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Metal-Polymer Nanocomposites By Plasma Immersion Ion Implantation And Deposition Technique

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To Cathy and our beloved parents.

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Summary

Plasma immersion ion implantation and deposition (PIII&D) is used to fabricate metal-polymer nanocomposites with metal nanoparticles with sizes of 5 – 20 nm embedded in a polymer matrix. Because of quantum confinement effects from these metal nanoparticles as well as their interactions with the surrounding polymer matrix, metal-polymer nanocomposites possess novel mechanical, electrical, optical and biomedical properties that are not obtainable in their bulk forms. This thesis is dedicated to the fabrication, characterization, application and stability of these high performance polymers.

PIII&D applies a negatively pulsed bias voltage in the range of 1 – 50 kV to the substrate. Together with metal plasmas generated from a filtered cathodic vacuum arc (FCVA) system, various types of metal-polymer nanocomposites have been fabricated. The formation of metal nanoparticles is controlled by the cooperative effect of ion implantation and ion condensation incorporated in the PIII&D process, resembling conventional ion beam mixing (IBM).

The first material fabricated was titanium-polyethylene terephthalate (Ti-PET) nanocomposite. The topography of Ti-PET nanocomposite was changed from a smooth and flat surface to a “self-organized” pattern with arrays of conical “hillocks” and “craters” at the nanoscale. Such a surface pattern was ascribed to the interplay between ion sputtering and surface re-deposition processes caused by ion implantation in the PIII&D process. The conductive-probe atomic force microscopy (CP-AFM) measurements showed that Ti nanoparticles with sizes of 10 – 20 nm were randomly embedded in the PET matrix. The measurement of temperature-dependent electrical conductivity revealed that electron transport in

Ti-PET nanocomposites was controlled by the variable-range hopping (VRH), as predicted by Mott's law with a stretched-exponential relationship of conductivity σ and temperature T . In addition, other effects such as "ageing" and the influence of the supporting polymer on the electrical conductivity were also investigated. Finally a new equation considering both temperature and the "ageing" effect was proposed.

A Ti-polystyrene (Ti-PS) nanocomposite on commercial PS substrates was the next material fabricated by PIII&D. X-ray photoelectron spectroscopy (XPS) results revealed complex compositional and chemical states on the surface layer. XPS depth profiling showed that Ti nanoparticles were only oxidized at the top surface layer (~ 10 nm) but kept their metallic state in the embedded part. It was proposed that the surrounding PS matrix inhibited the migration of oxygen to react with them. It was the first time that the excitation of localized surface plasmon resonance (LSPR) at the interface of Ti nanoparticles and a polymer matrix has been observed without annealing. The position of the LSPR peak at 337.5 nm was consistent with the condition provided by the Mie theory. Broadband absorption ranging from ultraviolet (UV) to near infrared was observed and was attributed to the fractal nature of the nanocomposites.

Next, Ti-PS nanocomposites fabricated on PS thin films were utilized as a biomaterial to enhance protein immobilization. A peroxidase protein assay based on the enzymatic property of soybean peroxidase (SBP) to the oxidation of 3,3',5,5'-tetramethylbenzidine (TMB) has been carried out to quantify the amount of protein immobilized on solid surfaces. This assay showed that SBP immobilization had increased from 1.73 ng/cm² on pristine PS thin films to 3.0 ng/cm² on Ti-PS nanocomposites. The mechanisms of enhancement has been

attributed to the altered physiochemical properties of Ti-PS nanocomposites, such as roughness, surface energy and surface functional groups.

Finally, the stability of polymer thin films upon the PIII&D process was studied. It was found that when plasma density was high, even thermodynamically stable, thick PS films may degrade and undergo dewetting in the PIII&D process. The time evolution dewetting patterns were captured and the mechanism was determined to be heterogeneous nucleation, in contrast to spinodal dewetting in thermodynamically unstable films. In addition, regular polygonal rims were found to be abundant on dewetted films on narrow experimental conditions, mostly 3 – 4 min processing time. This has been attributed to fingering instability of rims where a balance was established between the driving force of the temperature gradient induced surface stress and the resistive forces of friction, surface tension and the Laplace pressure.

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Abbreviations

AFM	Atomic force microscopy
ATR	Attenuated total reflection
BE	Binding energy
CA	Contact angle
CASING	Cross-linking by activated species of inert gas
CNT	Carbon nanotube
CP-AFM	Conductive-probe atomic force microscopy
DNA	Deoxyribonucleic acid
DW	Distilled water
FCVA	Filtered cathodic vacuum arc
FET	Field-effect transistor
HRP	Horseradish peroxidase
IPA	Isopropanol alcohol
LET	Light emitting diode
LET	Linear energy transfer
LW-AB	Lifshitz-van der Waals/acid-base approach
PA	Polyacetylene
PANI	Polyaniline
PC	Polycarbonate
PDI	Polydispersity index
PE	Polyethylene
PET	Polyethylene terephthalate
PI	Polyimide

Abbreviations

PIII	Plasma immersion ion implantation
PIII&D	Plasma immersion ion implantation and deposition
PMMA	Polymethyl methacrylate
PP	Polypropylene
PPy	Polypyrrole
PS	Polystyrene
PVC	Polyvinyl chloride
QD	Quantum dot
R _g	Radius of gyration
RNA	Ribonucleic acid
SAED	Selected area electron diffraction
SBP	Soybean peroxidase
SEM	Scanning electron microscopy
SP	Surface plasmon
SPP	Surface plasmon polariton
SPR	Surface plasmon resonance
SRIM	Stopping range for ions in matter
TEM	Transmission electron microscopy
T _g	Glass transition temperature
TMB	3,3',5,5'-tetramethylbenzidine
VRH	Variable-range hopping
XPS	X-ray photoelectron spectroscopy

CHAPTER 1 **Introduction**

1.1 Background

The word “*polymer*” is derived from the Greek where “*poly*” means “many” and “*mer*” means “part”. This word explicitly describes the structure of a polymer, i.e., a group of macromolecules connected by monomers via covalent bonds. Various polymers have been applied in industries due to their excellent bulk properties, such as flexibility, low density, high strength-to-weight ratio, chemical resistance and ease of formation. However, further applications are severely limited by inferior surface properties, e.g., low surface energy that leads to poor adhesion to metal films, inherent softness that leads to relatively high wear rate, etc. These limitations can be overcome largely by surface modifications. In the past, many modification techniques have been developed, such as flame treatment, corona discharge, chemical etching, ultraviolet, plasma treatment, and ion implantation (see Ref. [1, 2] and references therein). The properties that can be altered or improved include surface morphology, surface energy, hydrophobicity or hydrophilicity, surface functional groups, electrical conductivity, etc. Unlike the synthesis of new polymeric materials such as conductive polymers and hydrogels which may take many years to develop, polymer modification provides a faster track in obtaining optimized conditions on suitable polymers.

Recently, nanoscience and nanotechnology has opened an effective way of obtaining polymers with promising mechanical, electronic, optical, and magnetic properties [3, 4]. One of the most popular products is the polymer nanocomposite which has a structure of nanosized constituents embedded in a polymer matrix [5-

8]. These nanosized constituents as well as their interactions with the surrounding polymer matrix give the product combined properties that are not obtainable from their bulk counterparts. Furthermore, the macroscopic properties of polymer nanocomposite can be tailored through adjusting the microscopic parameters, such as size and shape of the constituents, the distance between two neighbouring constituents, and arrayed or disordered arrangements, thus assuring it an important role in nanotechnological applications as well as fundamental studies.

A short list of the constituents includes layered clay, fibres, carbon nanotubes (CNTs), metal nanoparticles, metal oxide nanoclusters, semiconductor quantum dots (QDs), biological components, and so on. In recent years, metal-polymer nanocomposites where metal nanoparticles with sizes of 1 – 50 nm embedded inside a polymer matrix have received considerable interest. Many interesting properties, such as photoluminescence, surface plasmon resonance (SPR), superparamagnetism, and dielectric relaxation, have been exploited for a number of present and future technological demands.

In this section, brief descriptions on bulk polymers and polymer thin films will be firstly given, followed by a review on polymer modifications. The fundamentals and applications of polymer nanocomposites will also be introduced.

1.1.1 Bulk Polymers

The historical development of polymers has experienced several stages [9]. In the ancient time, humans used natural polymers, such as food, wood, and fibres, for their basic life survival. These natural polymers are still extensively used in modern society. As early as the 19th century, studies of polymers in a scientific way had emerged. The fabrication of the first synthetic polymer *Bakelite*[®] in 1909

was the next milestone. Synthetic polymers developed rapidly in the following years and eventually led us to the “plastic” industry. Today, synthetic polymers are one of the mostly produced and used materials. [Table 1.1](#) lists some common natural and synthetic polymers together with their structure formulae, including silk, rubber, deoxyribonucleic acid (DNA), protein, polyethylene (PE), polystyrene (PS), polyimide (PI), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polymethyl methacrylate (PMMA).

In the 1970s, new kind of polymer were synthesized; conjugated organic polymers, also known as “synthetic metals” or conductive polymers [\[10\]](#). These polymers, although showing insulating or semiconducting properties in their intrinsic state, become highly conductive after proper doping [\[11\]](#). The conductivity through degenerate π -bonds in the molecules can be 10 orders higher than that of their undoped states. The undoped structures of three conductive polymers, polyacetylene (PA), polyaniline (PANI), and polypyrrole (PPy), are given in [Table 1.1](#). Conductive polymers have many interesting properties and are of particular importance in plastic electronics, a subject that aims to manufacture integrated circuits using organic materials. I am not going to discuss them further as they are out of the scope of this thesis.

Another type of important polymers are biopolymers, including starch, protein, deoxyribonucleic acid (DNA), ribonucleic acid (RNA) and hydrogel [\[12\]](#). Biopolymers play pivotal roles in biological related processes, e.g., most biological syntheses use enzymes, a kind of protein, as catalysts. A particular feature of biopolymers is that their functionalities are closely related to their structures. Taking proteins as examples, most proteins have at least three levels of structure, primary, secondary and tertiary. Once their native structural conformations are

lost upon external disturbance (e.g., temperature), their biological activities may also be lost, a phenomenon known as protein denaturation [13].

Name (Abbr.)	Structure	Name (Abbr.)	Structure
<i>Natural polymers</i>		<i>Synthetic polymers</i>	
Silk		Polyethylene (PE)	$\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$
Rubber	$\left[\begin{array}{c} \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array} \right]_n$	Polystyrene (PS)
DNA		Polyimide (PI)
Protein*		Polyethylene terephthalate (PET)
<i>Conductive polymers</i>		Poly(vinyl chloride) (PVC)	$\left[\begin{array}{c} \text{CH} \quad \text{CH}_2 \\ \quad \\ \text{Cl} \end{array} \right]_n$
Polyacetylene (PA)	$\left[\begin{array}{c} \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$	Polytetrafluoroethylene (PTFE)	$\left(\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \text{C}-\text{C} \\ \quad \\ \text{F} \quad \text{F} \end{array} \right)_n$
Polyaniline (PANI)		Poly(methyl methacrylate) (PMMA)	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C}-\text{CH}_2 \\ \quad \\ \text{O}=\text{C} \quad \text{O}-\text{CH}_3 \end{array} \right)_n$
Polypyrrole (PPy)

*The protein shown here is soybean peroxidase (SBP) protein, from Harris, N. and Gijzen, M. See: <http://www.expasy.org/cgi-bin/niceprot.pl?Q9XFI6#ref>.

Table 1.1 A list of some common polymers and their structures.

The process of synthesizing polymers is called polymerization. Two ways of polymerization are often found, condensation polymerization and addition polymerization. Condensation polymerization occurs when monomers react together with the elimination of small molecules whereas addition of

polymerization does not involve any elimination of small molecules and the long chain is joined together by breaking of the original double or triple bonds. Polymerization is usually carried out with catalysts [14]. The final product of polymerization contains chains with a range of lengths and it is only possible to specify an average molecular weight such as the number-average molecular weight M_n , or the weight average molecular weight M_w :

$$M_n = \frac{\sum M_i N_i}{\sum N_i} \quad (1.1)$$

$$M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i} \quad (1.2)$$

where M_i and N_i are the molecular weight and relative number of the species containing i repeating units respectively. Polymers can have a broad range of molecular weight ranging from 1,000 to 2×10^6 g/mol, and in some cases it may reach 10^7 g/mol. The ratio of weight average molecular weight to the number average molecular weight, or M_w / M_n , is called the polydispersity index (PDI), a measure of the distribution of molecular mass in polymers.

In contrast to ceramics or metals which have microstructures containing a large amount of small molecules compacted in a certain volume, the structures of polymers comprise linear or branched chains with or without side groups attached to them. As the intermolecular forces are weak van der Waals interactions, polymers are usually associated with physical properties like softness, lightness, and flexibility. The main element in polymer chains is carbon (C) which has four valence electrons. All electrons can form covalent bonds with neighbouring carbon or other atoms, inducing a large variety of polymer chains. Other common elements in polymers include oxygen (O), hydrogen (H) and nitrogen (N). It is

noticed that the microstructure of polymers is of paramount importance in determining their physical and chemical properties. Two polymers having the same molecular composition may exhibit very different properties if their microstructures are different. The structural parameters include, but are not limited to, the chain linearity, the tacticity, and the crystallinity. A discussion of these follows.

There are three different shapes of polymer chains, linear, branched and grafted. Linear chains consist of one single chain in each molecule whereas branched chains have one or more constituent branches attached to the main chain. Compared to linear chains, long side branches in branched chains may induce entanglements hence increase polymer strength, toughness, the glass transition temperature T_g (defined as the temperature point for polymers to transit from the glassy state to the rubbery state), and so on. If the side branch has a different composition or configuration from the main chain, it is then called a grafted polymer. If four or more distinct chains emanate from the same branch point, a crosslink is suggested. A high volume of crosslinks can turn a polymer matrix into a network, as in the extreme case of a gel where all chains have linked into one molecule. Gels are an important material in modern protein and tissue engineering while a surface with grafted polymers has wide application in biomedical engineering [15, 16].

The tacticity of a polymer describes the relative stereochemistry of chiral centers in neighbouring structural units within a macromolecule. Three different tacticities, isotactic, syndiotactic and atactic, are often identified. Figure 1.1 shows the tacticities using polypropylene (PP) as an example. The properties that can be

influenced by tacticity are rigidity, flexibility, crystallinity, melting point, solubility, etc.

Figure 1.1 The tacticity of PP: (a) isotactic (b) syndiotactic and (c) atactic.

Most polymers are amorphous, i.e., the chains are randomly arranged. However, there are also semi-crystalline polymers which have three-dimensional (3-D) ordering at the atomic scale, e.g., intramolecular folding or stacking of adjacent chains. An increased degree of crystallinity tends to give polymers an opaque appearance, rigid structure, and lower gas permeability, as demonstrated by amorphous and semi-crystalline PET [17].

1.1.2 Polymer Thin Films

Polymer thin films are formed when the size of bulk polymers is reduced into the micro- or nano-metric scale in one dimension. They have been applied in many fields, e.g., photoresists, packaging, gas barriers, membranes, biosensors, thin film transistors, etc [18-23]. Many methods for the synthesis of polymer thin films have been developed over the past few years, such as solvent casting, thermal spray, spin-coating, self-assembly, floating, Langmuir-Blodgett method, evaporation, sputtering, laser deposition, and plasma polymerization [23-33]. The

selection of a suitable method is dependent on the requirements of thickness and composition of polymer thin films. In brief, solvent casting and thermal spray usually give “thick” films with high roughness; spin-coating is well suited for preparing single and multilayer polymer thin films with high quality; Langmuir-Blodgett is used for polymer molecules with polar groups; plasma polymerized polymers usually have high density of crosslinking, are pin-hole free, and can be grafted with various functional end groups.

Polymer thin films have unique microstructures that are different from bulk polymers. Likewise, the microstructures undoubtedly affect their macroscopic mechanical, physical, and chemical properties. For example, the conformation of polymer chains changes from an isotropic-coil form in the bulk structures to an elliptical form, with the orientation of chain segments parallel to the surface [34, 35]. This is caused by the proximity of the gravity point to the surface of the polymer chains. The range of the influenced regions is about $2R_g$ to the surface, where R_g is the radius of gyration for polymer chains, given in the form:

$$R_g = \frac{1}{\sqrt{6}} a \sqrt{N} \quad (1.3)$$

with a the length of monomer and N the degree of polymerization. As a result of such a conformation, Ube *et al.* found that PMMA chains in thin films were not stretched with the elongation of films; instead, they slipped on the course of stretching [36].

Another feature in the microstructure of polymer thin films is that the density of chain ends is large at the surface due to entropic effects [37]. Chain ends from the region $2R_g$ are enriched at the surface of thickness d (typically 1-2 nm) according to:

$$\rho_e = 2a/d \times N^{1/2} \quad (1.4)$$

with a the sector length. This enrichment may affect the glass transition temperature T_g , the dielectric relaxation, as well as the kinetic behavior on the surface [38-40].

1.1.3 Polymer Modifications

Using various modification techniques to alter or improve the surface properties of polymers has been an area of intense research. Polymers with excellent bulk properties very often do not possess the surface properties required for specific applications. With proper polymer modification, the desired surface properties can be achieved without affecting their bulk properties. For example, PE is very inexpensive and easy to process, has excellent mechanical properties and good resistance to weathering. It has been used in huge quantities to make films in the packaging industry. However, its printability and bondability are far from satisfactory because of chemical inertness and low surface energy. Surface modifications, such as plasma treatment, have been successfully adopted to enhance the printability and bondability of PE [41]. Another example is that in printing and bioengineering, polymer films are required to be wettable on one hand so that inks or biomolecular solutions can be transferred onto the surface, but not wettable enough to induce smearing of the printed images. By using self-assembled monolayers of alkanethiols on gold to control surface wettability, *Tan et al.* obtained the optimized wettability for protein printing [42].

Conventional modification techniques include flame, corona discharge, glow discharge, chemical etching, plasma treatment, ultraviolet, gamma rays, surfactants and additives, ion and electron beams, self-assembled monolayers, and so on [2,

20, 43-48]. In literature, each modification technique and their respective capabilities of changing the property have been elaborated. Some examples are, *Chung et al.* used *p*-xylene diamine in methanol to chemically crosslink the polyimide phase in a polymer blend and found that the gas selectivity for H₂/CO₂ and H₂/N₂ has been significantly improved [20]; *Hutchings et al.* briefly reviewed the application of end-functionalized polymers on bulk polymers to obtained bespoke surface properties such as hydrophobicity, wettability, chemical resistance and biocompatibility [43]; *Lee* reviewed the fundamentals and applications for ion-beam modifications on polymers [45].

Among all of these techniques, plasma treatment is of particular interest because of its versatility [44, 46, 49]. The advantages of plasma treatment include simple setup (although the plasma process can be complex in the experiment), solution-free, efficient, uniform modification, etc. Common plasma sources used are inert gas plasmas (e.g., He, Ar, Ne, etc.), oxygen-containing plasmas (e.g., O₂, H₂O, etc.), nitrogen-containing plasmas (e.g., N₂, NH₃, etc.), carbon-containing plasmas (e.g., C₂H₂, CH₄, etc.) and fluorine-containing plasmas (e.g., SF₆, CF₄, etc.). Inert gas plasmas are normally used for cleaning or crosslinking of polymer surfaces, as in the technique named CASING (cross-linking by activated species of inert gas). Oxygen-containing plasmas are used to produce a variety of functional groups, including C-O, C=O, O-C=O, etc. There are usually two competing processes present in oxygen plasma modification, plasma etching and formation of functional groups. The competition between the two processes has been discussed by *Garbassi et al.* [49]. Nitrogen-containing plasmas introduce the amino groups to polymer surface to increase protein immobilization and cell adhesion through formation of covalent peptide bonds with the carbonyl bonds in the biomolecules

[50-52]. Fluorine-containing plasmas, on the other hand, produce low-energy fluorinated groups on the surface and surface hydrophobicity can be induced [53]. The depth of plasma modification is typically 1-5 nm.

One problem associated with plasma treatment and many other modification techniques is the “ageing” effect, where surface properties tend to return to their original values after a certain time [54]. This is due to the reorientation of surface molecules on the surface layer controlled by thermodynamic forces which drive the polar groups to the bulk side and low-molecular-weight molecules to the surface side. Adsorption of low-molecular-weight molecules from ambient environment after polymer modifications may also contribute to the “ageing” effect [55]. To mitigate or even inhibit the “ageing” effect remains as a challenge in polymer modifications.

1.1.4 Polymer Nanocomposites

Polymer nanocomposites offer the possibility of developing new classes of polymers with unique combinations of properties. Polymer nanocomposites are usually classified according to their constituents. Many components, such as nanofibres, CNTs, metal nanoparticles, metal oxide nanoclusters, semiconductor QDs, have been successfully integrated into various polymer matrices [56-58]. Their properties and relevant applications have also been extensively studied. For example, in mechanical engineering, polymer layered silicate nanocomposites where polymer and organically modified layered silicates are intercalated show high tensile modulus and strength with as little as 2 vol% silicates [8]. The reinforcement of polymers and the unaffected density at low loading make them promising materials in aerospace and automotive industries. In thermal stability

and flame retardance, polymer nanocomposites with CNTs were used to form a jammed network to improve both the physical and flammability properties [59]. In plastic electronics, metal-polymer nanocomposites have been developed as compatible passive elements, such as interconnects and electrodes, to be integrated into all-printed polymer organic transistors [60]. In plasmonics, a tunable multiple plasmon resonance response was realized using co-sputtered metal-polymer nanocomposites [61]. In the biomedical field, biosensors using metal-polymer nanocomposites have been found in molecular recognition devices [62].

One of the main difficulties in polymer nanocomposites is to establish structure-property relationship so as to design high performance polymer nanocomposites. In general, integrated constituents are found to affect the macroscopic properties in three ways [8]: the properties of the constituents themselves, the confinement effect of constituents to the polymer matrix, and the arrangements of constituents.

As the size of constituents approaches the fundamental physical length scale for physical properties, new mechanical, optical and electrical properties from the constituents themselves arise, e.g., photoluminescence in QDs, superplastic of nanograined ceramics, plasmon absorption in metal nanoparticles, and superparamagnetic response in nanosized magnets. These properties are likely to be preserved after mixing with polymer matrix. Another effect brought from the size reduction is the ultralarge interfacial area between the constituents per volume of material. Therefore a majority of polymer chains will reside near the surface of the constituents. The conformation of these adjacent polymer chains will be inevitably affected by constituents, a phenomenon known as the confinement effect on the polymer matrix. This confinement effect induces property changes in

molecular mobility, relaxation behavior, free volume, and thermal transitions such as the glass transition temperature T_g , etc. *Torkelson et al.* beautifully demonstrated that the confinement effect can be equivalently studied by a simple “model” polymer which has a “sandwiched” structure [63]. Finally, the arrangements of constituents also affect the physical properties of polymer nanocomposites. Uniform dispersion of constituents in a polymer matrix usually results in more prominent changes in properties with less loading. It has been also shown that by changing the arrangements in one-, two, or three-dimensional arrays, a large variety of systems can be realized [64].

1.2 Motivation and Objectives

Metal-polymer nanocomposites have received considerable interest because of their promising electrical, optical, magnetic and biomedical properties. They represent an adequate solution to many present and future technological demands. Despite the fact that the first metal-polymer nanocomposites date back to 1835 as reported by *Faraday* [65], challenges remain in handling tiny metal nanoparticles and integrating them into functional devices. It is known that metal nanoparticles tend to aggregate because of their high surface free energy. Moreover, reactive metal nanoparticles can be easily oxidized by air, moisture, SO_2 and so on [66]. Therefore, a novel technology that can prepare metal-polymer nanocomposite in a single step would be of great advantage to minimize these instabilities. In addition, when polymer thin films are used as supporting materials in the fabrication process, one has to pay attention to the intrinsic instability arising at the interface of polymer thin films and the substrate, especially when a harsh environment is present.

Another challenge in metal-polymer nanocomposites is the investigations of their structure-property relationships. Detailed studies on the structure and related properties is highly desirable for designing new types of metal-polymer nanocomposites. They also provide a better understanding of the materials and may stimulate future applications. In attempting to take up the above challenges, the main objectives of this thesis are:

1. To fabricate metal-polymer nanocomposites using the plasma immersion ion implantation and deposition (PIII&D).
2. To investigate the mechanism controlling the formation of metal-polymer nanocomposites with the aid of various surface characterization techniques.
3. To explore the electrical, optical and biomedical properties of different types of metal-polymer nanocomposites.
4. To study the instability of polymer thin films when they are exposed to energetic metal ions.

1.3 Major Contributions

The major contributions of this work are as follows:

1. The fabrication of various metal-polymer nanocomposites by PIII&D was achieved and the formation mechanism was addressed.
2. The electron transport in Ti-PET nanocomposites has been shown to be described by Mott's law on variable-range hopping (VRH).
3. It is the first time that the excitation of localized surface plasmon resonance (LSPR) has been observed from Ti-PS nanocomposites at room temperature.

4. Ti-PS nanocomposites have been utilized as biomaterials for enhancing protein immobilization.
5. A peroxidase protein assay has been employed to quantify the amount of proteins immobilized on the solid surfaces.
6. Dewetting of thermodynamically stable PS thin films was observed, with a highlight of the formation of regularly polygonal rims in dewetting patterns.

1.4 Organization

This thesis is organized in the following way:

Chapter one presents a background of bulk polymers, polymer thin films, polymer modifications and polymer nanocomposites and is followed by the motivation and objectives of this project. The main contributions of this thesis are also given in this chapter;

Chapter two introduces the main experimental and characterization techniques adopted in this project;

Chapter three presents the formation of Ti-PET nanocomposites and their structural and electrical properties. The mechanism controlling the formation of metal nanoparticles is also elaborated in this chapter;

Chapter four presents the surface structural and chemical properties of Ti-PS nanocomposites and the observation of LSPR;

Ti-PS nanocomposites using PS thin films as the supporting matrix and their applications in protein immobilization are given in chapter five;

The observation of dewetting of PS thin films and the analysis of the formation of regularly polygonal rims are given in chapter six;

The conclusions and some recommendations for further research are given in the last chapter, chapter seven.

CHAPTER 2 **Experimental and Methodology**

2.1 *Filtered Cathodic Vacuum Arc*

Cathodic vacuum arc as a technique for generating plasmas has been used for many years, as an alternative to other techniques such as glow discharge, radio-frequency (RF) capacitive/inductive coupling, microwave electron cyclotron resonance [67]. One unique feature in cathodic vacuum arc is that a wide range of metal plasmas can be generated. The setup of a cathodic vacuum arc is rather simple, i.e., the application of high-current, low-voltage power to a metal target, which acts as the cathode. By triggering the surface of the metal target with a refractory metal (e.g, Mo, W) or graphite in vacuum, high temperature and non-stationary “cathodic spots” can be initiated. These “cathodic spots” emit energetic electrons and ions. Notably, ions are normally emitted at high speed ($\sim 10^4$ m/s, or equivalent to 20 – 100 eV) and thus are supersonic. This is substantially different from other processes, such as evaporation or sputtering, where a “cold” plasma is usually produced.

A direct cathodic vacuum arc is not practically useful as the deposition source because of the co-production of metal macroparticles in the plasma. Metal macroparticles are metal clusters with large size up to micrometer scale. They are detrimental to the quality of the films, particularly when the film is ultrathin. To eliminate them, various filters have been devised in which the plasma is guided by a magnetic field through a curved duct by which the metal macroparticles are blocked [68, 69]. The combination of cathodic vacuum arc with the filter is therefore termed as filtered cathodic vacuum arc, or FCVA.

In our lab, a magnetic filter with a off-plane-double-bend (OPDB) geometry is used. The system is then called an OPDB-FCVA [70]. Figure 2.1 shows both the schematic and photo of an OPDB-FCVA. Briefly, the filter consists of three straight stainless steel pieces welded together into two tori of dimension approximately $40 \times 20 \times 10$ cm. Copper coils wrapped around the whole filter produce an axial magnetic field to guide the plasma. A flexible tube made of V-shaped blades is also placed inside the filter to further block metal macroparticles. When the cathodic vacuum arc is generated by a dc power source, the ion transport in the filter has been studied by both experiment and computer simulation, using carbon as the prototype ions [71, 72]. Our previous results showed that when “cathodic spots” were triggered at the surface of a metal target, the magnetic field (~ 10 mT) was sufficiently strong to guide electrons with the gyration radii r [73]:

$$r = mv / eB \quad (2.2)$$

where m , v and e are the mass, velocity and charge of the charged particle respectively, B is the magnetic field strength. Because of much smaller mass, electrons have smaller gyration radii than that of ions and will be guided to the chamber through the magnetic field. The transport of ions is then through the electric field created by the separation between electrons and ions.

Figure 2.1 (a) The schematic and (b) the photo of our FCVA system with the design of off-plane double bend (OPDB) filter.

While metal macroparticles are greatly reduced in FCVA, it is not difficult to see that the ion density and plasma transmission efficiency, defined as the ratio of plasma density at the exit of the filter to that at the entry of the filter, would be reduced as well. Specifically in our system, the typical values for ion density and plasma transmission efficiency were $2 \times 10^{11} \text{ cm}^{-3}$ and 30% respectively [70, 71]. Again, carbon was the prototype ion used.

Another feature in FCVA is that the charge state for metal ions is usually larger than unity and is dependent on the type of metal used. For example, Ti ions have an average charge state of 2.1 with a combination of Ti^{1+} , Ti^{2+} and Ti^{3+} ions, while carbon is mainly singly-charged [74]. In many FCVA processes, gases are used as either reactive or stabilizing species for arcing. The presence of an ambient gas can significantly reduce the kinetic energy of metal ions and change the distribution of ion energy, as pointed out by *Bilek et al.* [75].

FCVA as a deposition technique has been considered for various functional coatings e.g., metal oxides, nitrides, amorphous and diamond-like carbon, etc [76].

These coatings have been utilized in many applications such as data storage, microelectronics, tribological and optical engineering. For example [76-85], metal and metal alloy coatings have been used for protective purposes; amorphous carbon (*a-C*), tetrahedral amorphous carbon (*ta-C*) and diamond-like carbon (DLC) films have been used for tools protection and hard disk applications; nitride coatings such as TiN for tools protection and decoration, oxide coatings such as copper oxide (CuO) for heat transfer have been demonstrated; aluminium oxide for mechanical, optical and structural improvements and titanium oxide for optical, mechanical and electrical applications have been shown extensively. The coatings fabricated by FCVA usually have higher quality than those obtained by conventional physical vapor deposition (PVD) or chemical vapor deposition (CVD) methods.

While most of the substrates for coatings are metal, ceramic or semiconductor, FCVA depositions on polymer surfaces have been seldom reported. Notwithstanding *Abbas et al.* who used FCVA to deposit thin films on polymer as gas barriers [86, 87], most researchers focused on combining FCVA with PIII to modify polymer surfaces, as discussed later. This is probably due to the fact that by using FCVA alone it is difficult to deposit metal films because of the low condensation coefficient of metal atoms on polymer surfaces. Most polymer surfaces have low surface energy which discourages metal deposition and arriving metal atoms or ions may re-emit quickly. Even a metal film which is obtained by a long time deposition, the poor inherent interfacial adhesion between a metal film and polymer surface will be far from the requirements for practical applications. In contrast, when combined with PIII, the surface energy of polymers can be increased and hence also the interfacial adhesion.

Last but not least, it is worth mentioning that with the aforementioned efforts spent in technological development, FCVA has become a “mature” technique and been industrialized by some groups worldwide. In Nanyang Technological University, a spin-off company, Nanofilm Technologies International Pte Ltd, was set up in 1999 to implement this technology into the market place (See <http://www.nanofilm.com.sg>).

2.2 Plasma Immersion Ion Implantation and Deposition

Plasma immersion ion implantation (PIII or PI³), also known as plasma source ion implantation (PSII) or plasma based ion implantation (PBII), is a technique invented by *Prof. J. Conrad* of the University of Wisconsin–Madison in 1984 [88]. PIII was originally developed as a three-dimensional (3D) alternative approach for ion implantation to circumvent the expense of conventional beamline ion implantation and the restriction of “line-of-sight” principle. The setup of PIII is to apply a negative bias to the substrate. A plasma sheath is formed in the vicinity of the substrate surface upon the immersion of plasma [89]. Because all parts of the substrate are at the same potential, as long as the plasma is uniform and the feature size of the surface is much larger than the sheath thickness, conformal ion implantation can be achieved [90].

In our lab, pulsed bias is adopted in PIII. Along with a continuous metallic plasma generated from the FCVA, both ion implantation and deposition can occur in the process [91]. In brief, during the pulse-on period, ions inside the plasma sheath (a short layer in the vicinity of substrate surface) are accelerated and implanted into the substrate surface. The plasma sheath at this stage expands away from the surface at ion sound velocity in order to accommodate more ions for

restoring the screening effect. During the pulse-off period, ions are not accelerated and plasma deposition occurs on the surface instead. The two processes are schematically shown in Figure 2.2a. PIII can also realize pure metal ion implantation by synchronizing pulsed cathodic vacuum arcing with the applied bias, although the implantation is non mono-energetic due to the non-uniform charge state of ions in the cathodic vacuum arc and the finite rise and fall time in the applied bias [74, 92-94]. In general, PIII is useful for materials processing ranging from pure ion implantation to pure film deposition.

As recommended by Anders [92, 95], the acronym PIII&D (plasma immersion ion implantation and deposition) has been generically used for the whole family of plasma immersion processes including plasma ion implantation, plasma ion plating, plasma doping, plasma ion immersion processing, and other film-forming techniques; while PIII is used when referring to processes without film formation. In this thesis, we will follow the same nomenclature.

Figure 2.2b shows the photo of the PIII equipment used in our lab. The equipment comprises three components, the pulse supply, the substrate holder and the control unit. The pulse supply (*Spellman*) is capable of applying a bias up to a voltage of -50 kV and frequency of 2,000 Hz to the substrate. However, the maximum voltage used in our experiments is -25 kV, limited by the capacity of the ceramic insulator of the substrate holder. We also shield the chamber windows with leaded glass to prevent any possible x-ray emissions at the high-voltage PIII processing. The substrate holder is a long copper stick with a circular plate on its terminal made of aluminum. The control unit is from the *Australian National Science and Technology Organization* (ANSTO), Australia. It can set pulse parameters such as voltage, frequency, and pulse width. The ion fluence can then

be approximately determined from the plasma density, the pulse parameters, and the processing time using the 1-D *Child-Langmuir* law [96]. For a 1 min PIII&D processing time and assuming a plasma density of $1 \times 10^9 \text{ cm}^{-3}$, the nominal ion fluence is estimated to be about $4 \times 10^{16} \text{ cm}^{-2}$.

Figure 2.2 (a) The schematic and (b) the photo of PIII technique together with continuous metal plasmas used in our lab.

PIII processes on conductive substrates are straightforward. However, processing nonconductive substrates (e.g., polymers) can be difficult because of the surface charging effect, which is primarily induced by the emission of secondary electrons. Surface charging can severely reduce both ion energy and ion fluence, hence the efficiency of PIII processing. It may also lead to misunderstanding and misinterpretations of experimental results if it is not taken into consideration. To mitigate it, two different approaches have been proposed, a pre-coating of the conductive layer or use of a conductive mesh [97, 98]. The pre-coating of a conductive layer is done by depositing an ultrathin layer of conductive metals or carbons on the sample surface. This layer can then conduct the surface charges to the substrate holder effectively. The drawback of this method is that it may introduce extra contaminants. The other approach is to use a conductive

mesh. By putting this mesh in front of the substrate at a distance ~ 5 mm to the surface, a large amount of secondary electrons can be suppressed and both ion energy and ion fluence can be restored.

The role of energetic ions in film deposition is important for understanding the high quality films obtained by the PIII&D process. Without any biasing, low energy ions will condense on the substrate surface which has much lower temperature than ions. However, the mobility of these ions after condensation is low, making shadowing of adatoms and voids are formed in the film. This induces a tensile stress in the film. When the energy of ions increases a bit, they can modify the very top surface of the substrate and create a densified layer. This induces a compressive stress in film. The compressive stress can be larger than the interfacial energy between film and substrate, leading to self-cracking of film. If the ion energy is further increased, the compressive stress can be greatly relieved through the interactions of ion-matter and atomic rearrangement [99]. The qualitative tendency of compressive stress with respect to the ion impact energy is given by Figure 2.3 (from Ref [99]).

Figure 2.3 The schematics of generally observed ion impact energy and compressive stress (from Ref [99]).

Research related to PIII has kept growing since the invention of this technology. As mentioned above, PIII was initially considered as an implantation technique using gaseous plasmas, e.g., using N_2 PIII to form metal nitrides on metal or alloy surfaces so that the corrosion and wear resistance can be enhanced [100]. In semiconductor fabrications, PIII was adopted for shallow junction formation, silicon-on-insulator, trench doping, etc [101-103]. *Brown et al* firstly used cathodic vacuum arc as the plasma source in PIII for film deposition [91]. Since then, many coatings were realized, such as low- k materials, protective coatings on machining tools, and thick DLC films [73, 104, 105]. Recently, PIII modification on polymers was also extensively studied. Some highlights in this field are modification of polymer surfaces for biomedical applications, fabrication of nanostructures on the polymer surfaces, metallization of polymers as interconnects in microelectronics, improvements in optical properties, etc [96, 106-108]. Figure 2.4 plots the number of publications since the mid of 1990s (Source: *ISI Web of Science*). There is also an international conference named “International Workshop for Plasma-Based Ion Implantation & Deposition” held biennially to provide a fruitful platform for cross-disciplinary exchange of the latest scientific results in this research field.

Figure 2.4 Numbers of publications as a function of publication year from *ISI web of science* by searching with keyword “plasma immersion ion implantation SAME PIII”.

In summary, the PIII technique offers many advantages, such as 3D conformal modification, non-“line-of-sight”, cost-effective, high efficiency and large area plasma modification, making it a versatile technique for material processes requiring ion implantation and/or film deposition.

2.3 Stopping Range for Ions in Matter

The *stopping range for ions in matter* (SRIM) is a Monte-Carlo coded simulation tool for predicting ion implantations in various substances [109]. The theory of ion-polymer interactions states that when a primary ion is traveling inside a polymer, its energy will be dissipated in target atoms in two ways, electronic stopping and nuclear stopping [45]. The former arises from electromagnetic interaction between the incident ion and the target electrons while the latter is from collisions between the incident ion and target nuclei. Two types

of electronic stopping could occur, one is a glancing collision and the other is a knock-on collision. Glancing collisions are a distant resonant collisions with smaller momentum transfer and knock-on collisions are a close collision with large momentum transfer. The knock-on electrons are known as secondary electrons. Theoretical and experimental evidence suggested that approximately one half of the electronic stopping is due to glancing collisions and the other half to knock-on collisions, a phenomenon known as the *equipartition principle*. On the other hand, nuclear stopping also has two types, atomic displacements and phonons. The atomic displacements occur when the incident ions impart energy greater than a certain displacement threshold energy, or E_d , to a target atom. E_d is the minimum energy required to break the bonds and displace the atom over a lattice potential. For polymers, the value of E_d is in the range of 10 – 30 eV. The knock-on atoms in nuclear stopping are called recoils which can further transfer their energy to other target atoms through electronic stopping and nuclear stopping, provided that their energy is large enough. Phonons occur when the energy transferred is less than E_d and target atoms can not escape their sites. The energy then dissipates as atomic vibrations.

The aforementioned picture of cascade collisions is implemented by SRIM. In SRIM, the *Kinchin-Pease* approximation is used to calculate the energy partitioning. In this approximation, the recoils are not individually followed in the Monte-Carlo calculation. However, the flight paths of the incident ions are tracked and the energy losses are calculated using ZBL stopping powers, as shown below [45]. Assuming that elastic collision occurs for two spherical-shaped atoms, the transferred and the displacement energy, T and E_T , respectively, are given by:

$$T = \frac{4M_1M_2}{(M_1 + M_2)^2} E \sin^2\left(\frac{\theta}{2}\right) \quad (2.3)$$

$$E_V = \frac{T}{1 + k_d g(\varepsilon_d)} \quad (2.4)$$

where M_I and M_2 are the mass of the incident and target atoms, respectively. E is the kinetic energy of the incident ions, θ is the scattering angle in the center of the mass, k_d and $g(\varepsilon_d)$ are parameters accounting for the electronic loss. The electronic loss due to recoil, E_r , is obtained from T and E_V by:

$$E_r = T - E_V \quad (2.5)$$

SRIM is capable of providing both nuclear and electronic stopping power for most ions implanted into many elementary or compound materials over different energy ranges. The stopping power depends on the type and energy of the particle as well as the properties of the materials it passes through. It is also called linear energy transfer (LET), or S , given by:

$$S = -\frac{dE}{dx} \quad (2.6)$$

The stopping power profile is not constant over distance; instead, it usually increases towards the end of the range and reaches a maximum, shortly before the energy drops to zero. Three distances are found to be important in determining the ion distribution, projection range, longitudinal and lateral straggling range. The projected range is the distance from the surface to the point where ions stop. Longitudinal and lateral straggling ranges are the deviations in projection range in the parallel and perpendicular plane respectively. SRIM is also capable of giving the detailed ion distributions characterized by the three distances.

2.4 Characterization Techniques

The extent of the surface modification will not be fully understood without an in-depth investigation of the chemical and physical properties of polymer surfaces.

Therefore, characterization techniques which can reveal polymer surface structures at the molecular level are necessary. Common surface characterization techniques include contact angle measurement, x-ray photoelectron spectroscopy, atomic force microscopy, scanning and transmission electron microscopy, etc. In the following part we will briefly describe the basic principles and measurement capabilities related to these techniques. For those characterization techniques not described in this section but appearing, separate descriptions will be given depending upon the content.

2.4.1 Contact Angle Measurement

Contact angle (CA) measurement is one of the simplest yet most effective surface characterization techniques. It can be used to obtain the surface energy of a solid surface, to determine surface wettability, hydrophobicity or hydrophilicity, and even to qualitatively infer chemical compositions [110]. The sampling depth of CA measurement is a few atomic layers. The principle of CA measurement is based on that when a liquid droplet is on the solid surface, the contact angle θ , as shown in Figure 2.5a, is governed by the force balance at the three-phase (liquid, solid and vapor) boundary. This can be quantitatively shown by Young's equation:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (2.7)$$

where γ_{lv} is the surface tension of the liquid in equilibrium with its saturated vapor, γ_{sv} and γ_{sl} are the surface tension of the solid in equilibrium with its saturated vapor and the interfacial tension between the solid and the liquid, respectively.

Figure 2.5 (a) Contact angle measurement using a sessile drop method; (b) advancing angle θ_a ; (c) receding angle θ_r .

Young's equation can be improved by assuming that the intermolecular interaction across an interface between two phases occurs exclusively between the forces of the same type, i.e., dispersion forces and polar forces. The following equation is then implemented [111, 112]:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s^d \gamma_l^d} - 2\sqrt{\gamma_s^p \gamma_l^p} \quad (2.8)$$

where γ_s^d , γ_l^d , γ_s^p and γ_l^p are the dispersion and polar components for a solid and liquid respectively. By using at least two different testing liquids one of which has polar components, it is possible to calculate the dispersion and polar components of a solid surface using Eqn. (2.7) and Eqn. (2.8).

Three different types of contact angles can be measured, equilibrium, advancing and receding angles. The equilibrium angle θ is established when the system is in a thermodynamic equilibrium state, i.e., at the lowest energy state. However, in reality such a condition is seldom satisfied. The system may lie in one of the metastable states where CA could be larger or smaller than the equilibrium angle. The advancing angle, θ_a , is the angle at the onset of a sudden advance, e.g., when enough liquid is added to the droplet, whereas the receding angle, θ_r , is the contact angle at the onset of a sudden retraction, e.g., when enough liquid is subtracted. The difference between θ_a and θ_r is defined as CA hysteresis,

which is closely related to surface roughness, surface heterogeneity, as well as the re-arrangement of surface functional groups [49, 113].

Dataphysics OCA20 is the system for carrying out contact angle measurements in this work. It uses the sessile drop method, i.e., by dispersing liquid drops onto a solid surface using a microsyringe. The equilibrium angle is measured by waiting 60 s for the droplet to stabilize on the surface. A video camera attached to the system is then used to capture the shape of the droplet and calculate the angle. Advancing and receding angles are obtained by increasing or decreasing the volume of the droplet until the three-phase boundary moves on the surface, as shown in Figure 2.5 b & c. It is noticed that other methods, such as the tilted solid surface, can also be used to measure the dynamic advancing and receding angles [114].

CA is known to be affected by surface conditions, especially surface roughness and surface heterogeneity. Surface roughness can enlarge surface hydrophobicity or hydrophilicity through larger contact areas, i.e., higher surface roughness gives higher CA if the original surface is hydrophobic and smaller CA if the original surface is hydrophilic. Such a relationship is given by *Wenzel's* equation [115]:

$$\cos \theta = r \cos \theta_0 \quad (2.9)$$

where θ and θ_0 are the contact angles for actual and “flat” surfaces respectively and r is the roughness or the ratio of actual surface area to a flat surface. When a surface is heterogeneous and comprised of both high- and low-surface energy components, the overall contact angle is given by *Cassie's* equation [116]:

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (2.10)$$

where f_1 and f_2 are the ratio of surface areas for high- and low-surface energy components respectively and θ_1 and θ_2 are the contact angles for the two components respectively.

It is worth noting that recently *McCarthy et al.* pointed out that *Wenzel* and *Cassie* were wrong in the sense that the contact angle behavior is determined by interactions of the liquid and the solid at the three-phase contact line alone and that the interfacial area within the contact perimeter is irrelevant [117]. We can still use Wenzel's or Cassie's equation in the sense that the structure of the contact area reflects the ground state energies of contact lines and the transition states between them.

2.4.2 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a powerful technique for surface chemical characterizations. The schematic of a XPS system is shown in [Figure 2.6a](#). XPS measurements use x-rays, usually emitted from Al or Mg anodes, to impinge the sample surfaces and measure both the kinetic energy (E_k) and numbers of photoelectrons excited from the core levels of each element, as demonstrated in [Figure 2.6b](#).

The sampling depth of XPS is determined by the attenuation length of photoelectrons which in turn depends on the energy of incident x-ray, the XPS take-off angle, and the nature of surface structures. In general, it is a few nm for polymers, thus making it very surface sensitive. XPS measurements can be used to determine both compositional and chemical bonding states on the surface. Chemical composition can be identified by XPS survey-scanning because the

binding energy (BE) is unique for each element. Chemical bonding states are revealed by an XPS narrow-scan. The spectra of a narrow-scan are usually complex in shape and require special analytical tools to deconvolute them [118]. XPS measurements can also be adopted for depth profiling by using low-energy ions, e.g., Ar^+ , to sputter the surface gradually in a controlled manner. The quantification of each element in XPS measurement is given by [1]:

$$C_i = \frac{A_i / S_i}{\sum_j^m A_j / S_j} \quad (2.11)$$

where C_i is the atomic concentration of an element i , m is the number of elements in the sample, and A_i and S_i are the peak area and the sensitivity factor for element i , respectively. Sensitivity factors for some common elements in polymers, e.g., C, N, O, Si, have been previously determined by Vargo and Gardella [119].

Figure 2.6 (a) The schematic of a XPS system: (1) x-ray tube; (2) sample; (3) electronic focusing system; (4) spectrometer; (5) detector; (6) data acquisition. (b) Excitation of photoelectrons in XPS measurement.

In this work, XPS measurement was carried out by a *PHI Quantera SXM* system equipped with an Al $K\alpha$ (1486.6 eV) x-ray source and a take-off angle of 45° . The base vacuum pressure was 2×10^{-9} Torr. The survey-scan was recorded in

the range of 0 – 1200 eV with 1 eV resolution and the narrow-scan for each element was recorded with 0.1 eV resolution. The depth profiling was carried out by using low-energy Ar⁺ to sputter the samples at a constant rate of 9.86 nm/min.

2.4.3 Atomic Force Microscope

Atomic force microscope (AFM) belongs to the family of scanning probe microscopes (SPM) [120]. AFM is widely used for imaging, measuring and manipulating matter at the nanoscale. It measures the atomic forces between the tip attached to a cantilever and the surface. The lateral resolution of AFM is usually several 10 nm, limited by the tip size. However, the depth resolution can be up to the atomic scale of 0.1 nm. Two operational modes are usually employed in AFM, constant force mode and constant height mode. In constant force mode, the tip is either contacting the surface or tapping the surface at a certain frequency. The induced atomic forces cause the cantilever to deflect on the tip approaches the surface. This deflection is then kept constant by using a laser spot reflected from the top of the cantilever into an array of photodiodes together with a feedback circuit. Surface topography is therefore obtained by recording the movements of the tip. In contrast, when the scan is in constant height mode, the distance between the tip and the surface is kept constant and surface topography is obtained by measuring the deflection of the cantilever in the vertical direction. In this work, the AFM instrument used is a NanoScope IIIa, *Digital Instruments*, and the operation is in tapping mode as it can minimize the damage of the tip on the soft surface and keep the probing resolution as high as possible.

2.4.4 Electron Microscopes

Electron microscopy including scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are useful tools for imaging the sample surface. SEM uses an electron beam in a raster-scan and normally detects the secondary electrons emitted from the sample surface whereas TEM uses a high energy electron beam to impinge upon samples to provide information of size, shape and arrangement of the particles in the sample as well as their relationship to each other on the atomic scale. The SEM and TEM systems used in this work are SEM 5910LV, *JOEL* and TEM 2010, *JOEL*, respectively.

The preparation of the TEM specimens for commercial polymers is done by cutting the samples into 100 nm thick cross-sectional specimens using an ultramicrotome, *Leica* with a diamond knife. These specimens are then attached to a copper grid and dried in air. The preparation of the TEM specimens for polymer thin films consists of several steps: first, the samples are cut to the size of a copper grid and secured with epoxy; then, they are cut into 600 μm thick slices with a low speed diamond saw and ground to approximately 20 μm by a dimple grinder; after that, the specimens were thinned in a precision ion polishing system using Ar^+ at 5 kV and an incident angle of 4° . A hole was finally created at the center of the specimen to provide a large transparent area for observation.

CHAPTER 3 **Formation of Ti-PET Nanocomposites and Their Surface and Electrical Properties**

3.1 *Introduction*

Modern electronic fabrication has been steered into two different directions [121]. One is to launch fast and powerful electronic circuits towards the limits of information processing. The other is to exploit electronic circuits with modest performance but are cheap to fabricate and easy and flexible in handling. The latter is known as plastic electronics, or organic electronics, a subject of intense research in recent years. Plastic electronics normally use organic materials to fabricate all components in integrated circuits, such as transistors, interconnects, electrodes, substrates, etc [122]. When the requirements in device performance are not so strict, plastic electronics aim to act as a substitute for conventional Si-based microelectronics. The advantage of plastic electronics over Si-based microelectronics is obvious: the manufacturing uses simple devices such as inkjet printers instead of billion-dollar fabrication facilities. The system integration for plastic electronics is also simpler and easier, in contrast to steps like high vacuum deposition and photolithograph required in Si-based fabrication process.

The most popular materials as semiconducting electronic components in plastic electronics are conductive polymers. Conductive polymers such as PANI and polythiophene belong to a group of polymers with special electrical properties – they show insulating properties in the intrinsic state but semiconducting or conductive behavior when properly doped. Therefore, they can make most of the

functional components in an electric circuit, e.g., source, drain, channel, gate, interconnect and electrode [22, 23, 26, 30]. Over the past few years, plastic electronics using conductive polymers have become increasingly interesting because of low-cost all-polymer integrated circuits [123-126]. Commercial products based on plastic electronics have also been demonstrated, e.g., Philips successfully manufactured identification tags that are used as anti-theft stickers for retail goods (<http://www.philips.com>).

Other promising materials used in plastic electronics are the hybrid materials – composites of organic and inorganic molecules that combine the benefits of each. The hybridization can be at either the molecular-scale or the nanoscale. A good example for the hybridization at molecular-scale is the semiconducting perovskite $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{SnI}_4$ used as semiconducting channels in thin-film FET [127]. On the other hand, metal-polymer nanocomposites comprised of metal nanoparticles embedded in a polymer matrix have received considerable interest for hybridization at the nanoscale [18, 60, 128, 129]. Compared to conductive polymers, metal-polymer nanocomposites provide an even cheaper and easier way for device manufacture of electronic devices. So far, some electronic components and devices utilizing metal-polymer nanocomposites have been achieved, e.g., $\text{Ni}_{1-x}\text{Fe}_x$ nanocrystals in PI were applied as nonvolatile flash memories, in which electrons were trapped in $\text{Ni}_{1-x}\text{Fe}_x$ nanocrystals [128], metallic conductive Au-polymer nanocomposites were used as interconnects and electrodes in plastic electronics [60], etc.

In this chapter, we use an alternative technique, PIII&D, to fabricate electrically conductive Ti-PET nanocomposites in a single step. We will characterize the surface structure of Ti-PET nanocomposites using SEM, AFM and

conductive-probe AFM (CP-AFM). Moreover, the temperature-dependent (T-dependent) conductivity will be measured and the electron transport will be investigated according to the Mott-law variable-range hopping (VRH) mechanism. Other effects, such as “ageing” effects and the supporting material, on the influence of conductivity will also be discussed.

3.2 Experiments

Amorphous PET films (transparent, 250 μm thick, *Goodfellow*) were degreased in isopropanol alcohol (IPA) under sonication and put into the PIII&D processing chamber. The base pressure was 1×10^{-5} Torr while the working pressure was 1×10^{-3} Torr after feeding in the Ar flow. The Ti plasma was generated from the FCVA system at a density $\sim 10^{10} \text{ cm}^{-3}$. The operation parameters of PIII&D were a voltage of -10 kV, frequency of 600 Hz, duty time of 20 μs and processing time was 5 min.

The contacting electrodes for electrical conductance measurements were made in two ways. The first way was by depositing a $1 \times 1 \text{ mm}^2$ metallic layer consisting of 50 nm Ti and 200 nm Au on the four corners of the samples using an electron-beam evaporator (AUTO360, *Edwards*) with a shadow mask. This configuration was used to measure the T-dependent conductance using the van der Pauw method [130]. The measurements were done by placing the samples on a probe station (*Cascade MicroTech*) equipped with a semiconductor parameters analyzer (*HP 4156B*) and a heating device (*Temprotronics*). For the electrical measurements, temperature steps of 10 K starting from room temperature were used with a 10 min waiting time for the stabilization of temperature for each step. The second configuration for electrical measurement was by using silver paste to make two

Ohmic contacts with a distance of 5 mm. This configuration was used to measure time-dependent (t-dependent) conductance using a standard 2-point probe station equipped with an electrometer (*Keithley 6514*).

Figure 3.1 Setup of CP-AFM measurements. W_2C coated Si tip is in contact mode with the sample, where the top shadowed region indicates conductive PET surface. A carbon tape was used to connect the sample surface to the conductive substrate holder to form the conductive pathway.

The spatial distribution of Ti nanoparticles on PET surface was investigated using a CP-AFM (*JOEL*). CP-AFM is the AFM system equipped with the appropriate electronic modules. It has been successfully adopted in molecular electronics, microelectronics, and device diagnostics [131-136]. The advantages of using CP-AFM are that both surface topographical and electrical information can be obtained at high lateral resolution (~ 10 nm) and the electrical conductive pathways can also be visualized. The setup of our CP-AFM measurements is shown in [Figure 3.1](#). A tungsten carbide (W_2C) coated Si tip was attached to the cantilever. The samples were put under a vacuum of 5×10^{-5} Torr to avoid passivation of the sample surface that is usually induced by high dc biasing between the tip and the polymeric samples. Only the surface of the PET was conductive but the bulk is insulating and therefore an additional carbon tape was

used to connect the surface and the conductive substrate holder to form the conduction pathway. All measurements were taken at room temperature and the tip was in contact mode with the surface.

3.3 Results and Discussion

3.3.1 Surface Topography

Modification of the PET surface by the PIII&D started from the investigation of surface topography. Pristine PET was smooth with a root-mean-square (*rms*) roughness less than 1 nm. However, surface roughness increased to ~5 nm after the PIII&D process, as shown by both SEM and AFM images in [Figure 3.2](#). More importantly, the surface structure turned into a “self-organized” nanostructure with arrays of conical “hillocks” and “craters” at the nanoscale. By adjusting the ion implantation parameters, such as kinetic energy, ion fluence, ion angular distributions, and ion incident angle, we found that the size and shape of the “self-organized” nanostructures could actually be controlled. It is noticed that similar observations have also been found on the surfaces of ion implanted semiconductors and metals [\[137-139\]](#). The formation of “self-organized” nanostructures was attributed to the dynamic balance between roughening induced by ion sputtering and smoothing due to surface diffusion [\[137, 140, 141\]](#). For ion implanted polymers, however, the balance is established between ion implantation induced surface sputtering and surface re-deposition [\[142\]](#). Because a large contribution due to ion implantation was present in the PIII&D process, we believe the same mechanism is responsible for our observations of surface topography modification here. The whole formation process is elaborated in the following.

Figure 3.2 Surface topography of PIII&D processed PET (a) SEM (scale bar: 200 nm), 5 min modification. (b) 3-D AFM image (area: $1 \times 1 \mu\text{m}^2$), 5 min modification. (c) 3-D AFM image (area: $1 \times 1 \mu\text{m}^2$), 10 min modification. (d) 3-D AFM image (area: $1.7 \times 1.7 \mu\text{m}^2$), 15 min modification.

Polymer is prone to be sputtered away by energetic ions. However, the sputtering yield, which is the number of surface atoms removed per incident ion, is different for different target atoms, e.g., H atoms are preferentially sputtered compared to C atoms. Eventually the surface is left with a large portion of C atoms and the sputtering yield reduces rapidly. This carbon-rich surface layer has been confirmed by both experimental (e.g., by characterization techniques like

Raman scattering, SIMS, XPS) and simulation results (e.g., Molecular Dynamics) [143, 144].

The sputtering yield is also affected by surface heterogeneity and curvature. It is known that even for an originally homogeneous and smooth polymer surface, energetic ions can change the polymer matrix in localized regions around the ion tracks, thus transforming the polymer surface into a highly heterogeneous structure [45]. The ion tracks comprised two separate regions, the physical core and the penumbra. The physical core is the radial extent of energy deposition from primary ions. It has a radius r_c given by:

$$r_c = \frac{V_{ion}}{\omega_p} \quad (3.1)$$

where V_{ion} is the velocity of primary ions and ω_p is the plasma frequency given by

$\omega_p = \sqrt{ne^2 / m_e \epsilon_0}$ with n being the electron number density of the target, m_e the mass of the electron and ϵ_0 the permittivity of free space. The penumbra is induced by electronic excitation and ionization due to secondary electrons and surrounds the physical core. *Seki et al.* studied the size and distribution of the physical core and the penumbra by measuring the crosslinking in ion implanted polymers [145]. Apparently the structure within the ion tracks would be different from that outside the ion tracks, hence the physical and chemical properties, e.g., solubility, are different. This surface heterogeneity would lead to different sputtering yield at the microscopic scale at the initial stage, increasing surface curvature upon ion implantation. Once a slight surface curvature is induced, it can be amplified by subsequent low-energy (<10 keV) ion implantation at normal incidence. This is because sputtering is preferred at “craters” but inhibited from

the “hillocks”, due to the inhomogeneous energy deposition of primary ions upon the curved surface[137, 140].

The surface curvature could not grow infinitely, however, but was balanced by surface diffusion in metals or semiconductors or surface re-deposition in polymers induced by ion implantation. It is known that energetic ions can transfer their energy to bulk atoms, thermally activating or inducing surface diffusion on metals or semiconductors. The surface height evolution h can be expressed at the establishment of such balance as [138]:

$$\frac{\partial h}{\partial t} = -F_0 + C \frac{\partial h}{\partial x} + \Gamma_x \frac{\partial^2 h}{\partial x^2} + \Gamma_y \frac{\partial^2 h}{\partial y^2} - B \nabla^4 h + \eta \quad (3.2)$$

where F_0 is the sputtering at normal incidence, $C \partial h / \partial x$ is the sputtering yield with respect to angle of incident, $\Gamma_x \partial^2 h / \partial x^2$ and $\Gamma_y \partial^2 h / \partial y^2$ are the surface curvature dependence of sputtering, $B \nabla^4 h$ is surface diffusion [146] and η is the noise term. For polymers, however, extra free radicals can be induced by ion implantation. As the number density of radicals is proportional to the energy deposition, a high density of radicals is expected to accumulate at regions of high sputtering rate, e.g., “craters”. These radicals are chemically reactive and can react with other molecules in the residual atmosphere, a process named surface re-deposition [142]. Surface re-deposition can become significant if the sputtering rate is not too high, thus mitigating the growth of surface curvatures by an ion sputtering effect. An extra term representing surface re-deposition could be added to the right side of Eqn. (3.2) so that it can be applied to the polymeric substrate. Overall, when the interplay between ion sputtering and surface re-deposition is established, a “self-organized” surface pattern with arrays of conical “hillocks” and “craters” is formed, in accordance with the observations in Figure 3.2.

When ion fluence increases, the size of these “hillocks” increase and a slight deformation is observed, as shown in Figure 3.2c. The increased size is consistent with other’s observations and agrees with the proposed mechanism [142]. The deformation probably arises from thermal heating of the surface when a large amount of Ti ions transfer their energy to the PET matrix. At even higher ion fluence, PET surface can be severely damaged as more energy has been transferred and the temperature can be very high (Figure 3.2d). Surface topography at this stage (high ion fluence) has also been studied by Moon *et al.* who used focused ion beam (FIB) to induce the wrinkles and cracks on polymer [147].

3.3.2 Fabrication of Ti-PS Nanocomposites

In the past years, many fabrication methods for metal-polymer nanocomposites have been proposed, including colloidal chemical reduction, vacuum evaporation and sputtering, pulsed laser ablation, and so on. The colloid chemical reduction method is a solution-based self-assembly process which involves two steps: first, solutions containing metal ions are transferred into a micelle solution; then, a reducing reagent is added to reduce metal ions to metal atoms [64, 148]. The reduced metal atoms can coalesce and form metal nanoparticles in a polymer matrix with appropriate thermal control. The size of the metal nanoparticles is normally stabilized by covalently attached thiol- or disulfide-functionalized monolayers because of their strong adhesion to metal surfaces, as seen in the Au-dodecanethiol ($C_{12}H_{25}SH$) system [64]. Furthermore, homogeneous metal nanoparticles can be achieved by careful control of experimental conditions (e.g., concentration, temperature, solvent, etc.). However, one of the disadvantages of this method is that only limited types of metal nanoparticles can be realized, with

noble metal nanoparticles (e.g., Au, Ag, Cu) the most common cases. Vacuum evaporation and sputtering involve the condensation of atoms produced by the evaporation of a metal target or the co-sputtering of both metal and polymer targets [61, 149]. If metal nanoparticles residing on the surface of a polymer substrate are desired, evaporating ultrathin (<10 nm) metal films results in well-defined island structures resembling colloidal metal nanoparticles. If embedded metal nanoparticles in the polymer matrix are desired, co-sputtering of both metal and polymer can be adopted. The principle of this method is based on the fact that metal-metal interactions are much stronger than metal-polymer interactions [149]. As a consequence, metal atoms prefer to form clusters when they are near enough. This method is capable of producing a large variety of metal-polymer nanocomposites; however, it is difficult to control the distribution of metal nanoparticles. Unless certain templates are used, metal nanoparticles are randomly dispersed in the polymer matrix. Laser ablation of metal targets can also produce metal nanoparticles and composite alloyed nanoparticles in either solid or aqueous environments [150]. The formation of metal nanoparticles can be visualized by the appearance of a surface plasmon absorption band. Various shapes of nanoparticles can be obtained by using different laser powers at selected wavelengths [151].

Despite the aforementioned efforts, challenges remain in the fabrication of metal-polymer nanocomposites, e.g., the prevention of agglomeration of metal nanoparticles and the oxidation of metal surfaces. A method that can fabricate metal-polymer nanocomposites in a single step would provide advantages such as simplicity, low cost, and minimization of external disturbance and thus is highly desired. We found that the PIII&D technique which incorporates both ion implantation and ion condensation processes simultaneously in a single step is

capable of fabricating various metal-polymer nanocomposites, as demonstrated by the fabrication of Ti-PET nanocomposites in this section.

The depth of Ti ions implanted into PET at 10 keV is 20 – 30 nm from the simulation SRIM. This value is approximately the thickness for the modified layer after the PIII&D process. We also characterized the surface conductance of PET by CP-AFM. [Figure 3.3 a & b](#) are the current image of pristine PET and the current curve along the diagonal direction. No conductance but noise can be measured for pristine PET. [Figure 3.3 c & d](#) show typical current images for PIII modified PET at different magnifications. A bias of 2 V was applied in the measurements. In both [Figure 3.3 c](#) and [d](#), there are many small “dark dots” scattered on the surfaces. These “dark dots” represent Ti nanoparticles which are more conductive comparing to the remaining of the surface. The size of these spots is estimated to be around 10 nm and is in consistent with others results [\[152\]](#). This figure clearly indicates that the surface of PET has transformed into Ti-PET nanocomposites.

Figure 3.3 (a) The current image of pristine PET measured at -5 V. (b) The current measurement along the diagonal direction in (a). The current image of PIII&D processed PET measured at -2 V with an selected area of (a) 1000 nm (b) 200 nm. The “dark dots” represent high conductive Ti nanoparticles surrounded by PET matrix.

The current-voltage (I-V) characteristic is useful for determining the basic parameters of metal-polymer nanocomposites and to model the behavior when integrated into an electrical circuit. Figure 3.4 shows the average I-V plots for the selected areas *a*, *b*, and *c* as indicated in Figure 3.3. All I-V curves are non-linear and show typical metal-semiconductor junction conductivity. However, there are large variations in current values in these regions. For example, for areas *a* and *c*, the current is smaller than in area *b*. This originates from the surface inhomogeneity and implies that the conductivity in these regions is different, rather than just probing different conductive pathways to the substrate holder. By

looking at Figure 3.4b, it is fairly reasonable to deduce that Ti nanoparticles are highly conductive. Furthermore, if we look at these curves carefully, especially in Figure 3.4a – c, the “turn-on” voltage, which is defined as when the current starts to have a polynomial increase, is smaller for positive bias than for negative bias. When the bias is positive, electrons flow from the conductive tip into the modified PET surface.

Figure 3.4 (a) – (c) are the average I-V plots of selected areas *a*, *b*, and *c* as shown in **Figure 3.3**, respectively. Note the scale for current is very different. All curves show the typical metal-semiconductor junction conductivity. The “turn-on” voltage is smaller for positive voltage than for negative voltage.

We attribute the formation of Ti-PS nanocomposite to the cooperative effect of ion implantation and ion condensation in the PIII&D process, resembling the ion beam mixing (IBM) technique. On one hand, using ion implantation to fabricate metal nanoparticles in a polymer matrix has been studied recently, mostly on the

formation of noble metal nanoparticles [153-156]. *Stepanov et al.* indicated that ion fluence was a parameter of particular importance in the formation process [153]: at low ion fluence, the stopped ions are dispersed in the polymer matrix. When ion fluence reaches the critical value ($\sim 1 \times 10^{15} \text{ cm}^{-2}$), the solubility of metallic implants in the localized surface area of a polymer is exceeded, leading to the nucleation and growth of metal nanoparticles. When ion fluence is even higher, the synthesized metal nanoparticles may coalesce to form metal aggregates with larger size or quasi-continuous films via Ostwald ripening in the surface layer [153]. The schematic picture of the whole process is shown in Figure 3.5a. On the other hand, the IBM technique was initially considered optimum in semiconductor and polymer metallization by utilizing energetic ions to overcome the energy barrier at the interface of two different materials and to promote the necessary chemical bonding formations for enhancing the interfacial adhesion [157, 158]. Recently, the IBM technique for fabricating metal-polymer nanocomposites was demonstrated by *Micolich et al.* [159]. In their study, 50 keV N^+ was used to produce a network of alloy grains with a pre-deposited 10 nm thick Sn:Sb (95%:5%) alloy on the surface of polyetheretherketone (PEEK). The formation of metal nanoparticles by IBM is a reverse process to that of ion implantation, as schematically shown in Figure 3.5 b. At the beginning, a thin metal film is deposited on the surface. When energetic ions impinge the surface, the metal film cracks into large pieces due to ion sputtering effects. As ion fluence increases, part of metal films is energetically mixed with the underneath polymer matrix and the size of metal pieces reduces further. Finally, at high ion fluence, a network of metal nanoparticles is formed.

Figure 3.5 The schematics for the formation of metal nanoparticles via (a) ion implantation (b) ion beam mixing (IBM) technique.

Ti ion implantation provided by negative bias during pulse-on period induces Ti nanoparticles when the ion fluence approaches the critical value ($1 \times 10^{15} \text{ cm}^{-2}$). As plasma density is high in the FCVA, this critical value could be easily achieved in our experiment. Moreover, Ti condensation occurs during the pulse-off period and produces a thin Ti film prior to Ti ion implantation in the next pulse. The ion condensation region is expected to be thin because of two factors. First, the PIII&D process was carried out in high vacuum. Second, it is also known that polymers usually have low surface energy and the condensation coefficient, defined as the ratio of atoms remaining on the surface to the total arriving atoms, is normally much less than unity [149, 160]. This thin layer of ion condensation allows ion implantation to penetrate and mix the two materials. The two processes of ion implantation and ion condensation are repeated in every pulse of the whole modification, resembling the IBM process. Finally, a layer of Ti-PS nanocomposites were formed, with complex chemical bonding formations promoted by energetic ions. It is noteworthy that when compared with the

conventional IBM technique, the pre-deposition of a metal layer is avoided in PIII&D, thus the steps in obtaining conductive metal-polymer nanocomposites are simplified.

We also noticed that besides Ti nanoparticles, another possible contribution to the conductance is π -bonded nanoclusters. The formation of π -bonded nanoclusters, or carbonization, is a common ion implantation induced phenomenon in polymers [161, 162]. As seen from the theory of ion-polymer interactions, energetic ions dissipate their energy through electronic and nuclear stopping [45]. When the electronic linear energy transfer (LET) is high, a considerable volume around the ion tracks is influenced and active chemical species such as cations, anions, radicals and electrons along the polymer chains are produced. If two neighbouring radicals in the same chain unite, double or triple carbon bonds are formed, i.e., the delocalized π -bonds. The electron transport through these π -bonds is therefore facilitated. In literature, there are many reports that attribute electrical conductivity of gaseous ion implanted polymers to these π -bond nanoclusters [162-166]. It is also known that at very high ion fluence, abundant π -bonds can induce a metallic luster on the polymer surfaces because of light scattering from these electrons and the electrical conductivity can be increased by 16 orders.

3.3.3 Variable-Range Hopping Mechanism

The above CP-AFM study reveals the formation of Ti-PET nanocomposites. However, in order to better take advantage of metal-polymer nanocomposites, a formidable effort is necessary to investigate the transport mechanism. The electrical conductance in metal-polymer nanocomposites is known to have a different mechanism from that in metals and semiconductors where band models

can be applied. In studies of the transport properties of solid materials with large variance in structure, the temperature-dependent (T-dependent) conductance is of particular interest since it is indicative of the underlying transport mechanism. Particularly, for the system of conductive grains embedded in a dielectric medium, such as granular metals and doped semiconductors, two mechanisms are normally responsible for the obtained experimental data, the simple thermal activation model and the variable-range hopping (VRH) model [167-169]. The former can be described by an Arrhenius relationship for zero-bias conductivity, $\sigma = A \exp(-U/kT)$, where A is constant, U is the activation energy and k is the Boltzmann constant. U is proportional to the Coulomb charging energy of an individual grain, $E_c = e^2 / 4\pi\epsilon\epsilon_0 a$, expressed in terms of grain radius a , permittivity of space, ϵ_0 , and dielectric constant of the surrounding medium, ϵ . This simple activated behavior dominates those systems with weakly coupled electron-electron interactions at the Coulomb blockade regime, implying nearest neighbour hopping. In contrast, thermally assisted electron tunneling, or VRH, is mostly observed for systems with strong electron-electron interactions. The interplay between tunneling and thermal activation results in VRH behavior characterized by a stretched exponential T-dependent conductivity, as given by [168, 169]:

$$\sigma = A \exp\left(-\left(\frac{T_0}{T}\right)^a\right) \quad (3.3)$$

where σ is the electrical conductivity, A is constant, T_0 is the characteristic temperature, T is the measurement temperature, and a is 1/2 for a one-dimensional (1D) network, as in the Efros-Shklovskii (ES) model, and 1/4 for a 3D network, as in the Mott-law VRH.

From the microscopic point of view of metal-polymer nanocomposites, the nonconductive network is the polymer matrix whereas the conductive grains come from Ti nanoparticles and π -bonded nanoclusters. The Mott-law VRH states that the conduction transport is dominated by electron hopping between nearby localized electron states near the Fermi level E_F , which are associated with the Ti nanoparticles and π -bonded nanoclusters. As temperature rises, more electrons are thermally activated and the probability of tunneling becomes higher, leading to higher conductance.

The conductivity for pristine PET is $<10^{-16}$ S/sq and is beyond our measurement range; whereas the conductance of Ti-PS nanocomposites, as shown in [Figure 3.6a](#), is considerably higher. The conductance is calculated from the method proposed by van der Pauw, which stated that the resistivity for a symmetric electrode configuration as in the present case can be given by $\rho = \pi d R / \ln 2$ [130] (where ρ is the resistivity of the material, d is the thickness of the conductive layer, and R is the resistance measured by applying a current to two electrodes and measuring the voltage at the other two electrodes). Good ohmic curves are observed in all measurements because of the large contact area. At first glance of [Figure 3.6a](#), the tendency of the conductance along the temperature axis is rather random. However, it becomes clear if we divide it into three regions. The first region (R1) is from room temperature to 350 K, which is approximately the glass transition temperature T_g for PET. The conductance in this region shows a quasi-exponential increase as temperature increases. The second region (R2) is from 350 K to 400 K and the conductance keeps fluctuating in this region. The third region (R3) is from 400 K to 425 K and the conductance keeps decreasing. Unfortunately for even higher temperature, PET becomes mechanically soft and it

makes the measurement unreliable. Regions R2 and R3 encounter structural changes such as polymer chain relaxation and phase transition under high temperature. These structural changes may influence the conductance by changing the distance between neighbouring Ti nanoparticles and the dielectric constant of the PET matrix.

Figure 3.6 (a) The T-dependent conductance of Ti-PET nanocomposites. This curve is divided into three regions, R1, R2 and R3. R1 is from room temperature to 350 K, the glass transition temperature of PET, R2 is from 350 K to 400 K and R3 is from 400 K to 425 K. (b) The fitting of $\ln(\sigma)$ to $1/T^{1/4}$.

We therefore limit our interest to region R1 as in this region the conductivity could be hardly affected by structural changes due to high temperature. From Eqn. (3.3) we predict that the plot of $\ln G$ against $1/T^{1/4}$ should be linear. This is shown in Figure 3.6b. A well fitted linear line is observed. It confirms that such electronic conductivity is indeed controlled by a Mott-law VRH mechanism.

3.3.4 “Ageing” Effect in Conductance

Figure 3.7a shows conductance measured as a function of time t . Conductance at $t = 0$ means the measurement taken immediately after PIII&D modification. A rapid decrease in conductance is observed at the beginning. The decrease then

slows down with time and approaches saturation in the long term. Such a change in conductance is similar to the “ageing” effect in contact angle measurements for many plasma modified polymers, or physical ageing in polymer thin films [54, 63, 170]. The “ageing” effects in contact angle are driven by the minimization of surface free energy at the interface of the polymer and surrounding medium, which causes the absorption of low energy molecules from the surrounding atmosphere as well as the re-orientation of surface molecules, i.e., polar groups tend to return to the bulk side and low energy molecules tend to migrate to the surface side. Physical ageing is induced by changes in properties of polymer thin films near the glass transition temperature T_g , including chain relaxation and density. There are, however, few systematic studies performed for t -dependent conductance in the literature [171]. Balakrishnan *et al.* noticed the conductivity degradation in 8 mol % YSZ (8YSZ) ceramics with different microstructures and ascribed it to the subtle displacement of oxygen ions at high temperature [172]. In contrast, the “ageing” effect in conductance observed in the present case is at room temperature.

In order to find out how fast the conductance “ages”, we assume that an exponential relationship exists between the conductance G and time t . A linear fit is then found by plotting $\ln G$ with $t^{1/4}$, as shown in Figure 3.7b. Combining with Eqn. (3.3), a new equation that considers both temperature and “aging” effects can be given:

$$\sigma = A \exp\left(-\left(\frac{T_0}{T} \cdot \frac{t}{t_0}\right)^{1/4}\right) \quad (3.4)$$

where A , T_0 , t_0 are a constant, the characteristic temperature and the characteristic time respectively. t_0 is introduced here to indicate how fast the conductivity degrades. Surprisingly the decay coefficient for time t is also 1/4, the

same as the temperature coefficient in the VRH model. The underlying mechanism is as yet unknown to us. However, we suggest that the PET chains may “memorize” their original shapes due to their excellent mechanical properties. The damaged PET chains can gradually “reverse” back to their original positions and free radicals generated by ion implantation can bond to each other, crosslinking PET’s chains and blocking the electron transport.

Figure 3.7 (a) The electrical conductance for Ti-PET nanocomposites as a function of time t . Conductance at time “0” means that the measurement took immediately after the process. (b) A linear relationship observed in the “aging” effect by plotting $\ln(G)$ to $t^{1/4}$.

3.3.5 Supporting Materials in Conductance

The electronic transport of a granular system is also known to be dependent on the nature of the polymer matrix. To explore this effect, the same experimental conditions were applied to modify semi-crystalline PET (*sc*-PET) which is denser than the above mentioned PET (amorphous PET). The surface topography and the distribution of Ti nanoparticles in PIII&D modified *sc*-PET are similar to those in amorphous PET. The T-dependent conductance of *sc*-PET was then measured, as shown in Figure 3.8a. Likewise, there are two distinct regions in this figure, R1 and R2. The temperature point separating the two regions is 473 K where *sc*-PET

starts to show significant structural changes. We are interested in region R1 where structural changes could hardly occur. It is found that although the initial conductance at room temperature was almost the same for the two supporting polymers (see Figure 3.6a), the Mott-law of VRH mechanism is not observed. Instead, a logarithmic relationship between G and T exists and the fitting line is plotted in Figure 3.8b. In the literature, a logarithmic relationship was also observed in granular Al-Ge thick films and other systems [167, 173]. Although the mechanism for such relationships remains in dispute, it is clear that different supporting materials affect the intensity of electron-electron interactions between conductive clusters, hence the discrepancy in T -dependent conductance.

Figure 3.8 (a) The T -dependent conductance for modified sc -PET. Two regions are shown, R1 and R2. (b) The linear fitting of G with $\ln T$.

3.4 Summary

In summary, the PIII&D technique has been adopted successfully to fabrication Ti-PET nanocomposites on commercial PET surfaces. The surface topography turned into a “self-organized” nanostructure with arrays of conical “hillocks” and “craters”. Such a formation was the result of the interplay or competition between ion sputtering and surface re-deposition. The spatial distribution of Ti

nanoparticles inside a PET matrix has been investigated by CP-AFM measurements and the principles for the formation of Ti nanoparticles were discussed based on the uniqueness of the PIII&D process, i.e., the cooperative effects of ion implantation and ion condensation, resembling the IBM technique. It is noted that such formation should be universal and can be applied to other metal PIII&D modification on other polymers. The T-dependent conductance of Ti-PET nanocomposites was measured and a stretched-exponential relationship has been found for G and T , in accordance to Mott's law of VRH. Furthermore on the influence of the conductance, other factors, such as the "ageing" effect and supporting material, were also discussed. It was found that conductance "ages" with the same exponential coefficient as for the temperature dependence. A new equation of conductance has been proposed by considering both T and t . Finally, when *sc*-PET was used instead of amorphous PET as the supporting matrix, a logarithmic relationship for G and T was found.

CHAPTER 4 **Structural and Optical Properties of Ti-PS Nanocomposites**

4.1 *Introduction*

A subject of active research for polymer nanocomposites is their potential applications in optical and optoelectronic devices. The nonlinear optical properties arising from nanosized constituents as well as their interactions with the surrounding polymer matrix allow the devices to have high performance in applications such as photodiodes, solar cells, bandpass filters, photodetectors and light emitting diodes (LEDs) [174-177]. For example, near-infrared photodetectors were realized by mixing low bandgap (LBG) polymers, such as poly(3-hexylthiophene) or polythieno(3,4-b)thiophene, with (6,6)-phenyl C61-butyric acid methyl ester (PCBM) as the electron acceptor [176, 177]. Conjugated polymers and indium arsenide-based nanocrystals were also used to create near-infrared organic light-emitting diodes (OLED) and the emission was tunable from 1 to 1.3 micrometers, a range that effectively covers the short-wavelength telecommunications band [175].

Recently, metal-polymer nanocomposites also showed their promising optical properties [153, 178-180]. The size of metal nanoparticles embedded is usually 1-10 nm. As the size reduces into the quantum confinement range, the energy levels inside the nanoparticles are quantized because of the physical constraint to electron wavefunctions. The optical excitation or adsorption of metal nanoparticles would be inevitably altered by the quantum confinement effect. In addition, metal nanoparticles show a particular optical property, the excitation of surface plasmons

(SP) or surface plasmon polaritons (SPP). SP is an important phenomenon responsible for many applications, such as biosensors, coupled fluorescence, photodetectors, and surface-enhanced Raman scattering (SERS) [181-184].

According to Maxwell's theory, SP is the coherent fluctuation of electron density which propagates at the interface of a metal and a dielectric material. In principle, both a surface plasmon resonance (SPR) wave and localized surface plasmon resonance (LSPR) are possible. The former is the excitation of SP at the interface of a planar metallic surface with adjacent dielectric material and the latter is the excitation of SP at the interface of metal nanoparticles with adjacent dielectric material. Because the dispersion relation of SP is different from that of light, i.e., it is "nonradiative", a special light-plasmon coupler is required for the excitation of the SPR wave in a planar metallic surface. For example, an attenuated-total-reflection (ATR) prism in either *Kretschmann* or *Otto* configuration is often used when light is used as the excitation source [185]. On the other hand, only direct light is required for the excitation of LSPR because the coupling can be realized by the scattering from metal "islands". While noble metal nanoparticles (e.g., Au, Ag, and Cu) have been widely studied for the excitation of LSPR, composites containing Ti nanoparticles have seldom been reported, despite the fact that Ti is an important element for the production of waveguide layers, optical filters and other optical applications [186]. This is probably due to the difficulty in synthesizing Ti nanoparticles in a polymer matrix and the high tendency of oxidation on the surface of Ti nanoparticles. Oxides covering metal nanoparticles can degrade the intensity of LSPR and sometimes may even inhibit it. In this chapter, we demonstrate that our Ti-PS nanocomposites synthesized by PIII&D are capable of generating a LSPR peak at room temperature. This is

substantially different from Ti/oxide nanocomposites where LSPR peaks were only seen after annealing the nanocomposites at high temperature ($>400\text{ }^{\circ}\text{C}$) [186].

4.2 Experimental Details

Commercial PS sheet, 2 mm thick ($\rho=1.05\text{ g/cm}^3$, $T_g=95\text{ }^{\circ}\text{C}$, Goodfellow), was cleaned in isopropanol alcohol (IPA) under sonication before the PIII modification. The samples were then transferred to the vacuum chamber and a metal mesh was used to cover its surface at a distance of $\sim 5\text{ mm}$. The purpose of this metal mesh was to mitigate the surface charging effect caused by ion implantation in the PIII&D process [187]. The base pressure was $1\times 10^{-5}\text{ Torr}$. The processing pressure was $1\times 10^{-3}\text{ Torr}$ when a Ti plasma was generated by the FCVA system at 90 A DC with the flow of Ar gas. The PIII parameters were a frequency of 500 Hz, pulse width of 20 μs , processing time of 3 min, and voltages of -5 kV, -10 kV and -15 kV in order to obtain different damages due to ion irradiation of the polymer.

The preparation of plane view TEM samples for Ti-PS nanocomposites is as follows: PS ($M_w=280\text{ }000\text{ g/mol}$, Sigma) was first dissolved into toluene at a concentration of 1%. The solution was then spin-coated on n-type Si (100) wafer. The same conditions of PIII&D process for bulk PS were then applied for the synthesis of Ti-PS nanocomposites. After that, Ti-PS (together with the Si wafer) was introduced into a carbon-coated copper grid and secured with epoxy. The composite was then sliced into 600 μm thick disks with the low speed diamond saw and the disks were then mechanically ground with a disk grinder to a thickness of about 100 μm . The centre portions of these disks were further ground by the dimple grinder to approximately 20 μm . The samples were then thinned in the

precision ion polishing system with argon ions at an accelerating voltage of 5 kV which incident at an angle of 4° . A hole was finally created at the center of the specimen to provide larger transparent areas for TEM observation at an accelerating voltage of 200 kV.

4.3 Results and Discussion

4.3.1 Surface Analysis of Ti-PS Nanocomposites

Figure 4.1 shows both the cross-sectional and plane-view TEM images for PIII&D modified samples at -15 kV. The preparation for cross-sectional TEM was done by slicing PIII&D modified samples into 100 nm thick specimens using an ultramicrotome (*Leica*) with a diamond knife while the preparation for plane-view TEM was done by firstly dissolving PS into toluene and then spin-coating the solution onto a n-type Si (100) wafer. The exact PIII&D conditions were then applied for the fabrication of Ti-PS nanocomposites. Two distinctive layers were observed in the cross-sectional image, i.e., pristine PS and Ti-PS nanocomposites, as labeled in Figure 4.1a. The thickness of the Ti-PS nanocomposite layer was approximately 70 nm, consistent with others results under similar experimental conditions [98]. Ti nanoparticles 5 – 15 nm in size embedded in a PS matrix were clearly shown in the plane-view TEM image (Figure 4.1b). The selected area electron diffraction (SAED) pattern of the sample (the inset in Figure 4.1b) comprised of characteristic rings, indicating the nanocrystalline nature of the hexagonal Ti crystal structure. The amorphous structure of the PS matrix was indicated by the opaque halo in the center of the SEAD pattern.

Figure 4.1 (a) Cross-sectional and (b) plane-view TEM images for PIII&D modified samples at -15 kV. The inset in (b) is the SAED pattern.

The formation of Ti nanoparticles is a result of the cooperative effect of both ion implantation and ion condensation in the PIII&D process, as elaborated in [Chapter three](#). The detailed chemical states in Ti-PS nanocomposites were revealed by XPS measurements here. [Figure 4.2](#) of the XPS survey-scan shows the successful incorporation of Ti atoms. In contrast to pristine PS where only a carbon (C) peak was present, prominent Ti and oxygen (O) peaks were also found in PIII&D modified samples at their corresponding binding energy (BE) positions. While detectable C atoms implied no continuous, thick Ti film covering the surface, the prominent O peak indicated a large amount of O atoms on the surface. It is noted that O atoms were often found in many plasma treated polymers even when the pristine polymers were not oxygen-containing [188]. The source of these O atoms in the present case came from the residual oxygen or water vapor which reacted with free radicals created by ion implantation. Another possibility is the oxidation of surface Ti nanoparticles when the PIII&D modified samples were exposed to atmosphere [55].

Figure 4.2 The XPS survey-scan of Ti-PS nanocomposites fabricated at - 15 kV. All elements have been labeled at the corresponding B.E. positions.

XPS narrow-scan spectra for each element, i.e., C 1s, O 1s and Ti 2p, are shown in [Figure 4.3 a – c](#) respectively. By taking values from the literature [189, 190], deconvoluted peaks in each spectrum were assigned to the corresponding chemical bonds, as summarized in [Table 4.1](#). A particularly interesting finding is that Ti atoms have three different chemical states, metal, oxide, and carbide. For example, in [Figure 4.3a](#), the peak at BE 283 eV is attributed to the formation of a Ti-C bond because Ti atoms have smaller electronegativity than C atoms. Ti-C bond is then shifted to lower BE with respect to C-C or C-H peak. Similarly, the peak at BE 529.8 eV in [Figure 4.3b](#) is assigned to Ti-O bonds. The assignments of both Ti-C and Ti-O bonds are confirmed in the Ti 2p spectrum, as shown in [Figure 4.3c](#). These results verify that Ti-PS composites have complex bonding structures, with three elements interacting with each other.

As the sampling depth of XPS characterization is only about 5 nm, XPS depth profiling is required to fully explore the chemical state in Ti-PS nanocomposites.

The detailed narrow-scan spectra for Ti atoms at different depth are shown in [Figure 4.4](#). We noticed that the intensity of some peaks reduced faster than others. For example, two peaks at BE 457.6 and 464.6 eV corresponding to Ti-O vanished at around 12 nm whereas Ti and Ti-C bonds persisted up to a depth of 36 nm. This result implied that only surface Ti atoms were oxidized and not the implanted Ti atoms. The same conclusion has been drawn from the depth profiling spectra for C and O atoms. It is proposed that implanted Ti atoms were surrounded by a PS matrix which inhibited their contact with O atoms while surface Ti atoms could easily get oxidized after the modified samples were exposed to the atmosphere.

Figure 4.3 (a) – (c) The XPS narrow scans and their deconvoluted peaks for C 1s, O 1s, and Ti 2p of PIII&D modified samples at -15 kV, respectively.

Spectra	Peaks (eV)	Bonds
C 1s	283	C–Ti
	285	C–H
	285.4	C–O
O 1s	529.8	O–Ti
	531	O–C
Ti 2p	454.5, 460.4	Ti 2p ₃ , Ti 2p ₁
	456, 463.1	Ti–C
	457.6, 464.6	Ti–O

Table 4.1 The assignments of peaks in **Figure 4.3** to corresponding chemical bonds.

Figure 4.4 Detailed Ti 2p spectra for PIII&D modified PS at -15 kV at different depth. Two peaks at BE 457.6 and 464.6 eV corresponding to Ti–O bond vanish at depth around 12 nm.

4.3.2 Excitation of LSPR

As mentioned, the embedded Ti nanoparticles are able to give a LSPR response when excited by light. The optical absorbance of both pristine PS and Ti-PS nanocomposite samples was measured by a UV-Vis transmittance spectrophotometer (UV-2501PC, Shimadzu) in transmission mode. The

measurements were carried out by putting a sample into one channel and blanking the other channel as the reference. The absorbance spectra shown in Figure 4.5a were plotted with respect to the reference channel and by ignoring any reflectance or scattering from sample surfaces. This is acceptable as the sample roughness was kept low. For PIII&D modified samples, the absorbance is the superposition of unaffected PS and its modified surface layer, i.e., the Ti-PS nanocomposites layer. To separate the absorbance from the two layers, the relative absorbance is used, which subtracts the absorbance of pristine PS from that of PIII&D modified PS. Specifically, the Beer-Lambert law for single-layered material is given by [191],

$$A = \alpha l \quad (4.1)$$

and for double-layered material,

$$A' = \alpha_1 l_1 + \alpha_2 l_2 \quad (4.2)$$

where A and A' are the total absorbance for single- and double-layered materials respectively, α , α_1 , α_2 are the absorbance coefficient for the corresponding layers and l , l_1 , l_2 are the distances the light travels through the corresponding layers. As the absorbance contributed by the layer of unaffected PS in PIII&D modified samples is almost the same as the absorbance of pristine PS samples, the relative absorbance of Ti-PS nanocomposites can be obtained by subtracting Eqn. (4.1) from Eqn. (4.2). The result is re-plotted in Figure 4.5b.

Figure 4.5 (a) The optical absorbance of both pristine and PIII&D processed PS at applied bias of -5kV, -10kV and -15kV. (b) The relative absorbance obtained by subtracting the absorbance of pristine PS from that of PIII&D processed PS. The relative absorbance is purely due to the Ti-PS nanocomposites layer.

Two interesting features are observed in all spectra in Figure 4.5b. One is that an absorption peak is found at 337.5 nm and the other is the extension of absorption tails from UV to the near infrared range. The former is due to the excitation of LSPR at the interface of the Ti nanoparticles and PS matrix. Assuming the nanoparticles are spherical in shape, the electrical field induced at the surface is related to the applied, external (light) field by [181]:

$$E_{induced} = \frac{\varepsilon_m - n_d^2}{\varepsilon_m + 2n_d^2} E_{light} \quad (4.3)$$

where ε_m is the real part of dielectric constant for a metal and n_d is the optical constant for dielectric material. Therefore, the condition derived from Mie theory that meets the SP resonance for metal-polymer nanocomposite is given by [186, 192]:

$$\varepsilon_m + 2n_d^2 = 0 \quad (4.4)$$

The optical constant for Ti can be found from Ref. [193]. At a wavelength of 337.5 nm, or 3.67 eV, n_{Ti} and k_{Ti} are 1.67 and 2.79 respectively. This gives $\varepsilon_m = n_{Ti}^2 - k_{Ti}^2 = -5$. On the other hand, n_d is 1.59 for PS, pronounced from the

supplier's specifications. We then get $-2n_d^2 = -5.05$. The good agreement between the two values indicates that the condition described by Eqn. (4.4) is fulfilled, implying that the absorption peak at this wavelength is indeed caused by the excitation of LSPR. Furthermore, the average radius of the metal nanoparticles can be estimated from [186]:

$$R = \frac{V_f \lambda_p}{2\pi c \Delta\lambda_p} \quad (4.5)$$

where V_f is the Fermi velocity of electrons in bulk metal ($\sim 10^6$ m/s), λ_p is the wavelength of the SPR peak, c is the light velocity in vacuum and $\Delta\lambda_p$ is the full width at half maximum (FWHM) of the LSPR peak. We obtain $R = 8.4$ nm for our Ti-PS nanocomposites. This result is consistent with the TEM image as shown in Figure 4.1b.

The above observation of LSPR response at room temperature is illuminating. To our knowledge, presently no LSPR response has been reported for Ti-polymer nanocomposites. There are, of course, observations of LSPR peaks from Ti/oxide nanocomposites when the nanocomposites were annealed at high temperature (>400 °C) [186]. The high temperatures provided the energy for isolated Ti atoms to move and coalesce into Ti nanoparticles via Ostwald ripening. In contrast, as polymer chains become mobile at relatively low temperature (the glass transition temperature T_g), implanted and condensed Ti atoms can diffuse to nucleate and grow into Ti nanoparticles at localized surface regions in a much easier manner. This again validates PIII&D as an efficient technique to fabricate metal-polymer nanocomposites.

The microstructures of Ti nanoparticles, such as size, shape, volume fraction, and so on, are also known to influence both the position and the width of the LSPR

peak [194]. For example, *Krebig et al.* studied the size-dependence of the LSPR peak and indicated that the excitation of SP can be strongly changed if the particles and the sample interact with each other [195]; *Yang et al.* studied the SP excitation in Cu-polymer nanocomposites and found that the SP peak positions shifted to larger wavelength when the size of the Cu nanoparticles was increased [196]. We also observe the structure-dependence of LSPR peaks in our samples. The peak intensity is larger in Ti-PS nanocomposites fabricated at -15kV than that in the other two samples, as shown in Figure 4.5b. It is expected that higher voltage can lead to higher Ti ion implantations and hence a higher Ti fraction in the nanocomposite. However, the peak position at 337.5 nm is not shifted at different voltages. Two possibilities may contribute to this. First, the averaged size and shape didn't change with the increasing accelerating voltage, but only the metal volume fraction. It is expected that the metal volume fraction in the PS matrix would increase at higher accelerating voltage [197]. Higher metal volume fraction tends to increase the absorption peak, which is consistent with our observation that the peak was the highest at 15 keV. Second, if the change in the size of metal nanoparticles did occur but the amount of change was not large, only slight shift to a few percentages (~5 nm) would be observed [195]. This value approached to the limit in the measurement (steps of 10 nm wavelength were used in the UV-Vis spectrometer), making the difference indistinguishable at different voltages.

The second feature in the absorbance spectra is the broadening of absorption wavelength ranging from UV to infrared. This is attributed to the fractal network of nanocomposites where Ti nanoparticles could be present in various sizes, irregular shapes, and different orientations [178] (the conductivity of this fractal network is controlled by electron tunneling between nanoparticles, as shown in the

previous chapter). As seen from Figure 4.1b, Ti nanoparticles show large variations in size, shape, and orientation (*c.f.*, the SAED pattern). Furthermore, short-range interactions due to the close proximity of nanoparticles, like in the present case, can also be responsible for the broadened absorbance [197]. While a sharp and distinctive LSPR peak is desired in some sensor applications, broadband absorbance ranging from UV to infrared can be important for potential infrared applications, including thermal imaging, high-efficiency solar cells absorbing as much as possible of the solar radiation, thermal photovoltaics, and infrared photodetector and sensors [178, 197]. In SERS studies, broadband absorbance could also provide the enhancement of optical signals from any molecular transitions.

4.4 Summary

Ti-PS nanocomposites were fabricated using PIII&D. XPS measurements revealed that Ti atoms had three different chemical states, metal, oxide, and carbide. While surface Ti atoms were oxidized, embedded Ti atoms kept their metallic states due to the surrounding PS matrix. The excitation of LSPR at the interface of Ti nanoparticles and PS matrix was shown by UV-VIS measurements. Two interesting features were identified in the absorbance spectra, an absorption peak at wavelength 337.5 nm and the broadening of the absorption wavelength ranging from UV to infrared. The former was a result of the average sized Ti nanoparticles and the latter was from the fractal network of Ti nanoparticles where Ti nanoparticles could be present in various sizes, irregular shapes, and different orientations. Potential applications of using the optical properties of the Ti-PS nanocomposites were also discussed.

CHAPTER 5 **Protein Immobilization on Ti-PS Nanocomposites**

5.1 *Introduction*

Protein immobilization on a solid surface is a common phenomenon that occurs in many fields, such as food, chemical, biotechnology, and medical diagnostic industries [198]. In certain applications, protein immobilization is desired to be high. For example, in protein microarray technology, one of the main obstacles is the low efficiency of proteins immobilized on the microscale, arrayed surface, which inhibits subsequent capture of analytes [199]. In the biomaterials field, protein immobilization is the first step in the integration of an implanted device or materials with tissue [200, 201]. Subsequent bioactivities (e.g., accumulation of bacteria into biofilm) are inevitably influenced by the amount and orientation of proteins immobilized on the surface. In nanotechnology, higher protein immobilization is pivotal in sensors, actuators, and other functional components at the biological and electronic interface.

Polymers have been utilized as surfaces for immobilizing proteins because of their lightness, strength, formability, stability, resistance to corrosion, and chemical resistance. For example, PS is used for microtitre plates which require formability, mechanical strength and impermeability. Unfortunately, many polymers do not always possess suitable physiochemical properties that can optimize protein immobilization. Various methods have been therefore proposed to alter the physicochemical properties of polymer surfaces, particularly versatile plasma treatments [170, 202]. Recently, PIII as a technique to strengthen the

interactions between biomolecules and solid surfaces has received considerable interest [203-205]. For example, N₂ and Ar PIII was used to modify PE to increase the immobilization of *catalase* and *poly-L-lysine* through creating covalent interactions [203]; C₂H₂ PIII was used to deposit a thin layer of *a-C* on PET to reduces bacterial adhesion [204-206]. In this chapter, we utilize the Ti PIII&D technique to fabricate Ti-PS nanocomposites on PS thin films and use them as the solid surfaces for protein immobilization. Ti was chosen because of its biocompatibility which may play an important role for the subsequent cell culture in some practical applications. PS was chosen because it is widely used in biomedical devices, is inexpensive, and has good mechanical properties.

5.2 Experimental

5.2.1 PS Thin Films

PS ($M_w = 280$ kg/mol, *Sigma*) was dissolved in toluene at different concentrations, namely, 2 w/v% and 3 w/v%. After complete dissolution, the solution was spin-coated on *n*-type to a Si wafer ($R = 0.01 \Omega\cdot\text{cm}$) without the removal of the native oxide layer (~ 2 nm). The spin-coating process was performed inside a class 100 clean room to minimize any surface contaminants. The spin-coated PS thin films were then cured in vacuum at 140 °C ($T_g=100^\circ\text{C}$ for PS) for 14 hours. The thickness of the PS thin films was measured at 142 ± 2 nm for 3% solution and 82 ± 2 nm for 2% solution using ellipsometry (VB 250, *J. A. Woollam, Co.*). We also confirmed the thickness by firstly using a razor blade to scratch a trough on the surface and then measuring the height of the trough using a surface profiler (*Tencor*). The two measurements were consistent with each other.

5.2.2 PIII&D Process

The operation parameters for PIII&D were a voltage of -10 kV, frequency of 500 Hz, duty time of 20 μ s and processing time of 3 min.

5.2.3 Peroxidase Protein Assay

The amount of protein immobilized on the solid surfaces was quantitatively measured using a peroxidase protein assay similar to the enzyme-linked immunosorbent assay (ELISA), as shown in [Figure 5.1](#). Briefly, 200 μ l of soybean peroxidase (SBP) (*Sigma*) was diluted in 10 mM sodium phosphate buffer (pH = 7.0) to a concentration of 1 μ g/ml. 200 μ l of such SBP solution was then incubated on a Ti-PS nanocomposite surface using a clamp with an O-ring seal (diameter 12 mm) in the center. After 1 hr incubation, the SBP solution was removed and the samples were transferred to sterile Petri dishes containing a sodium phosphate buffer (pH = 7.0) for washing. The washing step was repeated four times for 1 hr each time in fresh sodium phosphate buffer. After that, 200 μ l 3,3',5,5'-tetramethylbenzidine (TMB) was added to the Ti-PS nanocomposite surfaces using another clamp with an O-ring seal (diameter 12 mm) in the center. The color of the TMB solution changed from blue to yellow in the presence of SBP. After a 1 min reaction, 50 μ l of TMB from the surface of Ti-PS nanocomposites was pipetted to a 96-well microtitre plate and 50 μ l of 2 M HCl (*Sigma*) was added to stop the reaction. The color changed immediately from blue to yellow in this step. Finally, the absorbance of the solution was measured at a wavelength of 450 nm by using a microplate reader (*Bio-Rad*). The quantity of protein immobilization was

calculated with the aid of a standard curve plotted using the above peroxidase protein assay.

Figure 5.1 The steps and materials used in performing the protein assay. 1, Ti-PS were prepared by PIII&D technique; 2, 1 $\mu\text{g/ml}$ SBP solution was incubated on Ti-PS nanocomposites using clamps with O-rings seals in the center; 3, After four time washing in sodium phosphate buffer (pH=7.0), the samples were clamped again with O-rings in the center. TMB was pipetted to the center and the color changed quickly from transparent to blue; 4, the reaction was allowed for 1 min and then 2 M HCl is added to inhibit the reaction. The color changed from blue to yellow immediately. The color is stable for at least 1 hour and the absorbance at 450 nm was measured by the microplate reader.

This protein assay utilizes the enzymatic property of SBP to oxidize the TMB [207, 208]. In the presence of SBP/H₂O₂, TMB can be quickly oxidized and the color changes from transparent to blue. The reaction is shown in Figure 5.2. Another common protein that can be utilized in the protein assay is horseradish peroxidase (HRP).

Figure 5.2 The oxidation of TMB catalyzed by SBP. The color changes from transparent to blue after the oxidation.

5.3 Results and Discussion

5.3.1 Ti-PS Nanocomposites

Similar to the experiment for Ti-PS nanocomposites fabricated on commercial PS samples, we characterized Ti-PS nanocomposites on PS thin films using XPS and TEM (Chapter four). The successful incorporation of Ti atoms into PS thin films after PIII&D has been confirmed by XPS, as shown in Figure 5.3. Each peak in the spectra is identified with the respective element according to their corresponding BE. Again, the peak intensity of O 1s was largely increased, implying that the concentration of O atoms was increased in the Ti-PS nanocomposites. A large amount of O atoms is apparently interacting with the PS matrix and/or Ti atoms.

Figure 5.3 XPS survey-scan for (a) PS thin films (b) PIII&D processed 3% PS thin films. PIII&D processed 2% PS thin films have similar spectrum as in (b).

Figure 5.4 shows plane views of Ti-PS nanocomposites on both 2 w/v% and 3 w/v% PS thin films at different resolutions. The SAED patterns for both samples exhibited ring patterns, in agreement with the polycrystalline structure of α -Ti [209]. The size of the Ti nanoparticles in the 2% PS matrix was a bit larger than that in the 3 % PS matrix, i.e., 10 – 15 nm and 5 – 10 nm respectively. It is noteworthy that the Ti-PS nanocomposites did not dissolve in acetone which was used as a solvent to remove the epoxy in TEM preparation, while pristine PS thin films were soluble in acetone.

Figure 5.4 Plane-view transmission electron images of Ti-PS nanocomposites fabricated on 2% PS thin films: scale bar (a) 50 nm; (b) 5 nm and 3% PS thin films: scale bar (c) 50 nm; (d) 10 nm. The insets in (a) and (c) are the SAED patterns, indicating polycrystalline structure of Ti nanoparticles.

5.3.2 Protein Immobilization

Before the amount of protein immobilization on different solid surfaces can be quantified, a standard curve was plotted by measuring the absorbance of TMB in the presence of SBP with known concentrations, as shown in [Figure 5.5](#). This standard curve shows that the absorbance starts to increase at a SBP concentration of about 10^{-9} g/ml (lower limit of detection) and saturates at a SBP concentration above 10^{-7} g/ml. Therefore, it is desirable to have measurements on the absorbance range from 0.2 to 3.5 (arbitrary unit), which corresponds to the lower limit of detection and saturation respectively.

Figure 5.5 The standard curve plotted by measuring the absorbance of TMB in the presence SBP with known concentrations.

Figure 5.6 shows the absorbance from different solid surfaces by carrying out the aforementioned peroxidase protein assay. The absorbance for Ti-PS nanocomposites fabricated on both 2 % PS thin films (Ti-PS 2%) and 3 % PS thin films (Ti-PS 3%) was almost twice that of PS thin films. The amount of SBP immobilized is calculated to be approx. 3 ng/cm² on both the Ti-PS nanocomposites, in contrast to 1.7 ng/cm² on pristine PS thin films. It is clear that Ti-PS nanocomposites offer an enhanced protein immobilization.

Figure 5.6 The absorbance from pristine PS thin film and Ti-PS nanocomposites fabricated on 2% PS thin films and 3% PS thin films.

5.3.3 Enhancement Mechanism

It is known that protein immobilization is determined by the interactions between the protein and the solid surface [200]. Two types of interactions are usually present, nonspecific and specific interactions. The type and strength of interactions are in-turn determined by the physiochemical properties of the surface as well as the nature of the protein molecules. The key properties for protein immobilization include surface morphology, surface tension, hydrophobicity or hydrophilicity, functional groups, etc. Unfortunately, the effects of these properties to protein immobilization are not well defined and sometimes even controversial. For example, *Schneider et al.* found that roughened and grooved Ti surfaces showed significantly increased immobilization of transcription factor and gene expressions in cells [210]. *Malmsten et al.* found that fibrinogen, immunoglobulin (IgG), and human serum albumin (HSA) adsorbed more on a hydrophobic methylated silica surface than on a hydrophilic silica surface whereas lysozyme adsorbed more on a hydrophilic silica surface than on a hydrophobic methylated silica surface [211]. It is therefore necessary to investigate the relationship between surface changes and protein immobilization for a specific metal-polymer nanocomposite. The possible mechanisms which may have arisen from altered surface properties in the present case are analyzed as follows.

Figure 5.7 shows the AFM images of both pristine and Ti-PS nanocomposites on 3% PS thin films. The pristine PS thin film has a smooth surface with a root-mean-square (*rms*) roughness less than 0.3 nm. However, the *rms* roughness of Ti-PS nanocomposites increased to 1.5 nm. In addition, the surface topography shows “self-organized” nanostructures with arrays of “hillocks” and “craters”,

consistent with results reported in the previous chapter. The increased surface roughness may favor protein immobilization because it provides a larger surface area for higher interfacial adhesion.

Figure 5.7 AFM images of (a) pristine PS thin film ($5 \times 5 \mu\text{m}$) and (b) Ti-PS nanocomposites on 3% PS thin films ($1 \times 1 \mu\text{m}$).

The calculation of the surface tension of Ti-PS nanocomposites uses the Lifshitz-van der Waals/acid-base (LW-AB) approach, which breaks up the surface tension into three components, γ^{LW} , the nonpolar London-van der Waals component, γ^+ , the electron-acceptor surface tension, and γ^- , the electron-donor surface tension. By combining with Young's equation, the relationship between contact angle θ and surface tension components is given by [204]:

$$(1 + \cos \theta) \gamma_L = 2(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}) \quad (5.1)$$

where the subscripts S and L indicate solid and liquid respectively. The equilibrium CAs on Ti-PS nanocomposites were measured using the sessile drop method and by allowing 1 min stabilization of the droplet after dispersion. The average value from three different spots in each measurement was taken. The equilibrium angles were 65.1° , 30.2° , and 34.2° by using DW, diiodomethane and formamide as the

testing liquid respectively. The surface tension components for the three testing liquids, DW, diiodomethane and formamide, are listed in Table 5.1 [204]. By using Eqn. (5.1), the surface tension components for Ti-PS nanocomposites were determined to be 44.1, 7.9, and 1.3 mJ/m² for γ^{LW} , γ^+ , and γ^- respectively. Comparing this value with pristine PS thin film which has $\gamma^{LW} \sim 40$ mJ/m², apparently both the electron- donor and acceptor surface tensions increase. The increased surface tension may also contribute to the enhanced protein immobilization because it provides higher interfacial adhesion to protein molecules.

	γ_L	γ_L^{LW}	γ_L^+	γ_L^-
Water	71.8	21.8	25.5	25.5
Formamide	58.0	39.0	2.28	39.6
Diiodomethane	50.8	50.8	—	—

Table 5.1 Surface tension components for testing liquids (in mJ/m²) [204].

Lastly, surface functional groups were revealed by a XPS narrow-scan for C atoms, as shown in Figure 5.8. The spectra were deconvoluted and labeled for corresponding chemical bonds [118]. We found that besides the C-C and C-O bonds which exist on pristine PS thin films, carboxyl groups (COO-) are present on the surface of Ti-PS nanocomposites. The carboxyl group may interact with amino groups in protein molecules to form covalent peptide bonds. Both the amount and the strength of the protein-solid surface will be enhanced due to such bond formation. This is in agreement with recent results that a PIII modified surface induced covalent bonding to proteins [203]. It is noted that the π - π^* peak was eliminated after the PIII&D process, indicating that the phenyl ring was the primary site for oxidation or reaction with residual gases [212].

Figure 5.8 XPS narrow-scan of C 1s for (a) PS thin films (b) Ti-PS nanocomposites on 3% PS thin films. Carboxyl (COO-) functional groups were found on (b).

Further evidence of the generation of surface functional groups is through the study of CA hysteresis. [Figure 5.9](#) shows both the advancing and receding angles on Ti-PS nanocomposites (3%) using DW as the testing liquid. The method adopted in the measurements was given in [Figure 2.5](#). Several interesting features are found in this figure. First, comparing with the value of pristine PS thin film (108°), surface hydrophilicity was greatly enhanced in Ti-PS nanocomposites immediately after the PIII&D modification (e.g., $t = 1$ h). Although the “ageing” effect was observed, the angle stabilized at a value less than 108° ($\sim 85^\circ$). Secondly, the CA hysteresis was large ($\sim 50^\circ$). As CA hysteresis is the measure of re-orientation of surface groups, this large value could mean that a large portion of functional groups are present on the surface. It is suspected that before water was

dispensed, hydrophobic groups or low-molecular-weight molecules resided on the surface. The water front for the advancing angle therefore met these groups and a high CA was established. After the surface was immersed in water, hydrophilic or polar groups migrated to the surface and a smaller receding angle was established. The enhanced surface hydrophilicity and functional groups favor protein immobilization by higher interfacial adhesion on protein molecules.

Figure 5.9 CA hysteresis and aging effect for Ti-PS nanocomposites (3%): advancing (■) and receding (●) angles. The CA for pristine PS thin film is 108°.

5.4 Summary

In summary, Ti-PS nanocomposites fabricated on PS thin films have been utilized as a biomaterial to enhance protein immobilization. Ti nanoparticles with size of 5 – 15 nm were characterized by TEM. A peroxidase protein assay based on the enzymatic property of SBP on the oxidation of TMB has been carried out to quantify the amount of protein immobilized on solid surfaces. A comparison between pristine PS thin films and Ti-PS nanocomposites revealed that the amount

of SBP immobilization had increased from 1.7 ng/cm² on the former to 3 ng/cm² on the latter. The mechanisms of enhancement have been ascribed to the altered physiochemical properties of Ti-PS nanocomposites, such as surface roughness, surface energy, and surface functional groups.

CHAPTER 6 **Dewetting of PS Thin Films by Ion Implantation**

6.1 Introduction

Polymer films are becoming progressively thinner as science and technology try to exploit their advantages in applications such as organic electronics, photoresists, optical devices, biomaterials, etc. However, it is a technical challenge to produce uniform, continuous and defect free films. Moreover, some polymer thin films showing good quality right after preparation may degrade and become unstable to ageing or environmental perturbations (e.g., temperature). One of the most common instabilities is polymer dewetting [213]. Dewetting is a phenomenon related to the break up of polymer films and the subsequent exposure of the substrate surface. In contrast to wetting where liquids spread on a solid surface and form a complete layer [214], dewetting of polymer thin films occurs when the films are forced to coat on a non-wettable surface by techniques such as spin-coating and dip coating. In the past two decades, dewetting has been a subject of intense research not only because a profound understanding of dewetting can provide us the necessary knowledge to tailor the instabilities of the films, e.g., *Karim et al.* reported that both the addition of C₆₀ nanoparticles and polymer branching can inhibit polymer dewetting [215], but also because dewetting in a controlled manner represents a promising way for submicrometer non-lithographic patterning [216-220], e.g., the fabrication of polymer field effect transistors, the micropatterning of proteins, and the nanopatterning of polymer thin films.

There are usually two mechanisms controlling dewetting of polymer films, spinodal dewetting and heterogeneous nucleation [221-224]. The former is induced by the amplification of thermal fluctuations and the latter is induced by the impurities or defects in the films. So far, much work has been done on spinodal dewetting of ultrathin and thermodynamically unstable polymer films. A few “spinodal-like” dewettings of thermodynamically stable polymer films associated with special conditions such as structural forces and density fluctuations have been reported [225, 226]. Nonetheless, the thickness of the films in these reports was usually less than 50 nm. Here we demonstrate that thermodynamically stable, thick (~100 nm) polymer films could possibly undergo dewetting. We use PS as the model polymer which has been extensively utilized for the fundamental understanding of the dewetting phenomenon of polymer thin films. Ti ion implantation was chosen to induce dewetting of PS films. It is noted that ion implantation was previously utilized to dewet metallic thin films [227, 228]. The current study is motivated by the fact that in many industrial processes, such as photolithography and pattern transfer for microelectronic fabrications, plasma modification, thin film deposition, and space engineering, polymer thin films are very often exposed to an ambient environment including both high temperature and energetic metal ions.

6.2 *Experimental*

PS (Sigma) ($M_w=280,000$ g/mol, $M_w/M_n < 1.10$, corresponding to an unperturbed radius of gyration $R_g \sim 14$ nm) was dissolved in toluene at a concentration of 2 w/v%. The solution was then spin-coated on a *n*-type Si (100) wafer with a pre-deposited 100 nm thick gold (Au) layer using an e-beam

evaporator (AUTO 360, *Edwards*). The purpose of this Au layer is to effectively screen the influence of native oxide on the stability of PS films, as described later. Spin-coating was done in a class 100 clean room to minimize surface contaminations. The PS films were then annealed at 140°C in vacuum for 20 h (the glass transition temperature T_g of PS is ~100°C). The thickness of films was 100±2 nm as measured by an ellipsometer (VB 250, *J. A. Woollam Co.*).

Ti ion implantation was obtained by applying the PIII&D technique with a Ti plasma generated from the FCVA system. As the plasma density varies largely as a function of the distance between the exit of the bend and the sample surface, we fixed the sample much closer (~ 12 cm) to the exit of the filter than what we did in previous experiments in order to get a higher plasma density. We expected a plasma density of at least three-fold higher. The parameters of the PIII&D used were a voltage of -5 kV, frequency of 500 Hz, and pulse width of 20 μs. The processing time was varied from 1 to 5 min in order to get different ion fluences. The dewetting patterns of the PS films were examined by an optical microscope (Nikon E200) *ex situ*. In addition, the microstructures were characterized by TEM.

6.3 Results and Discussion

6.3.1 Heterogeneous Nucleation

The thermodynamic stability of polymer films is determined by the interfacial interactions between the polymer and the substrate, which normally consists of both long-range van der Waals interactions and short-range polar and molecular interactions [219, 222]. As demonstrated by the mostly studied system of PS on Si without the removal of the native oxide (~2 nm), i.e., the air-PS-SiO₂-Si system, the interfacial potential is given by [222]:

$$\Phi(h) = \frac{c}{h^8} - \frac{A_{SiO_2}}{12\pi h^2} + \frac{A_{SiO_2} - A_{Si}}{12\pi(h+d)^2} \quad (6.1)$$

where c is constant, A_{SiO_2} and A_{Si} are the effective Hamaker constant of PS on SiO_2 and Si respectively, and h and d are the thickness of PS and SiO_2 layers respectively. The first term on the right hand side of Eqn. (6.1) represents the short-range potential proportional to h^{-8} while the second and third terms are for the long-range van der Waals potential proportional to h^{-2} . Using values from the literature [219], $c = 5.11 \times 10^{-77} \text{ J m}^6$, $A_{SiO_2} = 2.24 \times 10^{-20} \text{ J}$, and $A_{Si} = -1.36 \times 10^{-19} \text{ J}$, a critical thickness of PS film can be found at approximately 4.5 nm. Below this critical thickness, $\Phi''(h)$ is negative and the system is thermodynamically unstable. Spinodal dewetting is therefore possible, as experimentally observed by many authors [219, 222, 229]. This leads one to increase the instability by depositing a “slippery” layer on the Si surface, such as polymethyl methacrylate (PMMA) or polydimethylsiloxane (PDMS) [217, 230-232]. In our system, however, an extra interlayer of Au is present between the PS films and the Si substrate. This 100 nm thick layer can effectively screen the influence of the SiO_2 layer on the PS and thus the system of interest is changed to air-PS-Au-Si. We therefore replace the term A_{SiO_2} in Eqn. (6.1) with A_{Au} , which is the effective Hamaker constant of PS on Au, to calculate the thermodynamic stability. In addition, as the thickness of the PS film h is large, only long-range van der Waals interactions are necessarily considered. Using $A_{Au} = -1 \times 10^{-19} \text{ J}$ [233], we obtained a positive value of $\Phi''(h)$, indicating that PS films are thermodynamically stable on Au layer at the given thickness (In fact, $\Phi''(h)$ is always positive regardless of the thickness of the PS films). The Au interlayer therefore effectively stabilizes the PS films. This is consistent with our

experiments that no dewetting of PS films was observed after 20 h annealing at 140°C (Figure 6.1a).

However, after PIII&D dewetting was observed on the thermodynamically stable, thick PS films. The dynamic dewetting patterns as a function of time are recorded in Figure 6.1. Clear holes (bright spots) together with rims (dark rings around the holes) scattered on the surface are obtained even after 1 min (Figure 6.1b). These holes grow to larger size as processing time increases (Figure 6.1 c – e). At sufficiently long times, say 5 min, the holes grow even bigger to contact with each other and the rims are usually destroyed (Figure 6.1f). The detailed plots for the number density of holes in a unit area (mm^2) and the average size of holes as a function of ion implantation time are shown in Figure 6.2. It is found that the number density of holes decreases while the size of holes increases with ion implantation time. This is probably due to the merging of small holes into big ones during the growth of holes.

Reiter et al. indicated that there were often three characteristic stages in the complete dewetting process in time evolution [213, 222, 234-237]: at the initial stage, holes are formed on the surface of films; at the intermediate stage, these holes grow bigger with asymmetric rims accumulated on their boundaries; as time increases, holes continue expanding until the rims contact each other and form ribbons in between; at the final stage, these ribbons are unstable and decay into smaller droplets via Rayleigh or fingering instabilities. The above surface features as a function of time are consistent with the characteristic stages of dewetting by thermal annealing [213], indicating the ability of PIII&D as an effective method to dewet PS thin films. However, the analysis of thermodynamic stability implies that spinodal dewetting is unlikely to be responsible for the observations. Indeed,

if spinodal dewetting occurred, a characteristic wavelength, λ , given by $\lambda = \left(-4\pi^2\gamma/\Phi''(h)\right)^{1/2}$ (γ is the surface energy of the film and $\Phi''(h)$ is the second derivative of interfacial potential with respect to the height of film, h) can be found [222, 231]. This wavelength results from the balance between two pressures in polymer films, the disjoining pressure arises from long-range van der Waals interactions and the Laplace pressure arises from surface curvature [213, 222, 234, 238]. The disjoining pressure drives the dewetting process whereas the Laplace pressure tries to keep PS films flat. There is no characteristic wavelength found in all of our images; instead, holes are randomly distributed. Such observation agrees well with heterogeneous nucleation controlled dewetting where holes can break up during the entire process [222, 234]. A continuous breakup of holes in heterogeneous dewetting is possible as some holes may have grown into large size while others just start growing.

We also tried to modify PS thin films without applying the bias, i.e., using only Ti condensation. We found no dewetting of PS films even after 10 min deposition time. This is in contrast to the “ring” formation in volatile, thin films containing organically passivated metal nanoparticles on a solid substrate, which was attributed to the hole nucleation associated with evaporation and/or disjoining pressure [239, 240]. We propose that Ti condensation does not change the surface layer to metal-polymer nanocomposites, but merely metal/polymer double layers. In another separate experiment, we conducted a 1 keV Ar^+ implantation into PS thin films. Again, no dewetting but only ion sputtering was observed. Therefore, both negative bias and Ti ions were necessary to induce the above dewetting patterns.

Figure 6.1 Optical micrographs for PS films after (a) thermal annealed at 140 °C in vacuum for 20 h, and (b) 1 min, (c) 2 min, (d) 3 min, (e) 4 min, and (f) 5 min Ti ion bombardment. Scale bar is 50 μm in all figures.

Figure 6.2 The plots for the number density (■) and size (●) of holes as a function of dewetting time. The number density decreases while the size increases at longer time.

It is known that the formation of holes in heterogeneous nucleation is initiated through thermal activation which overcomes the potential barrier for nucleation from defects or impurities present in the films. These holes then grow radially outwards until they contact with each other. We observe defects and Ti nanoparticles embedded in PS films after PIII&D, as shown by the plane-view TEM image in [Figure 6.3](#). Ti nanoparticles (dark spots) are found at high density in this image. The formation of Ti nanoparticles by PIII&D has been discussed previously and ion fluence is known as an important parameter in the process [\[153, 154\]](#). In our experiments, ion fluence is proportionally related to the processing time. Because of the high plasma density, Ti nanoparticles may form in a very short time (<1 min). These nanoparticles then serve as nuclei for subsequent dewetting of the PS films. The thermal activation energy for dewetting comes from ion implantation which transfers energy from the energetic ions to the PS matrix at localized regions near the ion tracks. We note that, some ultrathin metallic films which can adhere well on an inorganic substrate at room temperature, may also undergo dewetting by laser ablation or ion implantation, a phenomenon known as solid-state dewetting [\[241-243\]](#). These studies show that energy from ion implantation can be high enough to induce dewetting on thermodynamically stable polymer films.

Figure 6.3 A typical plane-view transmission electron image for PS films after PIII&D. The “Dark” spots represent Ti nanoparticles. Scale bar is 50 nm.

6.3.2 Fingering Instability

In addition to the observation of dynamic dewetting patterns, we also found a striking feature in the geometry of rims. Over a narrow range of ion implantation times, mostly between 3 – 4 min, a high density of rims with polygonal shapes was seen on the surface of the PS films. [Figure 6.4](#) shows examples of pentagonal, hexagonal, octagonal rims. These rims have regular sides and keep their regularity until they contact each other. After that, the regularity is destroyed and the rims decay into small droplets, similar to that in [Figure 6.1f](#). The regularity of the rims is comparable to some natural observations, such as snowflakes.

Figure 6.4 (a) Regular polygonal rims in dewetting patterns after 3 – 4 min Ti ion bombardment. Scale bar is 50 μm . (b) – (d) are examples of pentagonal, hexagonal and octagonal rims respectively. Scale bar is 25 μm .

The formation of regular polygonal shaped dewetting rims without the aid of pre-defined patterns is illuminating. It is substantially different from most observations in thermal dewetting which show irregular polygonal rims. We propose this feature is a result of fingering instability [244-246], in contrast to Rayleigh instabilities where polymer rims decompose into droplets due to surface tension alone. Fingering instability is a more complex phenomenon associated with applied forces, such as viscous or Marangoni, centrifugal, and gravitational forces [247-249]. *Cazabat et al.* studied the spreading of silicone oil on Si wafers driven by Marangoni forces and observed fingers at the advancing front [247]. They showed that the velocity of the spreading liquid, $V(x)$, was given by:

$$V(x) = \frac{h}{2\eta} \tau + \frac{\gamma}{3\eta} h^2 \frac{d^3 h}{dx^3} \quad (6.2)$$

where x is the direction parallel the solid surface, h is the height of the liquid film, $\tau = d\gamma/dx$ is the surface stress induced by the temperature gradient, η is the viscosity and γ is the surface energy of the liquid. The first term on the right hand side of Eqn. (6.2) describes the driving Marangoni forces while the second term describes the flow induced by the Laplace pressure, which is dependent on the surface curvature. At the advancing front where the surface curvature is large, balancing the two terms in Eqn. (6.2) leads to the formation of fingers with a characteristic wavelength [247].

Although dewetting of polymer films instead of spreading of liquid films is of interest in the present case, we believe Eqn. (6.2) holds its generality in both cases. We limit our analysis at the stage of “mature” rims [250], where the substrate has been exposed to ion implantation at the centre of holes and circular shaped rims have been developed. The driving force for hole expansion is unlikely to be long-range van der Waals forces as in spinodal dewetting. For thermodynamically stable polymeric films, long-range van der Waals forces are known to stabilize instead of destabilize PS films against height fluctuations [225]. We therefore propose the driving force to be a thermally induced surface tension gradient, resembling the Marangoni forces in liquid films. It is known that in the process of ion implantation, energetic ions transfer their energy to the substrate and dissipate as heat in both localized space (nanometers) and short times (picosecond) near the ion tracks; a concept known as thermal spikes [227, 228]. Thermal spikes lead to elevated temperature in both the PS films and the Au layer. However, most of the ion energy is converted to heat in the Au layers while a large portion of ion energy is devoted to structural changes, such as chain scission and crosslinking, in the PS films [45]. The temperature in Au could therefore be far above that of the PS

films. We propose that at the dewetting front, i.e., the three-phase contact line of air, PS, and Au, the temperature is above T_g whereas in regions in the PS films away from the dewetting front, the temperature is much lower. The thermally induced surface tension gradient, given by $\tau = d\gamma/dx = (d\gamma/dT)(dT/dx)$, is therefore established [247]. It drives the holes to expand.

On the other hand, the resistive forces include not only long-range van der Waals forces as mentioned above, but also the friction force and the Laplace pressure. Friction force is induced by the viscoelasticity of PS melts and is proportional to the size of the rims characterized by height H and width W , whereas the Laplace pressure is proportional to surface curvature. The resistive forces are small in the early stage of holes. However, they increase when holes grow to larger size with more and more PS material accumulated at the rims. This dynamic process is schematically represented in Figure 6.5a. A hole with diameter $R1$ is assumed to have rim a at the beginning. Note that the highly asymmetric shape of the rim is taken from Ref. [235]. After a certain time, the hole grows to a large diameter $R2$ with a corresponding rim b . Apparently, rim b has larger resistive forces than that of rim a because both size and surface curvature are increased. At a critical value R of the hole diameter, the driving force is balanced by the resistive forces. This leads to formation of fingers with a characteristic wavelength within each hole. The characteristic wavelength is responsible for our observations of regular polygonal rims.

We also use a model based on mass conservation to qualitatively explain the transition from circular to polygonal rims at the critical diameter R . As the vapor pressure of PS is small, the mass of PS in the dewetting process should be conserved, i.e., the removal of PS from holes is equal to the accumulation of PS on

the rims. In the early stage the size of the rims can grow larger to accommodate this accumulation. Rims therefore keep their circular shapes. However, when approaching the critical diameter R , the driving force may not be able to support larger H and W any more. If further PS is accumulated, the rims stop growing; instead, they change their shape from a single, circular shape into polygonal shapes with multiple edges according to fingering instability. Figure 6.5b illustrates the critical diameter R schematically. When a hole at the critical diameter R grows by an infinitesimal distance dR , the material removed is $\theta Rh dR$ (θ is an arbitrarily chosen radial angle for the rim and h is the thickness of the original PS film). Meanwhile, the accumulation in the new rim is $\theta HW dR/2$, assuming a triangular cross-section for the rim and height H and width W are at their maximum values [235, 236]. The condition for rims to collapse from a circular to a polygonal shape is given by $\theta Rh dR > \theta HW dR/2$, or $R > HW/2h$. If further energy for dewetting is supplied, the fingers can be enlarged because the thinner regions of the rim move at a faster rate than the thicker regions due to smaller resistive forces. Consequently, a regular polygonal shape can be observed at the dewetting front.

Figure 6.5 (a) The schematic representation for the expansion of holes (cross-sectional view). As a hole grows from diameter R_1 to R_2 ($R_2 > R_1$), the rim develops from rim a to rim b . Because more materials are accumulated to the rim, rim b has a higher surface curvature than rim a (dotted line). (b) The schematic representation for a circular hole at the critical diameter R grows by an infinitesimal radial distance dR . The rim

will collapse into polygonal shapes when it reaches the maximum values for the height H and the width W . θ is an arbitrary angle.

6.4 Summary

In summary, we report dewetting of thermodynamically stable, thick (~ 100 nm) polystyrene films by the Ti PIII&D process. The dynamic dewetting patterns with time evolution were recorded. The dewetting mechanism was determined to be a heterogeneous nucleation, where the defects and Ti nanoparticles formed by ion implantation serve as the nuclei. In addition, we observe abundant rims with regular polygonal shapes in the dewetting patterns. This is attributed to fingering instability, which results from the balance between the driving force arising from a thermally induced surface tension gradient and the resistive forces from the combination of friction force, Laplace pressure and long-range van der Waals interactions. Finally, a model based on mass conservation was used to qualitatively describe the transition from a circular to polygonal shaped rims at a critical diameter for the holes.

CHAPTER 7 **Conclusions and Future Work**

Recommendations

7.1 *Conclusions*

- The PIII&D was successfully adopted for the fabrication of various metal-polymer nanocomposites together with metal plasmas generated from the FCVA system. The formation of metal nanoparticles inside the polymer matrix was attributed to the cooperative effect of both ion implantation and ion condensation in the PIII&D process.
- The surface topography of Ti-PET nanocomposites was observed to have “self-organized” nanostructures with arrays of conical “hillocks” and “craters”. Such formations were explained as a result of the interplay between ion sputtering and surface re-deposition caused by ion implantation. Ti nanoparticles with size of 10 – 20 nm were shown to be randomly embedded in the PET matrix. Temperature-dependent electrical conductance measurements showed that the electron transport in this nanocomposite was controlled by the Mott VRH law, which has a stretched-exponential relationship for conductance G and temperature T . Other effects such as the “ageing” effect and supporting polymer on the influence of conductance were also investigated. A new equation considering both temperature T and “ageing” time t was proposed.
- Ti-PS nanocomposites on commercial PS substrates were fabricated in order to exploit their optical properties. The studies of surface

compositional and chemical states showed that only the surface layer (~ 10 nm) of Ti nanoparticles was oxidized whereas the embedded part of Ti nanoparticles in the PS matrix preserved their metallic states. It is the first time that LSPR excited at the interface of Ti nanoparticles and a polymer matrix at room temperature has been observed. The position of the SPR peak at 337.5 nm was consistent with the condition provided by the Mie theory. An extended absorption tail ranging from UV to near infrared was attributed to the fractal nature of the nanocomposites.

- Ti-PS nanocomposites fabricated on PS thin films have been utilized as a biomaterial to enhance protein immobilization. A protein assay based on the enzymatic property of SBP to the oxidation of TMB has been carried out to quantify the amount of protein immobilized. A comparison between PS thin films and Ti-PS nanocomposites revealed that the amount of SBP immobilization had increased from 1.7 ng/cm^2 on the former to 3 ng/cm^2 on the latter. The mechanism of enhancement has been ascribed to the physiochemical properties of Ti-PS nanocomposites, such as increased surface roughness, increased surface energy and formation of carbonyl functional groups.
- For the first time, dewetting of thermodynamically stable PS films by ion implantation has been reported. The dewetting patterns as a function of time were captured. The dewetting mechanism was controlled by heterogeneous nucleation; therefore no characteristic wavelength for the spatial distribution of holes could be identified. Moreover, regular polygonal holes were found abundantly on the surface. This has been attributed to fingering instability of the rims where temperature gradient

induced surface stress act as the driving force and surface curvature induced Laplace pressure and friction forces acting as the resistive forces. By using a model based on mass conservation and the assumption that the driving forces are not big enough to support the growth of rims any more, we demonstrated that at a critical value R_c for the diameter of circular holes, the formation of polygonal holes is preferred.

7.2 Future Work Recommendations

7.2.1 Polymer Nanocomposites for Protein Microarrays Technology

The results of [Chapter five](#) show that protein immobilized on Ti-PS nanocomposites were enhanced due to the surface physiochemical properties that favor protein immobilization. As one of the obstacles in current protein microarrays technology is the inefficient protein immobilization for capturing reagent, such as antibody, we propose that arrays of Ti-PS nanocomposites could be used. [Figure 7.1](#) demonstrates the steps in fabricating the arrays of Ti-PS nanocomposites on Si or glass substrates: first, a Si or glass substrate is prepared and cleaned; then, a thin layer of PS is pin-coated on this substrate; after that, PIII&D together with Ti plasma is used to modify the PS thin film through a shadow mask. The feature size on this shadow mask could be down to the micrometer range; finally, the whole sample can be washed with acetone as the unmodified area is soluble to acetone while the Ti-PS nanocomposites are not. The pattern from the shadow mask is transferred and the product is ready to be used in protein microarrays.

Figure 7.1 Proposed steps in fabricating arrays of Ti-PS nanocomposites on Si or glass substrates for protein microarrays technology. **1**, Si or glass substrate is prepared and cleaned; **2**, a thin layer of PS is spin-coated; **3**, PS thin films are modified by Ti PIII&D process with a shadow mask; **4**, unmodified PS is washed by acetone while Ti-PS nanocomposites are left on the surface. The product is then ready to be used as protein microarrays.

7.2.2 Microfabrications utilizing dewetting of polymer thin films

Dewetting of polymer thin films is a spontaneous process that creates micropatterns without lithography and pattern transferring. If the spatial arrangements of dewetting holes can be controlled, such as by using physical constraints or bi-layers [251], microfabrication on some electronic devices could be greatly simplified. The next interesting step after this project could be the realization of arrays of electronic components by utilizing dewetting of polymer thin films.

Appendices I List of Publications

Journals

1. **Z. J. Han**, B. K. Tay, P. C. T. Ha, M. Shakerzadeh, A. A. Cimmino, S. Prawer, and D. McKenzie, Electronic conductance of ion implanted and plasma modified polymers, *Appl. Phys. Lett.* **91**, 052103 (2007). (Also available in *V. J. Nanoscale Sci. & Technol.*, volume 16, issue 7, 2007)
2. **Z. J. Han** and B. K. Tay, Electrical conductivity of polyethylene terephthalate (PET) modified by titanium plasma, *J. Appl. Polym. Sci.* **107**, 3332 (2007).
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