite crystal is observed in the Raman spectrum as a peak at 1582 cm^{-1} [36]. Disorder associated with the implantation-induced lattice

damage causes a broadening of this Raman allowed (G) line, giving rise to a disorder-induced (D) line with a peak near 1360 cm^{-1} . A deconvolution of the broad peak into two Lorentzian lines can be performed using the fitting program in the Raman spectrometer [102, 129]. The ratio of the two peaks' intensities, I_D/I_G provides a sensitive characterization of the implantation-induced disorder.

3.2 X-ray Photoelectron Spectroscopy (XPS)

The XPS technique uses X-rays to irradiate the surface of the sample. An X-ray photon interacts with an inner-shell electron of an atom. The interaction causes a complete transfer of the photon energy to the electron, which then has sufficient energy to leave the atom and escape from the surface of the sample. This electron is referred to as a photoelectron [130]. The kinetic energy, E_k , of the photoelectron is determined by the difference between the X-ray photon energy, $h\nu$ (h is the Planck's constant and ν is the X-ray frequency) and the binding energy E_b of that inner-shell electron. With E_k measured by the XPS's electron analyser and X-ray energy is known, the binding energy of the inner-shell electron, E_b , can be determined. The binding energy of a particular shell of an atom is unique for each element and allows identification of the element. With the exception of hydrogen, it can detect elements in concentrations to about 1 at% and with an error of $\sim 20\%$ [51].

XPS analysis was performed using a Kratos AXIS spectrometer with monochromatic Al K α (1486.71 eV) X-ray source. The survey spectra range from 0 eV to 1100 eV

and were recorded in 1 eV steps for each sample. This was followed by high-resolution spectra scans over different element peaks in 0.1 eV steps. Charge correction was done by assuming that the binding energy of the C 1s core level was located at 285 eV for the polymers used [130].

Quantitative ratios of atomic composition can be computed from the XPS peak areas using atomic sensitivity factors tabulated in the Perkin-Elmer Handbook of X-ray photoelectron spectroscopy [131]. XPS has been primarily used here for the analysis of chemical bonds and their atomic concentration information.

Peak synthesis, or curve fitting has been used to resolve and identify chemical bonds in composite profiles obtained from high-resolution scans. XPS Peak Fit software was used to aid the curve fitting. A linear background was chosen and several peaks were assumed and fitted with a mixed Lorentzian-Gaussian profile. All the peaks were optimized giving a standard deviation of $\chi^2 < 1$ from the original spectra.

3.3 Scanning Electron Microscopy (SEM)

The surface morphologies of the samples were observed using a JEOL (JSM-5910LV) scanning electron microscope (SEM) with the electron gun operating at 6 kV. A bent tungsten wire filament is heated by passing an electrical current through it, and at an optimum temperature, thermionic emission of electrons will form. The electrons are accelerated by passage through electrical fields and focused to a first optical image of the source. The electron beam is scanned across a sample and produces secondary

electrons, back-scattered electrons, and X-rays. The SEM images are formed from the detection of the secondary electrons. The vacuum in the chamber is about 10^{-6} Torr.

3.4 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a common characterization method used for phase identification in both crystalline and non-crystalline materials. It detects reflected diffraction beam caused by X-rays scattered off the lattice planes of the sample. It is able to distinguish different phases as the interferences between X-rays scattered from the planes are unique. Furthermore, the areas under the peaks of XRD diffraction patterns are related to the amount of each phase present in the sample. Its main advantage is non-destructive on the materials and simplicity as no vacuum system is required. Peaks in the diffracted intensity are identified according to d spacing in (in nanometers) or by identifying the diffracting planes (hkl) of the materials [132].

In this work, the use of XRD has been used for detecting crystallinity of nickel ion modified PET samples. As PET is a semi-crystalline polymer, several PET XRD peaks are also observed to have changed after ion implantation. But these diffraction lines are broadened significantly due to the small crystallites size. The breadth of the diffraction lines can be used to measure the thickness of lamellar crystals using the Scherrer equation. Further details are covered by Alexander in his book: X-ray Diffraction Methods in Polymer Science [133]. The crystallinity of the ion modified samples were characterized using the Siemens D5005 X-Ray diffractometer (XRD) with a glancing incident mode by using $\text{CuK}\alpha$ ($\lambda = 0.154$ nm) radiation (40 kV, 40 mA). The incident angle was fixed at 1° , the 2θ scanning step size was set at 0.05°

and the counting time at each step was 2 seconds. The grain size was calculated from the full width at half maximum (FWHM) of the peak (radians) using Scherrer's equation: $t = C\lambda/B\cos\theta$, where λ is the x-ray wavelength (nm), B is the FWHM of the peak (radians) corrected for instrumental broadening, θ is the Bragg angle, C is a factor (typically 1.0) that depends on the crystallite shape, and t is the crystallite size (nm).

3.5 Surface profiler

The surface profiler (Tencor P10) is a useful and simple instrument in measuring depth profiles (deposition rate), root-mean-square roughness of the surface after polishing and wear profiles after a tribological test. The unit is a stylus-based surface profiler, with a motorized XY stage with variable speed, capable of a lateral resolution of 10 nm at 1 $\mu\text{m/s}$ scan speed and vertical resolution of 7.8 nm at a range of 13 μm . It uses a stylus that traverses the surface in direct contact at low force (5 mg), moving up and down as it rides over the surface peaks and valleys. The instrument converts the vertical motion of the stylus to an electrical signal, by optical displacement-sensing techniques, thus producing the surface profile $z(x)$.

3.6 Conductive Atomic force microscopy (CAFM)

Conductive atomic force microscopy (CAFM) offers the possibility of probing the local electrical properties of disordered systems, and has been utilized to image oxide-based nanocomposite materials [134, 135]. This characterization technique is applied to study the transport properties of ion implanted PET.

Figure 3.1 Picture of the CAFM with nitrogen cold finger

Figure 3.2 Schematic of the setup for a CAFM measurement

Figure 3.1 and 3.2 show a picture of the JEOL 4200 Scanning Probe Microscopy (SPM) and the schematic setup of the CAFM measurement, respectively. In order to accommodate the insulating nature of the bulk substrate, there are a number of specific steps taken:

- 1) The sample was secured to the AFM sample holder using special highly thermal conducting grease to improve the thermal conductivity.

- 2) Silver conducting paint was applied to two edges of the sample to provide a conducting path for the current.

The samples were measured at room temperature under atmospheric pressure initially but it was difficult to obtain a clear and reliable image. This was possibly due to measuring a soft polymer substrate in contact mode, which contaminant the tip easily and giving intermittent electrical contact to the sample. In order to harden the polymer samples, liquid nitrogen was utilized to cool the substrate holder in a vacuum at 5×10^{-5} Torr. Below 273 K, the sample was found to be sufficiently hard that data could be obtained reproducibly with several AFM measurements. The AFM is operated in contact mode using W_2C -coated Si cantilevers with a force constant of 0.35 Nm^{-1} to obtain topographic and current imaging simultaneously. In contact mode, the tip and sample remain in close contact throughout the scanning area. The tip-sample interaction remains in the repulsive regime as shown in Figure 3.3 and the tip's vertical deflection is used as a feedback signal to adjust the tip-to-sample distance to maintain a constant force. A position-sensitive photodiode detects the reflection in the laser beam that has been focused on the tip's cantilever and creates a topographic image of the surface from the changes in z direction (normally perpendicular to the surface of samples).

Figure 3.3 Tip-sample interaction force in atomic force microscopy

3.7 Mechanical Testing

3.8.1 TriboScope Nanoindenter

Nano-indentation was carried out using Hysitron Inc. TriboScope[®] Nanomechanical Test Instrument, which could continuously measure the force and displacement of an indenter with resolutions of 1 nN and 0.0002 nm, respectively. The TriboScope module was attached to a Digital Instruments atomic force microscope and is capable of taking images of the indentation area. Nanoindentation offers the lightest loads and smallest displacements possible and the ability to separate the mechanical behaviour of different material constituents. This is essential in the measurements of thin films and thin modified layers to minimise substrate effects. However, in the case of very thin layers (< 50 nm) or multilayer thin films, it is still not always easy to avoid the substrate effects when displacements with the smallest loads can reach more than 10 % of the modified layer. This happens in the experiments where TRIM predicts the implantation depth of about 50 nm and indentation is made on much softer polymers.

The use of low loads in experiments may also result in great discrepancies. Yet, despite these limitations, the nano-hardness of the carbon-implanted UHMWPE was measured using the nano-indentation method because it provides the only possible qualitative determination of relative nano-hardness between the reference sample and the implanted samples. This method has also been adapted by several researchers for thin films, elastic polymers and multilayer (nano-scale) polymer films [136-139].

Nanoindentation experiments

Four to six indentations were made on each sample using a sharp Berkovich diamond tip with an average radius of curvature of about 200 nm. The total included angle on this tip is 142.3 degrees, with a half angle of 65.35 degrees. This makes a very flat tip. The tip geometry has been used as the standard for nanoindentation. A computer controlled the scan speed and scan area of the AFM and the loading and displacement of the diamond tip. A typical experiment involved using the AFM to image the original topography, then switching to the load-displacement transducer to indent the surface while collecting load-displacement data, and finally resuming AFM scanning. The experimental details of the TriboScope are described in references [140-142]. The contact area is a function of contact depth and it is determined experimentally through a tip calibration procedure based on multiple indentations on a reference fused silica (specified by the manufacturer) over a range of contact loads. Since the modulus and hardness of the standard sample are known, the surface area versus contact depth function (referred to as the area function) can be determined empirically.

The indentations on the carbon-implanted UHMWPE are carried out at a load of $100 \mu\text{N}$ using a trapezoidal loading curve with a loading/unloading rate of $20 \mu\text{N} / \text{s}$. The load-displacement data were acquired in real time by a computer and saved for further analysis.

Determining hardness from load-displacement curve

For hard materials, it is possible to calculate the hardness and elastic modulus directly from the imaged indentation area. However, for softer viscoelastic materials such as polymers, relaxation and recovery was exhibited after indentation and this is a reason why indentation area images could not be shown. Instead, the unloading data was used to determine the nano-hardness in terms of Oliver and Pharr Method [143]. According to classical indentation theory, the initial unloading portion of the load-displacement curve represents purely elastic recovery [137]. The slope of this unloading segment, S , is a measure of the material stiffness, also known as the contact stiffness. The reduced elastic modulus can be written as

$$E^* = \frac{1}{2} \left(\frac{\pi}{A_{\max}} \right)^{1/2} S \quad (3.1)$$

Based on the above equation, the elastic modulus can be directly calculated from the known unloading slope. The material hardness, H , is defined as the maximum load, $P_{\max}$, divided by the projected area of the indentation under this load, i.e.,

$$H = \frac{P_{\max}}{A_{\max}} \quad (3.2)$$

Figure 3.4 Schematic of the nanoindentation process and analysis: (a) indentation under maximum load and (b) typical nanoindentation curve for a polymer illustrating the unloading slope used to measure the material elastic stiffness [137]

3.8.2 Tribometer

The CSEM Pin on disk tribometer was used to study the wear rates of the virgin UHMWPE and carbon-implanted samples. These tests were carried out on a platform rotating at the speed of 5 cm/s and the friction partner used was an alumina (Al_2O_3) ball with a diameter of 6 mm. A load of 1 N was applied for a duration of 1000 cycles on a wear track with a radius of 8 mm. The cross-sectional area of the wear track was then measured using a stylus profilometer and the wear volume was calculated from the track's cross-sectional area. The wear rates were then calculated using the following relation [93]: Wear rate, $k = V / (W.S)$ where V is the wear volume in mm^3 , W is the normal applied load in Newton and S is the sliding distance in metres.

Chapter 4:

Carbon Ion Modification of Ultra-High Molecular Weight Polyethylene

Ultra-high molecular weight polyethylene (UHMWPE) is a polymer used in the application of orthopedic applications. It is used in particular as a socket in the hip-joint replacement. It has several advantages as a socket as it can be easily molded and is light-weight. However, the implant material in the femur is often made of metal alloys such as Ti alloys which are harder than polymers. The friction causes the hip-joint replacement to fail within a short period of time. The wear of the UHMWPE socket cup is a major cause of failure. Thus, it is essential to “protect” the UHMWPE surface by modifying its mechanical properties and study the wear behavior of a modified UHMWPE surface. This chapter discusses the experiments and characterization of surface modified UHMWPE by carbon plasma immersion ion implantation and deposition.

4.1 Introduction

The polymer used in this work was UHMWPE (5 mm thick sheet) with semi-crystalline structure and was purchased from Goodfellow. The monomer (repeating unit) of the UHMWPE is shown in Figure 4.1 and consists of carbon and hydrogen atoms. UHMWPE is an ultra-high molecular weight polyethylene, which gives it outstanding toughness, wear resistance and very good chemical resistance over lower weight polyethylene. The density and the average molecular weight, quoted by the manufacturer, are 0.94 g/cm³ and 4.5 x 10⁶ g/mol, respectively. FCVA is used to produce dense and highly ionized carbon plasma while the substrate holder is negatively pulse biased using a high voltage pulser unit. The surface modification process occurs when carbon ions are accelerated through the plasma sheath towards the substrate and implanted into the polymer. The structural and mechanical changes made by carbon PIIID on the surface of UHMWPE were studied as a function of pulse voltage and modification time.

Figure 4.1 Basic structure of a UHMWPE monomer

4.2 Experiment

The UHMWPE sheet was cut into square pieces with an average size of 3 cm x 3 cm. The pieces were then mechanically polished to achieve an average surface roughness of less than 100 nm using alumina solutions with particle sizes of 0.3 μm and 0.05

μm. The polished pieces were thoroughly cleaned in acetone followed by distilled water in an ultra-sonic bath. They were then placed in an oven set at 60 °C for drying.

In the chamber, the substrate was placed parallel to the incoming plasma to minimize the deposition [9] since there is likely some deposition that occurs during the process. A deposition layer was not desirable in this study of modified surfaces as a built up of deposition layer would eventually reduce the number of ions interacting with the polymer surface. After implantation, the surface profiler was used to check if any thin layer of deposited film might have formed on the surface. There was no measurable layer of deposited film and this may be likely due to the formation of a deposited layer less than the roughness of the polymer's surface (100 nm).

The conducting grid is placed 5 mm above the substrate. The substrate holder was then connected to the PIII by a high-voltage, insulating feed-through. Carbon ion modification was achieved when ions were accelerated through the grid into the substrate.

An estimate of the average dose rate, calculated by the PIII system from the time-averaged ion current density, was read from the controlling software. Based on the dose rate (range from 10^{13} to $2.41 \times 10^{14} \text{ cm}^{-2} \text{ sec}^{-1}$), the dose for a sample implanted at a pulse voltage of 10 kV for an implantation time of 1 min was estimated to be between 6×10^{14} to $1.45 \times 10^{16} \text{ atoms/cm}^2$. In this technique, two parameters can be directly controlled: the negative pulse voltage and implantation time. For the first set of samples, the pulse voltages varied from 3 kV to 12 kV with a constant modification

time of 10 min. This set of samples studied the effects of increasing pulse voltages during implantation. For the second set of samples, the modification time varied from 1 min to 20 min with a constant pulse voltage of 10 kV. As the modification time increased, the ion dose proportionally increased from 1.45×10^{16} atoms/cm² to 2.9×10^{17} atoms/cm². The pulse voltages were applied with a constant pulse frequency and width of 900 Hz and 10 μ s, respectively. The pulse voltage was applied in short pulse width of 10 μ s to avoid excessive heating of the polymer by reducing the heating effect from ion bombardment. The plasma temperature is below the working temperature of the UHMWPE at 95 °C and therefore the temperature effect from the plasma on the polymer would not be significant.

The pulse voltages have been chosen according to the maximum rating of the insulator (Teflon) feed through in the connection of the substrate holder. Substrate pulse voltages can be increased from 3 kV to 12 kV without any electrical breakdown that makes the PIII system unstable. Other advantages of working with low voltages are: it can reduce high X-ray emission, excessive charging and heating effects on the polymer.

4.3 Results and Discussion

4.3.1 Raman spectroscopy

For the virgin UHMWPE, several sharp peaks at 1060, 1127, 1293 and 1440 cm⁻¹ were observed as shown in Figure 4.2. The bands at 1060 and 1127 cm⁻¹ with weak intensities are from the C-C skeletal stretching. The band at 1293 cm⁻¹ with medium

intensity is in CH₂ in-phase twisting mode and the band at 1440 cm⁻¹ originates from the CH₂ deformation stretching [28, 102, 129].

The Raman spectra of carbon-implanted UHMWPE for different pulse voltages and different modification time are shown in Figure 4.2 and 4.3 respectively. In both cases, the relative intensities of the bands at 1060, 1127, 1293 and 1440 cm⁻¹ decrease, indicating that the chemical structures of the modified polymer change after surface modification. In particular, the intensity of the band at 1293 cm⁻¹ is related to the n value of the [-CH₂-] _{n} bond in virgin UHMWPE. Therefore, the decrease of the relative intensity of the band at 1293 cm⁻¹ in the spectrum indicates that the polymer chains in the samples have broken and the length of the chain becomes much smaller than that of virgin UHMWPE [102].

Figure 4.2 Raman spectra for carbon ion modified UHMWPE at different pulse voltages for 10 min

More importantly, a broad peak similar to that of amorphous carbon [144] was observed in both the spectra, indicating that the formation of sp^2 bonds has occurred on the surface of the samples [102]. The broad band around 1560 cm^{-1} was fitted by Lorentzian shape [102, 129] and the fitted results are shown in Table 4.1. The fitted results showed a general upward shift in the G peak, D peak and the intensity ratio, I_D/I_G , which corresponded with the increasing pulse voltage and modification time.

Figure 4.3 Raman spectra for carbon ion modified UHMWPE for different modification time at 10 kV

Table 4.1 Fitting results of Raman spectra

Sample	G peak (cm ⁻¹)	D peak (cm ⁻¹)	I _D /I _G
3 kV	1549	1366	0.776
5 kV	1583	1330	0.847
8 kV	1584	1334	1.194
12 kV	1577	1324	0.737
1 min	1549	1303	0.659
3 min	1581	1334	0.902
6 min	1583	1330	0.851
12 min	1585	1335	1.087
20 min	1581	1326	1.159

4.3.2 X-ray photoelectron spectroscopy

Figures 4.4 and 4.5 show the plots of the variation in C 1s peaks as a function of pulse voltage and modification times, respectively. In the case of the carbon ion modified UHMWPE, the spectra showed the presence of another two peaks centred at 285.8 eV and 288.2 eV and these had been identified as C-O and C=O bonds, respectively [145]. A standard fit of the C 1s spectra is shown in Figure 4.6.

Figure 4.4 XPS C 1s spectra for carbon ion modified UHMWPE as a function of pulse voltage

Figure 4.5 XPS C 1s spectra for carbon ion modified UHMWPE as a function of modification time

The analysis of the XPS results was complicated by the fact that the two primary bonding states of interest, namely the C-C and C-H bonds, were very close in their binding energies. For the C-C bond, the binding energy is 284.6 eV [28, 129, 145] while for C-H, the binding energy is 284.8 eV [146]. This difference of 0.2 eV in energy is close to the resolution limit of most detectors used for XPS. Since it is not possible to resolve the C-C and C-H bonding states clearly, one peak centred at 284.6 eV has been fitted. However, from observations in the Raman spectra, there is a strong presence of amorphous carbon peak on the surfaces of the carbon ion modified UHMWPE, which indicates an increase in the presence of C-C bonds. Other researchers suggested that it was the energetic carbon ions which led to the breaking of C-H bonds in virgin UHMWPE (chain scission) [102, 129]. The formation of free radicals through this process led to graphitization and oxidation [7]. Graphitization occurred when the free radicals react with the carbon plasma to form C-C bonds. The formation of C=O and C-O bonds (oxidation) are likely to occur during the process as the free radicals enables bonds to be formed easily. It is less likely to occur during the XPS analysis as the XPS analysis was performed at ultra-high vacuum (10^{-9} Torr), at much lower than in the high vacuum (5×10^{-6} Torr) conditions of the process chamber.

Figure 4.6 Fitting of XPS C 1s spectrum for carbon ion modified UHMWPE at 3 kV for 10 min

Table 4.2 Fitting results of XPS C 1s of UHMWPE

Modification Conditions	Bonds	Position (eV)	Total Area (%)
Virgin UHMWPE	C-C, C- H	284.6	100
3 kV, 10 min	C-C, C-H	284.6	75.0
	C-O	285.8	17.4
	C=O	288.2	7.6
5 kV, 10 min	C-C, C-H	284.6	70.5
	C-O	285.8	23.4
	C=O	288.2	6.1
8 kV, 10 min	C-C, C-H	284.6	76.8
	C-O	285.8	19.7
	C=O	288.2	3.5
12 kV, 10 min	C-C, C-H	284.6	82.1
	C-O	285.8	14.2
	C=O	288.2	3.7
10 kV, 1 min	C-C, C-H	284.6	68.9
	C-O	285.8	24.1
	C=O	288.2	7
10 kV, 3 min	C-C, C-H	284.6	77.2
	C-O	285.8	15.4
	C=O	288.2	7.4
10 kV, 6 min	C-C, C-H	284.6	71.2
	C-O	285.8	21.1
	C=O	288.2	7.7
10 kV, 12 min	C-C, C-H	284.6	68.1
	C-O	285.8	24.4
	C=O	288.2	7.5
10 kV, 20 min	C-C, C-H	284.6	60.6
	C-O	285.8	31.3
	C=O	288.2	8.1

4.3.3 Mechanical properties of carbon ion modified UHMWPE

4.3.3.1 Nano-hardness tests

The nano-hardness of the samples as a function of pulse voltage and modification time is shown in Figure 4.7 and 4.8 respectively. The ion modified UHMWPE all show an increase in the nano-hardness when compared with the virgin UHMWPE. The sample that was modified at a pulse voltage of -10 kV for 12 min showed the best improvement with an increase in surface nano-hardness from 0.35 GPa (virgin UHMWPE) to 1.6 GPa. In Figure 4.7, the increasing trend in nano-hardness as a function of pulse voltage suggests that higher pulse voltage could be applied to achieve higher nano-hardness. However, there was no significant improvement in the nano-hardness when the modification time increased beyond 12 min at a pulse voltage of -10 kV. This saturation point has been attributed to a possible exhaustion of cross-linking sites and the subsequent predominance of scission [147].

Figure 4.7 Nano-hardness of carbon ion modified UHMWPE as a function of pulse voltage

Figure 4.8 Nano-hardness of carbon ion modified UHMWPE as a function of modification time

4.3.3.2 Wear rates

The wear rates as a function of pulse voltage and modification time are shown in Figure 4.9 and 4.10, respectively. The wear rate of the virgin UHMWPE was $67.5 \times 10^{-5} \text{ mm}^3/\text{Nm}$. With the application of only a pulse voltage of 3 kV for 10 min, the wear rate decreased significantly to $16.5 \times 10^{-5} \text{ mm}^3/\text{Nm}$. There was also a decrease in wear rate to $22.5 \times 10^{-5} \text{ mm}^3/\text{Nm}$ for a sample modified at a pulse voltage of 10 kV for 1 min. However, it was observed that the decrease in wear saturated at approximately $10 \times 10^{-5} \text{ mm}^3/\text{Nm}$ when the pulse voltage was applied beyond 5 kV for 10 min. There was also no significant decrease after a modification time of 6 min at a pulse voltage of 10 kV. These results indicated that a slight structural change of the surface by low pulse voltages and low modification times could decrease the wear rate significantly and the wear rates did not decrease correspondingly to an increase in nano-hardness. This is explained by considering two possible factors that can aid the improvement of wear resistance during a wear test of PIII treated UHMWPE. Firstly, there might be an establishment of a low shear strength boundary film, which effectively reduced the probability of direct contact between asperities on the surface of the polymer and the friction partner [2]. Formation of C-C bonds in the surface modified layer is likely contributed to this establishment. The second factor was the improved abrasion wear resistance of the surface due to increased hardness. With low ion energy used in this technique, the modified surface was very thin and the nano-hardness of the carbon-implanted layer was still much lower than the friction partner. Therefore, the increase in nano-hardness could not fully account for the reduced wear rate. Instead, the establishment and maintenance of a thin film of low shear boundary film during the wear test can aid in achieving a high wear resistance. Taking this into

account, the wear resistance of the polymer may improve with PIII treatment but would not continue to improve significantly with increase in nano-hardness.

The observed improvements in the nano-hardness may be attributed to formation of a cross-linking layer on the surfaces of the samples induced by ion bombardment. Several researchers have suggested that the cross-linking of polymer chains by the reaction of free radicals with ions, strengthens the surface properties through the formation of a three-dimensional connected network [4, 8, 28, 129, 148].

Figure 4.9 Wear rate of carbon ion modified UHMWPE as a function of pulse voltage

Figure 4.10 Wear rate of carbon ion modified UHMWPE as a function of modification time

4.3.4 SEM

The surface morphologies of the samples observed by the SEM are shown in Figure 4.11(a-h). Figure 4.11(a) shows featureless and smooth surface morphology of a virgin UHMWPE. Figure 4.11(b-d) shows the surface of modified polymers changes as the modification time increased from 3 min to 12 min at a pulse voltage of 10 kV. The carbon ion modified UHMWPE in Figure 4.11(b-c) shows increasing surface tension and roughening. Figure 4.11 (d) shows for a longer modification time of 12 min, the surface of the polymer were severely damaged.

Figure 4.11(e-h) shows the changes in surface morphologies as the pulse voltage was increased from 3 kV to 12 kV at a fixed modification time of 10 min. At 3 kV, the SEM image showed a smooth surface similar to the virgin UHMWPE. With increasing pulse voltage, the surfaces showed heavier structural damage. However, when the sample's surface for modified polymer at 10 kV for 12 min in Figure 4.11 (d) was compared to the modified polymer at 12 kV for 10 min in Figure 4.11 (h), the former showed greater surface damage and roughening. This indicates that polymer surfaces are more susceptible to a longer modification time beyond 12 min (ion dose of about 1.73×10^{17} atoms cm^{-2}).

Figure 4.11 SEM pictures showing the structure changes in carbon ion modified UHMWPE

4.4 Summary

The use of FCVA combined with substrate pulse biasing has successfully modified the surface properties of UHMWPE. Using this technique, carbon ions were implanted at sufficiently high energies to break the polymer chains during the pulse “on” time of the pulse voltage. It is likely that the polymer surface, with an abundance of free radicals caused from the bombardment of polymer chains, reacted with the carbon ions to form a modified layer with formation of new bonds. This was observed from the Raman and XPS spectra. The strong presence of the G and D peaks was observed from the Raman spectra of modified polymers. Although it was difficult to quantify the C-C bonds using XPS, there was a strong presence of the C-C peaks. The existence of C-O and C=O bonds was observed and attributed to oxidation when the samples were exposed to the environment.

The nano-hardness and tribological properties of carbon modified UHMWPE improved and this was attributed to cross-linking bonds formed from the modification process. It was likely that highly ionized carbon plasma produced by FCVA enabled the polymer surface react readily with carbon ions to form strong cross-linking bonds. By varying the pulse voltage and modification time, the changes of these properties were shown under different surface modification conditions. The wear resistance of the modified polymers was observed not to have improved significantly with a higher pulse voltage or longer modification time. Thus, it was suggested that another factor that reduced the direct contact of wear asperities by the formation of a low shear strength film during the wear test might be able to explain this phenomenon.

Chapter 4 Carbon ion implantation of UHMWPE

However, it was also observed that energetic ion bombardment caused serious degradation and roughening of the polymer surfaces with high ion dose, as observed in the SEM images. The increased surface roughening observed by SEM for a longer modification time of 12 min might pose an adverse effect in the case of biomaterials.

Chapter 5:

Nickel Ion Modification of Polyethylene Terephthalate

An advantage of using cathodic arc source as a plasma source is that the technique can be extended to metal cathodes and using metallic ions to modify the surfaces of polymer in a similar manner to that described in the last section. Chapter 5 discusses the experimental details and data analysis of Ni ion modified polyethylene terephthalate (PET) to modify its electrical resistivity. The electrical properties of PET can be modified to a greater extent by metal PIIID. The PIIID parameters such as pulse frequency and pulse width were kept constant at 900 Hz and 10 μ s, respectively. The chemical and electrical properties of the Ni ion modified samples have been characterized by XPS, XRD and two-point electrical resistivity measurements.

5.1 Introduction

The basic structure of a PET monomer is shown in Figure 5.1 and it consists of carbon, oxygen and hydrogen atoms. PET was also purchased from *Goodfellow* and the density is quoted by the manufacturer as 1.4 g/cm³. It is in a biaxially oriented form, is a hard, stiff and strong material and has good gas barrier properties and good chemical resistance except to alkalis, which will hydrolyse it.

Figure 5.1 Chemistry structure of a PET monomer

Metal plasma ion implantation is not as commonly carried out by PIII research groups until recent years as most plasma sources deal with gaseous based plasma discharge utilizing Ar [6, 109, 149-151], N [8, 27, 129, 152] and H [95, 153, 154]. In using a metal cathodic arc source, PIII technique is extended to metal PIII (MePIII) with a range of metals i.e. Mg, Ti, Ni, Zn, and Al [42, 94, 155]. The added advantage of using condensable (e.g. metal) plasma is that deposition occurs on the substrate which allows thin film deposition and a wider range of surface structures to be formed on the substrate. However, in this work, metal plasma immersion ion implantation and deposition is carried out with minimal deposition to understand the interaction of ions with polymer and the modified layer.

In Chapter 4, irradiation effects from ion modification of UHMWPE lead to intense graphitization and improvements in mechanical properties. In the nickel ion modification of polymers, the heavier Ni ion is likely to cause similar irradiation effects and graphitization. Another process that may occur with metal ions is the agglomeration of implants as metal is insoluble in the polymer matrix and is less likely to bond with the free radicals caused by ion bombardment. The presence of implants at sufficiently high doses also contributes to electrical conductivity due to hopping mechanism between precipitates of the implanted species [36].

5.2 Experiment

FCVA system and PIII parameters

The nickel plasma was produced from a vacuum arc spot on a 60 mm in diameter cathode target. The cathode target has a 99.95 % pure nickel content with the macro-particles and neutrals in the plasma filtered out by the FCVA system. Argon gas has been added to the cathode area to stabilize the arc. The flow rate of Ar is 7 sccm. There are unlikely any effects of Ar^+ implantation because the Ar gas is in a molecular state and there are no Ar element detected during the analysis by XPS.

The sample was placed in a vacuum chamber parallel to the incoming plasma to minimize deposition and then pumped down to 2×10^{-5} Torr. When Ar gas is introduced, the working pressure of the system is 5×10^{-4} Torr. The pulsed voltages

applied to the substrate holder were varied from 8 kV to 12 kV but a fixed pulse frequency and pulse duration at 900 Hz and 10 μ s were maintained respectively.

Substrate preparation and initial observation

The semi-crystalline PET (Goodfellow, 0.1 mm thick film) was cut into an average size of 2 $\times$ 2 cm. Lithography is used to pattern the polymer film to leave defined regions of exposed surface. Nickel ion modifications on these substrates' surfaces turned the insulating regions into conducting regions. The photo-resist surrounding the regions was later removed by ultra-sonic bath, cleaning the modified samples in acetone for 10 min. This was followed by another ultra-sonic bath of 10 min in a beaker of distilled water to cleanse away the acetone stained onto the samples. This left behind resistor-like modified regions where electrical resistivity could be characterized with the two-point probe method as shown in Figure 5.2. The modified samples had different sizes of resistor patterns on them and two small drops of silver paste were applied on the two ends. The surface resistivity was then measured using a multi-meter by probing onto the silver contacts and the length and the width of the resistor was measured by a surface profiler.

Figure 5.2 Resistor-like patterns on PET by lithography

Initial observation after ion modification included a change of colour from transparent white to metallic colour. There may be a very thin layer of Ni deposition expected during the “off” pulse duration. However, the thickness of the deposited layer could not be determined using the surface profiler because the thickness could not be differentiated from the surface roughness of the virgin PET. The surface roughness (RMS) of the PET was about 10 nm. This indicated that by placing the substrate away from the direct line of sight of the incoming plasma, the deposition is effectively reduced.

Characterization by TEM

Cross-sectional TEM using a JEOL JEM-1010, was carried out to estimate the modified depth of Ni modified PET. Details of the sample preparation were as followed [156]: Firstly, the sample was embedded in the centre of a polymer resin and hardened over two days. Secondly, Leica ultramicrotome EM UC6 was used to prepare thinly cut samples of about 80 nm using a diamond blade with an angle of 45°. Lastly, the sample floated into a water catchment area beneath the blade and copper grid was used to scoop up the samples. As polymer samples were fragile and susceptible to radiation damage, many samples were easily disintegrated by the energetic beams (100 kV) and thus, magnification was kept at a low of 15,000 times.

At low resolution, it is difficult to observe any details from the cross-sectional TEM. From Figure 5.3, the modified depth for a Ni ion modified PET at a pulse voltage of 10 kV could only be estimated to be about 60 nm. This is much larger than the projected range predicted by TRIM ($27 \pm 7\text{ nm}$).

Figure 5.3 Cross-sectional TEM of Ni ion modified PET

Characterization by XPS and XRD

These samples were then characterized for their nature of chemical bonding using XPS. High-resolution spectra were measured for different element peaks in 0.1 eV steps and surface composition in the samples was calculated. The crystalline structures of the nickel ion modified PET were also characterized by XRD.

5.3 XPS

Figures 5.4 and 5.5 show the C 1s of Ni ion modified PET at different pulse voltages and modification times. The C 1s spectrum of the virgin sample is composed of three main components: C_I (284.6 eV) is attributed to C-C bond of benzene rings, C_{II} (286.6 eV) is attributed to carbon atoms in group C-O and C_{III} (288.9 eV) is attributed to carbon atom in O=C-O [130, 157, 158]. The intensities of all the peaks decreased after Ni ion modification and this indicates significant chain scission of the carbon bonds.

From Figure 5.5, a comparison between modification time of 10 min and 20 min was made for two pulse voltages. It is observed that for a longer modification time (indicating higher dose), the reduction in C 1s peaks intensity is not as significant. The reason might be that new C-C bonds are formed with a higher dose.

Figure 5.4 C1s spectra of Ni ion modified PET as a function of pulse voltage

Figure 5.5 C1s spectra of Ni ion modified PET as a function of modification time

Figure 5.6 O 1s spectra of Ni ion modified PET as a function of pulse voltage

The O 1s spectra of Ni ion modified PET at different pulse voltages are shown in Figure 5.6. Virgin PET has two main peaks: O_I is attributed to C=O bonds (O 1s binding energy is 582.1 eV) and O_{II} is attributed to C-O bonds (O 1s binding energy is 533.7 eV) [130]. The peak positions have been corrected for shifts caused by charging to O_I at 582.1 eV. This peak can be verified by examining C 1s spectra in which only C=O peak remains after ion modification. After ion modification, the peak O_{II} disappears completely and the peak O_I broadens slightly.

Figure 5.7 shows the Ni 2p spectra of samples ion modified at different pulse voltages. The samples were modified for 20 min. The Ni 2p spectra of the samples are composed of three main peaks which are identified: Ni_I (852.96 eV) is attributed to the Ni 2p_{3/2} spin orbital, Ni_{II} (855.56 eV) is attributed to the presence of Ni (OH)₂, Ni_{III} (860.42 eV) is attributed to NiO (nickel oxide formed during the modification process or due to reaction with the environment) and Ni_{IV} (870.20 eV) is attributed to the Ni 2p_{1/2} spin orbital [158]. Fitting of the Ni 2p spectra (as indicated in Table 5.1) showed that the area ratio of Ni_{III} generally increased from 16 % to about 21.5 % as pulse voltage was increased from 8 kV to 12 kV. This suggests the formation of NiO increased with pulse voltage and modification time.

The element atomic percentages were also shown in Table 5.1. The Ni at% did not increase expectedly with the pulse voltage and modification time. The highest Ni content was found in sample ion modified at pulse voltage of 10 kV and modification time of 10 min. There were no major change in C content in the polymer surface if C and O at% were renormalize to 100%.

As only the surface analysis was performed in these ion modified polymer, it is not conclusive if the Ni at% is directly dependent on the pulse voltage and modification time. It is possible that there is Ni implanted to a greater depth with high pulse voltage but that the surface concentration remains the same. This would result in more Ni ions being implanted but it will not be observable from the surface composition. However, from the depth profiles that were seen in Figures 2.1 and 2.2, it is likely that the maximum Ni content is seen from the surface analysis.

Figure 5.7 Ni 2p spectra of Ni ion modified PET as a function of pulse voltage

Table 5.1 Fitting of Ni 2p of Ni ion modified PET at different modification conditions

	C (at%)	O (at%)	Ni (at%)	Ni _I Area ratio(%)	Ni _{II} Area ratio(%)	Ni _{III} Area ratio(%)	Ni _{IV} Area ratio(%)
Virgin PET	77.63	22.37	-	-	-	-	-
8 kV 20 min	66.87	17.82	15.31	22.64	19.1	15.97	8.81
10 kV 10 min	56.11	25.54	18.35	20.6	17.25	19.6	9.66
10 kV 20 min	63.23	20.88	15.89	18.38	15.1	21.5	6.8
12 kV 20 min	69.03	16.90	14.07	22.22	15.65	20.2	6.3

5.4 XRD

XRD measurements indicate the existence of two strong diffraction peaks for the semi crystalline PET samples as shown in Figure 5.8 where the XRD peaks are plotted normalized to the main peak’s intensity, I_0 . These two peaks correspond to the diffraction from (100) (main peak) and (200) (weak peak) planes [157, 159]. The (100) diffraction peak is centred at $2\theta \approx 26.10^\circ$ and the (200) diffraction peak is centred at $2\theta \approx 23.10^\circ$. The strong appearance of these crystallographic planes may be due to their relatively simple indices. The simple indices enable the plane to be more densely populated with lattice points and it is more likely these planes are observed as actual crystal faces [133]. Two other PET broad peaks at $2\theta \approx 47^\circ$ and $2\theta \approx 54^\circ$ are also observed [13, 35, 160]. The broadness and high intensities of the main peaks in virgin PET indicate that the crystalline regions in PET are made up of small but vast numbers of crystallites.

In Ni ion modified PET, the relative intensity of the XRD peaks is reduced as compared to the virgin PET, indicating a decrease in the crystallinity of the polymer [159]. In addition, a small and broad Ni (111) is observed at about 44.5° . This indicates that some amount of crystalline Ni appears in our samples. However, the modified layer is only about 60 nm thick and the diffracted signals from such a thin film are observed to be buried in the peaks from the semi-crystalline PET substrate [161]. It is difficult to quantify the size of the Ni crystallites. Another sharp diffraction peak appears at about 54.5° , which is due to the silicon substrate holder used in XRD.

The different pulse voltages used in the samples were observed to have little effect on the size of crystals in the modified samples. It is suggested that crystallinity in the polymers is affected to a larger extent by temperature-stress induced mechanism [132]. As the range of energies used here is small and the samples were not annealed, the small difference in crystallinity can be expected.

Figure 5.8 Normalized intensities of XRD peaks for Ni ion modified PET as a function of pulse voltage

5.5 Electrical Resistivity

The resistances of the Ni ion modified PET films were measured using the 2 point-probe method. The sheet resistivity of the PET film decreases by a magnitude of 9 orders, from $10^{13} \Omega/\text{sq}$ (virgin PET) to $10^4 \Omega/\text{sq}$ (Ni ion modified PET). The resistivity of the Ni ion modified PET was reduced to $17 \text{ k}\Omega/\text{sq}$ at a pulse voltage of 10 kV for a modification time of 10 min. The reduction in electrical resistivity was not closely related to the PIII parameters. Thus, no correlation could be shown here. Instead, the electrical resistivity was related to the Ni content (at%) in the PET as

shown in Figure 5.9. However, it is noted that XPS cannot accurately resolve the small difference in atomic concentration.

Figure 5.9 Sheet Resistivity of Ni ion modified PET as a function of Ni content

5.6 Summary

The polyethylene terephthalate films (PET) were surface modified by Ni plasma immersion ion implantation and deposition. The substrates are negatively pulse biased and immersed in highly ionised plasma produced by a filtered cathodic vacuum arc. Effects of the pulse voltages and modification time on surface characteristics of the modified samples are observed using a number of characterization methods. XPS C 1s spectra shows chemical changes in the carbon bonds found in PET and the Ni 2p spectra shows the various Ni bonds formed. Ni 2p3 and Ni 2p1 atoms were detected

from the Ni 2p spectra suggested that some Ni atoms exist as precipitates and not only as NiO. From X-ray diffraction measurement, a change in crystallinity in PET and formation of a Ni peak are observed. The electrical sheet resistivity was also found to have fallen significantly to about 17 k Ω /sq.

However, it is not conclusive if the Ni content (at%) varies as a function of pulse voltages and modification time from the present data. XPS cannot accurately resolve the small difference between the Ni content found in modified polymers at these conditions. There might be implanted Ni atoms that affect the total Ni concentration in the modified films and further characterization such as Ni dose measurements will be required.

Chapter 6:

Conductive Atomic Force Microscopy

Conductive atomic force microscope (CAFM) measurements at low temperature were carried out on Ni ion modified PET samples with different electrical resistivities. The measurements offer insights into local electrical properties of Ni ion modified PET. A comparison was made with a carbon ion modified sample at similar PIII parameters and a Ni film deposited on PET by PIID technique. These reference samples showed a contrast in their current profiles. The measured current data at a range of temperature further provide a qualitative analysis into the transport properties of samples with different resistivities.

6.1 Conductive AFM images

Figure 6.1 shows the topography of a virgin PET sample taken with a CAFM probe at a temperature of 250 K. Figures 6.2 and 6.3 show the topography and current images of two Ni ion modified samples of different electrical conductivities at varying temperature between 160 K and 273 K. The two Ni ion modified samples are labelled as Sample I (sheet resistivity $\sim 75 \text{ k}\Omega/\text{sq}$) and Sample II (sheet resistivity $\sim 17 \text{ k}\Omega/\text{sq}$). The currents were found to decrease as the temperature was lowered at a fixed bias voltage, indicating a temperature dependent surface conductivity but no change in the spatial distribution of current was observed.

Figure 6.1 Topography of a virgin PET sample taken with CAFM

Chapter 6 Conductive atomic force microscopy measurements on Ni implanted PET

Figure 6.2 Topography and current images taken with CAFM at different temperatures for insulating Sample I

Chapter 6 Conductive atomic force microscopy measurements on Ni implanted PET

Figure 6.3 Topography and current images taken with CAFM at different temperatures for conducting Sample II

6.2 Profiles of topography and current images between the insulating and conductive samples

The CAFM results were first analysed by comparing the profiles between the insulating and conductive samples. CAFM images taken for the virgin PET, carbon ion modified PET and Ni film on PET were also presented in this section.

6.2.1 Profiles of insulating Ni ion modified PET and carbon ion modified PET

Figure 6.4 illustrates the topographic and current images for sample I (Ni ion modified PET), obtained with $V_s = 3.2 \text{ V}$. V_s is the potential applied to the CAFM probe. The surface topography as shown in Figure 6.4 (a) is observed to be similar to that of a virgin film. Observed pits in the topography can be found as insulating features in the corresponding current image in Figure 6.4 (b).

The current image of insulating Sample I was placed along with a current image for Sample III, a carbon ion modified PET at similar PIII parameters. The selected current image was taken at a lower temperature ($T = 175 \text{ K}$) because it was the clearest image taken for the sample. The current images for the sample did not vary significantly at different temperatures. Although the two samples were modified at similar conditions, the Ni ion modified PET has lower electrical resistivity ($17 \text{ k}\Omega/\text{sq}$) than the C ion modified PET ($1.5 \text{ M}\Omega/\text{sq}$). This is reflected in the current images in Figure 6.4 (b)

and (c) as the Sample III has much lower current values. The conducting clusters are also smaller than Sample I.

Figure 6.4 (a) Topography of insulating Sample I Ni ion modified PET, (b)

Current images of Sample I and (c) Sample III C ion modified PET

6.2.2 Profiles of conducting Ni ion modified PET

Topographic and current images for sample II (conducting Ni ion modified sample), obtained with $V_s = 2.6 \text{ V}$, are illustrated in Figure 6.5. V_s has to be varied for the samples because the saturation points for the measurement of the current were different. The profile of the current image reveals a well-defined granular structure, with conducting features of about 35 nm in dimension, which exhibit high conductivity compared to the surrounding matrix. The surface topography in Figure 6.5 (a) appears to be modified when compared to the virgin film in Figure 6.1 as there

are regular patterns that can be observed. This correlates with the corresponding current image in Figure 6.5 (b).

Figure 6.5 Profiles of (a) topography and (b) current images of conducting Sample II of Ni ion modified PET at $T = 250$ K are plotted

6.2.3 Profiles of CAFM images for Ni film deposited on PET

CAFM was done on a 50 nm thick Ni film was deposited on PET to compare the topography and current profiles with Ni ion modified samples. The substrate biasing conditions were similar at 10 kV, with pulse frequency 900 Hz and pulse duration $10 \mu\text{s}$. Ni film deposition occurred when the sample faced directly to the incoming plasma. During CAFM measurements at similar temperatures, it was found that the Ni film has a constant current distribution, as shown in Figure 6.6. This topography and current distribution is not similar to insulating Sample I or conducting Sample II.

Figure 6.6 Topography and current images of Ni film deposited on PET

6.2.3 Discussion

Ion implantation of C-based materials can also lead to the formation of conducting sp^2 rich clusters, particularly at elevated sample temperatures during implantation [162]. The sample temperature was not monitored during the process. However, the effects of any significant sample heating during implantation should be also evident for sample I, for which these data shows no evidence of clustering. In addition, for carbon ion modified PET (Sample III), CAFM images indicate no evidence of conducting clusters in Figure 6.4 (c). Data has also been presented for Ni film deposited on PET. These results suggest that the conducting features observed for sample II do not arise

from sp^2 clustered carbon, but are thought to be Ni nanoparticles which form an interconnected conducting network.

6.3 Insulator and semi-metallic behavior in Ni ion modified PET

6.3.1 Temperature dependence of electrical properties

The temperature dependence of the local electrical properties can reveal the nature of electronic transport. The limited temperature range of the CAFM experiments permits the qualitative comparison of the electronic behaviour arising in the Ni ion modified samples. For each sample, current images were obtained as a function of temperatures, at a fixed sample bias. Drift to a different location during temperature variation prevents the measurement of current for a defined Ni nanoparticle site, so the temperature dependence of the maximum current, i_T , was considered and evaluated for each current image. The drift occurs because the AFM probe will expand or contract with temperature changes.

Figure 6.7 Histograms showing the current distribution in insulating Sample I and conducting Sample II at $T = 160$ K

A histogram was also obtained from current images showing the current distribution in Sample I and II. Figure 6.7 shows an even distribution of current values in the Ni ion modified PET.

6.3.2 Results and discussion

Many high conductivity features are found to be within a typical range of 100 nA of the measured maximum current, which is taken as the error in i_T . To compare samples I and II, the variation with temperature of a reduced current, $i(T) = i_T / i_{273K}$, is considered, as shown in Figure 6.8. The $i(T)$ data for sample I reveal strong temperature dependence, with $i(T)$ tending towards zero as $T \rightarrow 0$, typical of an insulating phase exhibiting hopping conductivity. Conduction in sample I presumably may arise from tunnelling between both charge centres generated by chain scission and isolated Ni impurities too small to resolve by CAFM. Sample II demonstrates weaker temperature dependence, $i(T)$ tending towards a finite value, of about 0.5, as $T \rightarrow 0$, which is typical of a semimetallic phase. The high contrast in current observed between conducting nanoparticles and the surrounding matrix as shown in Figure 6.5 (b) is consistent with the nanoparticles forming an interconnected conducting network.

Figure 6.8 Temperature dependence curve of insulating Sample I and conducting Sample II

Electronic behaviour of disordered metallic systems have been successfully described by weak localisation and interaction effects [86]. While the presented data in Figure 6.8 is insufficient to quantify the conduction mechanism, including dimensional properties that may exist below the measured temperature range, it is instructive to examine the expected form of $i(T)$ for a system undergoing an I-M transition. For a semimetal, $i(T)$ would take the form $i_D + i_1 T^{1/2} + i_L \ln[\sinh(T/c)^{3/2}]$, where i_D is a constant current, arising from the Drude conductivity and the additional terms arise from interaction and localisation effects [86]. In Figure 6.8 this model is fitted to the data for sample II, making use of the fitting parameters $i_D = 0.35$, $i_1 = 0.035$, $i_L = 0.01$, and $c = 55K$. Values of c and $i_L/i_1 \sim 10$ are in accord with bulk sheet conductivity measurements performed on carbonised ion-implanted polymer films [83], for which $c = 56 - 59K$.

For the experiments described in this section, when $T \gg c$, any weak localisation effect was expected to therefore be 3D at these temperatures. In contrast, the insulating system $i(T)$ takes the form, $i_0 \exp[-(T_0/T)^\gamma]$, which is fitted to the data for sample I in Figure 6.8 using the parameters $i_0 = 6.5$, $\gamma = 0.64$, and $T_0 = 700\text{K}$. γ is consistent with bulk sheet-resistivity measurements of ion-implanted polymers, which have shown $\gamma = 0.25 - 0.74$ with increasing dose [84, 163].

6.5 Thermal spikes effects due to ion modification in polymers at medium energies

Metal ion implantation of polymers causes precipitation and cluster formation as observed from the CAFM measurements. Thermally induced diffusion may be used to explain this phenomenon since thermal spikes are also associated with melting and formation of amorphous regions [61, 78]. Thermal spikes create a larger modified volume where the melt region will eventually quench into an amorphous state. The quench time depends on the size of the thermal spike radius and the thermal conductivity of the target. The thermal spike size and quench time caused by a Ni ion implanted into PET are of interest and are examined in detail in this section.

Many recent papers discuss the thermal spikes from ion implantation of light and heavy swift ions [79, 164-166] in different materials. Lower ion energies may be used in plasma source ion implantation [42, 90] and at such energies, there is a higher proportion of nuclear energy loss in the target. However, some thermal spike models

ignore the mechanism of thermal spike due to nuclear energy loss because the electronic stopping power far exceeds the nuclear stopping power. In the case of a Ni ion modified polyethylene terephthalate (PET), the nuclear stopping power is dominant. In Figure 6.9, the nuclear and electronic stopping power is plotted as a function of ion energies and it shows that nuclear stopping power is dominant for energies up to 600 keV. Thermal spike models that focus on thermal spikes by electronic stopping power becomes insufficient to explain any thermal related effects of ion implantation using lower energies.

Figure 6.9 Nuclear and electronic stopping powers for nickel ion implanted into PET using TRIM at a range of ion energies

The modification process viewed at the atomic level consists of the formation of vacancies and recoils through primary and secondary collisions of incident ions with target atoms. Along the ion's trajectory, there is the degradation (chain scission) and gelling (cross-linking between the free radicals and target atoms) of the polymers. The extent of chain scission and cross-linking in the modified layer is correlated to the electronic and nuclear energy loss mechanisms of the ion through the polymer. In

electronic energy loss, most of the energy of the incident ion is transferred to the target atoms' electrons and materials with strong electron-phonon coupling are sensitive to electronic energy loss [165]. Nuclear energy loss arises from collisions between the ion and the target nuclei, which cause atomic displacements and phonons. Displacement occurs when the colliding ion imparts energy greater than a certain displacement threshold, E_d , to the target atom. If the knock-on atoms are unable to be displaced from their sites, their energy dissipates as lattice vibrations i.e. phonons. E_d is the energy that a recoil requires to overcome the binding forces and to move more than one atomic spacing away from its original site [167].

A mechanism for the formation of thermal spikes by nuclear energy loss of a heavy ion in polymers is examined through a discussion on energy loss mechanisms and related thermal spike effects. Light ions are not considered as their magnitudes of nuclear energy losses are much smaller and the damage distributions are different with light ions. Nuclear collisions between the ion and the target atoms are the main cause of recoils atoms and these recoil atoms also loses their energy through nuclear and electronic processes until all excited electrons and atoms are thermalized by dissipating energy through phonons and plasmons. Lee [167] discussed the contributions of the recoils atoms in the ion-beam modification of polymers and calculated the electronic losses of the recoil atoms using an approximation to the LSS theory developed by Norgett *et al.* [168] It was also noted that the phonon contribution from the ion is small compared with that of the recoils because one ion produces many recoil atoms. Thus, in the ion implantation of polymers, the recoil atoms play an important role as a large percentage of energy losses occur through

recoil atoms. Using TRIM, the ion's energy losses to recoil atoms by Ni ion implantation are compared at different ion energies and these results are summarized in Table 1. The main energy loss at 20 keV is by the recoils through phonons (strong lattice vibrations). High nuclear collisions results in a large energy loss to recoil atoms and in a polymer target such as PET, the recoil atoms are made of lighter elements such as H, C and O. It becomes clear that at medium energies, nuclear collisions between the ion and target atoms play a role of displacing target atoms and transferring most of the ion's energy to the lighter polymer atoms. In this process, recoil atoms are created. Although they have lower energies than the incident ion, they continue to transfer their energy to other nearby atoms, forming a collision cascade. As the recoil atoms' energies are less than the incident ion, their nuclear energy losses are still more significant than their electronic energy losses and energy losses occur mainly through phonons.

Table 6.1 Calculation of the stopping powers and the percentage energy losses by ions and recoils

Energy (keV)	$\frac{dE}{dx}_{nuclear}$	$\frac{dE}{dx}_{electronic}$	% Energy Loss by ion			% Energy Loss by recoils		
			Ionization	Vacancies	Phonons	Ionization	Vacancies	Phonons
2	3.370	0.119	4.69	3.29	9.37	19.80	2.99	59.86
20	5.751	0.375	8.03	1.16	4.13	29.26	3.28	54.15
200	4.615	1.542	10.14	0.19	0.59	53.64	2.31	33.13
2000	1.430	4.376	40.43	0.08	0.32	50.77	0.51	7.89

6.5.1 Estimation of a thermal spike's radius

The cylinder shape model is derived from a typical single Ni ion trajectory implanted at the maximum ion energy of 20 keV into polyethylene terephthalate (PET). The cylindrical-shaped thermal spike is used rather than the hemispherical model as this shape closely resembles a single ion cascade. This cylindrical volume acts like a heat source where it is assumed to have obtained a molten form and heat is diffused out from the centre of the heat source. The projected range for a Ni ion implanted into PET was found to be $\lambda = 277 \text{ \AA}$ by TRIM. The radius r_o of the molten thermal spike (initial source radius) is calculated using the following equations which assumed all the energy provided in a single ion went into the melting of the polymer uniformly across the spike volume (from the law of energy conversation):

$$mc_p(T_m - T_o) = eE_o \quad (6.1)$$

$$m = \pi r_o^2 \lambda \rho \quad (6.2)$$

Combining the two equations give us

$$r_o = \left[\frac{eE_o}{c_p \pi \lambda \rho (T_m - T_o)} \right]^{1/2} \quad (6.3)$$

where e is the electron charge, E_o is the incident ion energy, T_m is the melting point of PET, T_o is the room temperature, ρ and c_p is the density and specific heat capacity of the polymer, respectively. The thermal spike now resembles a two dimensional cylinder with source radius r_o and projected length λ . r_o is taken to be zero at the surface of the polymer at the point of ion impact.

The heat diffusion equation is used to simulate the diffusion process of the thermal spike to its surroundings and is written as:

$$\nabla^2 T = \frac{c\rho}{\kappa} \frac{\partial T}{\partial t} \quad (6.4)$$

where c_p and ρ is similar to the terms described in equation (3) and κ is the thermal conductivity of PET. Using Femlab [169], a cylinder model has been built and the software applies the finite element method to solve the equation. It is convenient to assume that the temperature is constant within the spike boundaries and drops to the ambient value of 297 K at the boundaries [78, 170].

The boundary conditions are as follows:

1. The boundary above the point of ion impact is assumed to be a heat insulator and no heat diffuses out of that boundary. In practical experiments, this area is exposed to vacuum and radiation conduction is not considered here.
2. At $t=0$, within the cylinder whose dimensions are $r_o = 83.7\text{\AA}$ and $\lambda = 277\text{\AA}$, the temperature is the melting point of PET at $T_m = 583\text{K}$.
3. Outside the cylinder, the temperature is assumed to at room temperature, $T_o = 297\text{K}$.

6.5.2 Estimation of quenching time

Firstly, several physical aspects of the PET were considered. PET is a type of semi-crystalline thermoplastic, which will soften when heated. It has a density of $1.397 \times 10^3 \text{ kg m}^{-3}$, specific heat capacity of $1.3 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$ and thermal conductivity at room temperature of $0.275 \text{ W m}^{-1} \text{ K}^{-1}$. There is no distinct glass transition temperature

(T_g) because crystalline and amorphous structures have slightly different T_g . The amorphous chains go through the glass transition transformation but the crystalline portions may remain rigid until it reaches a higher temperature. Thus, at 343 K there is movement of the amorphous regions which indicates the start of the glass transition period. This indicates that in plasma conditions where the temperature is about 358 K, the polymer substrate has already started to soften. The main transition is at the melt temperature ($T_m = 583$ K) where the crystalline regions will break down and the polymer will be in the liquid state.

Figure 6.10 Cooling profile calculated by the analytic model for a thermal spike in PET

Figure 6.10 shows the cooling rate as a function of time at the point of impact of the ion on the polymer. The surface temperature is taken at $r_o = 0\text{\AA}$. From this figure, the quench time is the period where temperature drops from 583K to 343K and is determined as $t_q = 628\text{ps}$. In comparison with an earlier simulation, this quench time is about twelve thousand times longer than in ta-C films.[78]

Figure 6.11 Simulation showing the heat dissipation from a cylinder shaped thermal spike at different times (a) $t = 1 \text{ ps}$ and (b) $t = 628 \text{ ps}$.

Figure 6.12 Temperature profile at the centre of the cylinder (point of impact) is shown at $t = 628 \text{ ps}$.

The diffusion of heat from the heat source towards the polymer substrate is illustrated in Figure 6.11. Fig 6.11 (b) illustrates that at $t = 628\text{ps}$, the entire cylinder has reached a temperature of 343K or lower. In Figure 6.12, the temperature profile shows the spread of the thermal spike at $t = 628\text{ps}$ as the thermal spike cools towards room temperature.

6.5.3 Discussion

By considering the dose rate used in experiments, where a dose rate of $3.3 \times 10^{14} \text{ ions.cm}^{-2}.\text{s}^{-1}$ was used to implant Ni ions into PET, the possibility of another ion arriving within the spike area during the thermal spike is determined. Each thermal spike has a radius of $83.7\text{\AA}$ (size of area, $\pi r_o^2 \approx 22000\text{\AA}^2$), which quenches in 628ps . Based on the dose rate, it is determined that one ion arrives in approximately 1.4ms within the thermal spike's effective area. Thus, it is highly likely for the thermal spike to quench completely before another ion can arrive in the vicinity, limiting the thermal spike effect to a single ion. Thus, the thermal spike based on a single ion is sufficient because the quench time is found to be sufficiently short that the thermal spikes of multiple ions do not overlap each other and cause heat accumulation. However, the same concept may not be applied to the damage defects actually caused by ion implantation because at high dose i.e. $10^{16} \text{ atoms/cm}^2$, the damage regions will overlap each other.

It is also noted that the modification of PET by PIII can result in a range of ion energies due to real pulse rise time but only the maximum energies are considered in

an ideal thermal spike model. The insulating nature of the polymer and the real pulse rise time is likely to cause a lower pulse voltage that affects the ion energies during ion implantation.

Metal ion implantation of polymers causes precipitation and cluster formation as observed from the CAFM measurements. Evidence of a longer quench time found in the simulation may allow thermal induced diffusion to occur and this may affect the formation of clusters. A mechanism for the implanted atoms to form precipitates or larger cluster is illustrated in Figure 6.13.

Figure 6.13 Diffusion process induced by an incident ion (a) low dose phase, (b) high dose phase and the induced thermal spike radius and (c) cluster formation.

Diffusion of metal precipitates can be encouraged by two factors: ion dose and temperature. Thermal spikes by incident ions cause melting of the polymer and a molten region is formed. Implanted Ni atoms or precipitates have a higher melting temperature and is unlikely to be affected by the thermal spike. During the quench time of a thermal spike, the molten region allows a greater movement of atoms and this assists in cluster formation.

In the experiments results as discussed in above sections, it was shown that large clusters does not form in carbon ion implanted PET, although there are smaller precipitates observed and the overlapping of highly graphitized regions promotes conductivity. The reason for this may be that carbon ions easily form bonds with the carbon-based polymer, resulting in sp^2 bonds rather than clustering of precipitates.

6.6 Summary

In this chapter, CAFM has been used to perform nano-scale current imaging at low temperature of Ni-ion implanted PET, which demonstrated a reduction in bulk sheet resistivity as the Ni dose was increased. The profiles of the current images was compared with CAFM images for carbon ion modified PET (Sample III) and Ni film deposited on PET. The Ni ion modified samples (insulating and conducting) have shown different profiles from Sample III and Ni film. There is preliminary conclusion that the conducting clusters are Ni nanoparticles which form an interconnected conducting network. Temperature dependence of the local electrical conductivity was next examined by measurement of currents between 273 K and 160 K. The analysis of profiles of current images and the temperature dependence graphs suggest that there is evolution in local conductivity from a spatially homogeneous insulator (Sample I) to an interconnected network of Ni nanoparticles (Sample II).

Thermal spike due to single ion in ion implantation of polymers was then examined to explain a mechanism for the formation of Ni nanoparticles. The thermal spike radius for a single Ni ion at 20 keV was estimated with the aid of TRIM. A cylindrical model

Chapter 6 Conductive atomic force microscopy measurements on Ni implanted PET

was used to represent the thermal spike. Heat diffusion equation was used to simulate the diffusion process of the thermal spike to its surroundings. The quenching time was determined from the simulated results and was found to be significantly longer than for metals or semi-conductor materials because of the low thermal conductivity of PET. A mechanism for the formation of Ni nanoparticles was illustrated.

Chapter 7:

Conclusion and Recommendations

7.1 Conclusion

The surface modifications of polymers by carbon and nickel plasma immersion ion implantation were carried out successfully using the combined technique of FCVA and PIII. In the experiments, deposition was minimized by the substrate's orientation to the plasma and the modified layer enabled the characterization of the changes in the surface properties due to ion-polymer interactions.

XPS was used to determine the chemical bonds before and after surface modification. In both polymers, there was disappearance of some original chemical bonds and oxidation. For C implanted UHMWPE, there was some oxidation as observed by the formation of C-O and C=O bonds which is attributed to environmental oxidation after removing the samples from the vacuum chamber. There was a reduction in C-H bonds and there was formation of C-C bonds as observed by Raman spectroscopy. For Ni implanted PET, there was the reduction of C-O and O=C-O bonds as shown in C 1s spectra. Formation of new Ni peaks and the Ni atomic concentration could be determined by XPS. However, the XPS cannot accurately resolve the atomic concentration for the samples modified at different conditions as the difference in atomic concentration is small.

Another major consequence of the surface modification of polymers was the increase in electrical conductivity for both carbon and nickel ions modified polymer. The electrical characteristics of Ni ion modified polymers were examined in greater details. Ni implanted PET was examined under the CAFM and it was found that the more conducting sample has well-defined conducting clusters of about 35 nm that could be seen in the current images. Attempts were made to determine if the conducting clusters were Ni nanocrystallites. However, XRD measurements were not conclusive to determine this because the PET diffraction patterns were more distinctive than the Ni peaks. However, from comparing the profiles of different samples under CAFM, it is very likely that the conducting clusters are Ni nanoparticles from a modified layer rather than sp^2 conducting clusters or a layer of Ni film deposited on PET. The electronic transport mechanism could be induced from measurements of the currents during CAFM experiments and supported theories made by previous researchers on ion-implanted polymers.

Finally, a mechanism for the formation of Ni nanoparticles in Ni ion modified polymers was proposed. Thermal induced diffusion is a likely process for the Ni precipitates to form larger and well-defined conducting nanoparticles. Thermal spikes that occurred during ion implantation might allow for diffusion and the thermal spikes concept in PIID was examined. Thermal spikes provide sufficient energy and heat transfer to the substrate, causing the melting of polymer into a liquid state before quickly quenching and solidifying. Polymers have a lower thermal conductivity and melting point compared to materials like Si and metals and it was insightful to examine the quenching time of a thermal spike in polymer. Using a cylindrical model

for the thermal spike and heat diffusion equations, the thermal spike quenching process was simulated. The quenching time was found to be significant, providing good evidence that thermal spikes are relevant to the surface modification process.

7.2 Recommendations for further research

In this section, recommendations for further research are briefly discussed. Firstly, it has been difficult to provide a good depth profile using TRIM due to its differences with the conventional ion implantation. The use of the integrated current to estimate the dose rate is reasonable but may not provide a good estimate of the retained dose which is affected by many parameters due to the high pulse voltages. Thus, the surface modification process by PIID process can be further optimized by examining these characteristics in greater detail.

Another area for future development is the characterization of polymers by TEM. The analysis can be supported by Electron Energy-Loss Spectroscopy (EELS) to improve spatial resolution and provide chemical information.

The potential of this surface modification technique for polymers have been demonstrated. This can be extended to other insulator materials such as fused silica. Carbon PIID may be applied in the area of forming nanocrystalline diamond (NCD) films [171-173]. In past work [174, 175], it has been demonstrated that carbon ions, in the order of MeV energies, implanted into fused silica and subsequently annealed in forming gas (4% H₂ in Ar) will form NCD. NCD was formed under a depth of 140

nm with cluster size ranging from 5 to 40 nm. Carbon ion implantation on fused silica using PIII can result in a much shallower depth (about 50 nm) and it will be interesting to see if formation of NCD on the surface of materials can be achieved by PIII. The use of PIII technique also has the advantage of allowing high dose-rate implantation on large substrates, which can easily be patterned or used for large area protective coatings. Initial experiments have led to the formation of carbon nanoclusters with good mechanical properties [176]. Optimization of the process by varying process temperatures and improving the conditions for formation of NCD, e.g. reducing the oxidation of implanted carbon at high temperature may lead to higher sp^3 content.

Metal PIIID has much potential in the electrical applications of surface modified polymers. Future work can focus on developing a method to enable buried electrodes, especially in arrays, in polymeric materials for attractive applications in flexible electronics and biosensors. The possibility of fabrication of a sandwich structure insulator/conductive layer/insulator by ion implantation have been demonstrated in implanted polyethylene and polyamide-6 films with 60 to 100 keV B^+ ions [68, 177]. One alternative to developing buried electrodes is the use of ion modified electrically conductive polymers such as metal PIIID modified PET demonstrated in this thesis. A spin coated layer [178] or further modification can be done to the surface of the ion modified polymers to embed the conducting layer. This structure can be applied in the development of biosensors where the ability to attach biomolecules covalently to precise areas of a surface is desirable [179]. A buried electrode can provide an electrostatic force for manipulation and immobilization of proteins [179]. However,

the embedded electrode has to be very near the surface with a thin layer of insulator. The precision of the insulator thickness (~ 50 nm) can be controlled using this surface modification technique. Plasma immersion ion implantation has an added advantage of enabling large area modification for biosensor arrays [180, 181].

Figure 7.1 Principle of operation of a biosensor consisting of a biological sensing element in close contact with a physico-chemical transducer such as electrode which produces a quantifiable electrical signal [182]

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