CHAPTER 1

Introduction

1.1 Plasma: A Brief Introduction and Historical Background

The word \textit{plasma} was first introduced by Irving Langmuir (1928), and derives from the Greek \textit{πλάσμα} meaning \textit{something formed} to denote the state of gases in discharge tubes [1–4]. He wrote [5], “Except near the electrodes, where there are sheaths containing very few electrons, the ionized gas contains ions and electrons in about equal numbers so that the resultant space charge is very small. We shall use the name plasma to describe this region containing balanced charges of ions and electrons”. Plasma is characterized by quasineutrality and collective behaviour. Plasmas are many particles ensembles; electrons, positive and negative ions, neutral atoms and molecules, excited species, free radicals and photons. The most important distinction between plasma and a normal gas is the fact that mutual Coulomb interactions between charged particles are important in the dynamics of plasma and cannot be disregarded. Sir William Crookes (1879) suggested the concept of the \textit{fourth state of matter} for electrically discharged matter. Crookes published the results of his investigations of discharges at low pressure and remarked: “The phenomena in these exhausted tubes reveal to physical science of a new world, a world where matter may exist in a fourth state . . .” [6]. In addition to being important in many aspects of our daily lives, plasmas are estimated to contain more than 99% of the visible universe (figure 1.1). This estimate may not be very accurate but quite reasonable one in view of the fact that stellar interiors and
atmospheres, gaseous nebulae, and much of the interstellar hydrogen are plasmas [7]. However, the statement *fourth state of matter* often appears in the sequence: solid, liquid, gas, and plasma. This implies that plasma is another phase. Each state is achieved by adding heat to the previous state. The first three states are the common phases achieved via phase transitions. Hence, the statement that plasmas are the fourth state of matter could be examined considering phase transitions. It has been established recently that the transition from gas to plasma is not a phase transition similar to the other phase transitions at which transitions the differential of the Gibbs free energy equals zero. Therefore, plasmas are better not called the fourth phase of matter [8].

With the exception of most astrophysical and atmospheric conditions, gas discharge plasmas are always maintained and enclosed inside a vessel. Although stars are plasmas in thermal equilibrium, the light and heavy charged particles in low pressure processing discharges are almost never in thermal equilibrium, either between themselves or with their surroundings. There are large numbers of processes that may occur among active plasma species and also between the plasma and reactor wall which strongly affects the plasma itself. Gas phase collisions are dominant in low temperature plasmas. This is quite understandable, if we change the background feed gas in a low temperature plasma reactor, the nature of the plasma will change considerably. In highly ionized plasmas, the nature of the gas is relatively unimportant (unless thresholds for ionization change drastically), because they are dominated by charged particle collisions [4]. Electron collisions are particularly important, because they can produce new electrons and ions under most conditions and also generate the chemically active species required for numerous plasma applications. Plasma processes (sputtering, etching, plasma enhanced chemical vapour deposition, surface treatment etc.) require information about the surface reactions of active species and their probability as well as information on gas phase collision/reaction processes and their cross-sections [4,10]. As in any gas, temperature in plasma is determined by the average energies of the plasma particles (neutral and charged) and their relevant degrees of freedom (translational, rotational, vibrational, and those related to electronic excitation). Thus, plasmas, as multi component systems, are able to exhibit multiple temperatures. In contrast to the high temperature plasmas (e.g. fusion plasma), the classic low temperature plasmas are
divided into thermal and non-thermal plasmas [1-4,9]. The thermal plasma (e.g. arc discharge at atmospheric pressure) is characterized by the nearly equal temperature of the plasma species, $T_e \approx T_i \approx T_g$, where $T_e$, $T_i$, and $T_g$ are the temperatures of the electron, ion, and neutral gas atoms/molecules, respectively. In a high pressure gas discharge, the collisions between electrons and gas molecules occur frequently. This causes thermal equilibrium between the electrons and the gas atoms/molecules. Hence, such plasma is in a state of local thermodynamic equilibrium (LTE). By contrast, the non-thermal plasma (e.g. low pressure glow discharge) is weakly ionized (degree of ionization, $10^{-6} - 10^{-4}$) and is characterized by a significant non-equilibrium state [2,4,9]. The electron temperature is much higher than the ion and neutral gas temperature. This is the case of a partial thermodynamic equilibrium (PTE). The reasons are the small kinetic energy transfer in elastic collisions between electrons and heavy particles and the heavy particle confinement time. Because of the low collision frequency of electrons with heavy particles at low pressure, the heavy particle temperatures remain in the order of room temperature and we observe so called cold plasma. In such non-equilibrium plasma, the electrons represent the energetic particles with mean kinetic energy of a few eV. The high temperature electrons enhance the chemical reactions in the plasma [1,10]. In a low pressure glow discharge plasmas, the characteristic energy of the ion population is low, not far above that of the working neutral gas at a kinetic temperature of $\sim 0.025$ eV [11]. This low energy is the result of frequent ion–neutral collisions associated with a small ionization fraction, and the fact that the masses of the ion and neutral background species are comparable, allowing the ions to lose a large fraction of any energy they may have gained from electric fields in a single collision. The low ion energy greatly reduces the probability of their contribution to the formation of active species through inelastic collisions. The inelastic collisional processes of electrons are therefore of primary interest in industrial glow discharges [11].

Gas discharge plasmas are generated and maintained by the input of electrical power. The various electric power sources include devices running at direct current (DC), standard line frequency ($\sim 50$ Hz), low frequency ($\sim 50$ kHz), radio frequency (RF $\sim 13.56$ MHz) and microwave ($\sim 2.45$ GHz) [4,11]. The glow discharge is the best
known type of non-thermal discharge and has been widely used in plasma science for more than a century. The term *glow* indicates that the plasma is luminous in contrast to the relatively low power dark discharge. The DC glow discharge has been historically important, both in applications of weakly ionized plasmas and in studying the properties of the plasma. A DC discharge has one obvious feature, its macroscopic time independence and hence is simpler than RF discharges. RF discharges at frequency of 13.56 MHz or its first harmonic 27.12 MHz are widely used in plasma technologies for surface treatment and thin film deposition. The RF discharges operate by means of internal or external electrodes and they are classified into two types according to the method of coupling the high frequency power, capacitively or inductively. The discharge coupled by way of a capacitor to the RF power source is named capacitively coupled plasma (CCP). In the case of the inductive coupling, the high frequency current passes through a solenoid coil and leads to an oscillating magnetic field which induces the electric field. The induced electric field generates dense low temperature inductively coupled plasma (ICP) or transformer coupled plasma (TCP). The generation of dense low temperature plasma can be also achieved by microwave discharges, for example at 2.45 GHz. The microwaves produce much larger electric fields in the plasma bulk. On the other hand microwave plasmas (MWP) are of special interest in combination with magnetic fields. In such plasma, the power input reaches a maximum for the case $\omega = \omega_{ce}$, where $\omega_{ce}$ is the electron cyclotron frequency. This is called electron cyclotron resonance (ECR) plasma.

Plasmas have various uses in technology because of their unique electrical properties and ability to influence both physical and chemical processes. Plasmas play a key role in processing materials, including those related to the production of integrated circuits [12]. The production, processing and performance testing of any object or set of objects with at least one nanoscale dimension, composed of atoms of any chemical element and produced using plasmas is of interest of plasma nanoscience. Plasmas can also be used to process waste, selectively kill bacteria and viruses, and weld materials [12,13]. Achieving controlled nuclear fusion, which holds promise as an abundant and clean energy source, is essentially a plasma physics problem [14]. Thus plasma science
is essential both to understand the basic processes and advancing important technological applications.

1.2 Reactive Magnetron Sputtering

When a solid surface is bombarded with energetic particles such as accelerated ions, surface atoms of the solid are ejected due to collisions between the surface atoms and the energetic particles. This phenomenon is called sputtering. Bunsen and Grove (1852) first observed sputtering in a DC gas discharge tube [15]. They discovered that the cathode surface of the discharge tube was sputtered by energetic ions in the gas discharge, and cathode materials were deposited on the inner wall of the discharge tube. W. Thomson called this phenomenon, in analogy to the generation of drops out of a liquid surface by an impinging primary drop, spluttering [16]. The expression sputtering as a result of a printer’s error was soon adopted as scientific term. At that time, sputtering was regarded as an undesired phenomenon since the cathode and grid in the gas discharge tube were destroyed. Today, however, sputtering is widely used for surface cleaning and etching, thin film deposition, surface and surface layer analysis, and sputter ion sources [16,17]. Sputtering deposition and sputtering etching have become common manufacturing processes for a wide variety of industries [11]. First and foremost is the electronics industry, which uses sputtering technology to produce integrated circuits and magneto-optical recording media. The energetic particles in sputtering may be ions, neutral atoms, neutrons, electrons, or photons. The most relevant sputtering applications are performed under bombardment with ions. The sputter yield which is the removal rate of surface atoms due to ion bombardment is defined as the mean number of atoms removed from the surface of a solid per incident ion. The sputtered particles are emitted predominantly as neutral atoms in the ground state, and generally less than 5% are ions [18]. A certain fraction can be emitted as atom clusters. Sputtering is caused by the interactions of incident particles with target surface atoms. The sputter yield will be influenced by the energy of incident particles, target materials, incident angles of particles, and crystal structure of the target. In the energy range of sputtering, the interaction between the bombarding ion and the target surface
atoms, and the subsequent various interactions may be treated as a series of binary collisions [17].

As shown in figure 1.2, this process is often compared to the break in a game of atomic billiards, in which the cue ball (bombarding ion) strikes the neatly arranged pack (the atomic array of the target). The result is the scattering balls (target atoms) in all possible directions, including some back towards the player, i.e. out of the target surface (sputtered atoms). However, in the real situations, the variation of interatomic repulsion or attraction with the separation distance is rather different from the hard sphere billiard ball case. When an ion approaches a target surface, several processes may occur: the ion may be reflected and neutralized. The impact of the ion may result the secondary

Figure 1.2: (top) Sputtering may be viewed as the break in the game of atomic billiards, (bottom) interactions of ions with surfaces leading to a series of collisions.


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electron emission. Ion engineering is considered to be one of the most advanced technologies and is widely applied in the development of semiconductor materials. In particular, ion implantation is effective in modifying the electronic properties of silicon semiconductors [11]. When ion beams with lower energies of several to a few hundred eV are irradiated onto solid surfaces, these ions accumulate on the surface to form thin films similar to a snow covering on the ground. With energies of a few hundred eV to several tens keV, these ions sputter the atoms of the surfaces and when ion beams with higher energies than several tens keV are exposed onto solid surfaces, these ions are implanted within the deep bulk of the solid without any significant damage to the surface. The collision phenomena occurring in a target, often referred to as target kinetics are fascinating and important subject of study [19]. To obtain sputtering as a functional deposition process, a number of criteria must be fulfilled. Firstly, ions of sufficient energy must be created and directed towards the target to eject atoms from the target surface. Secondly, ejected atoms must be able to move freely towards the object to be coated called substrate or workpiece with little impedance to their movement. This is why sputter deposition is a vacuum process: low pressures are required to maintain high ion energies and to prevent many sputtered atom-gas collisions after ejection from the target. Low pressure sputtering is one of the most promising techniques for the production of thin film devices. A wide variety of thin films can be made with little film contamination and at a high deposition rate by the low pressure sputtering technique. This is usually achieved by magnetron sputtering. An electrode system equipped with a superimposed magnetic field is generally referred to as magnetron electrodes. The difference between a magnetron cathode and a conventional diode cathode is the presence of a magnetic field, $\mathbf{B}$ superimposed with the electric field, $\mathbf{E}$. Two types of magnetron sputtering systems are widely used for thin film deposition. One is a cylindrical type; the other is a planar type. The planar magnetron is a much favoured design because of its physical simplicity and the ability to extend the cathode to virtually any size required [20]. In planar magnetron configuration, permanent magnets (sometimes electromagnets are used) are arranged radially from the centre on the back of the target, in order to provide the magnetic field of several hundred gauss in front of the target [11,20]. In magnetron sputtering, electrons in the glow discharge experience
cycloidal motion, and the centre of the orbit drifts in the direction of $\mathbf{E} \times \mathbf{B}$ with the drift velocity of $\mathbf{E}/\mathbf{B}$. The magnetic field is oriented such that these drift paths for electrons form a closed loop. This electron trapping effect increases the collision rate between the electrons and the sputtering gas atoms/molecules. The magnetic field increases the plasma density which leads to increase in the current density at the cathode target, effectively increasing the sputtering rate at the target. Due to low working pressure, the sputtered atoms traverse the discharge space almost without collisions, which results in a high deposition rate. At present, planar magnetron is indispensable for the fabrication of semiconductor devices. Historically, magnetron sputtering was first proposed by Penning [21] in 1939. A prototype of the planar magnetron was invented by Wasa [22] in 1969, and a practical planar magnetron system was devised by Chapin [23] in 1974.

The industrial sputtering of thin films is done under vacuum at pressures (< 7.0 Pa) low enough that sputtered atoms are transported directly from the target to the substrate with few or no collisions. Plasma based sputtering methods are rarely operated at pressures lower than 0.13 Pa because it is difficult at such pressures to generate a plasma dense enough to induce sputter deposition at rates of commercial interest [11]. Sputter deposition, includes both physical sputtering and reactive sputtering. In the former, atoms are sputtered from a target material and are transported to and deposited on a substrate. In reactive sputtering, a feedstock gas whose dissociation products chemically react with the target material is present in addition to the bombarding ions. Hence the deposited film is a compound formed from the sputtered materials and the reactive gases. In strict sense, all sputtering is reactive because there are always residual gases in the chamber that will react with the sputtered species. However in reality, reactive sputtering occurs when a reactive gas is purposely introduced to the plasma chamber to react with the sputtered material. For example, when oxygen is injected into the chamber with the sputtering of titanium (Ti) to form titanium oxide or when nitrogen is added to form titanium nitride. In contrast to physical sputtering, where a model for the generation and transport of sputtered atoms from target to substrate is relatively straightforward, a reactive sputtering model involves surface reactions at both target and substrate in addition to sputtering at the target and deposition at the substrate [12]. It is the reactions on the target surface that leads to the classic reactive sputtering
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Problem [19, 24]. Reactive sputtering may be used in either the DC or RF mode. Sputtering discharges for conducting films are generally DC discharges, usually DC planar magnetrons; for sputtering insulating films, capacitive RF discharges or RF driven planar magnetrons are commonly used [12]. Reactive deposition may be a cheaper alternative to RF magnetron sputtering of compounds because DC power supplies and elemental target materials are cheaper. Reactive sputtering is widely used to deposit dielectrics such as oxides and nitrides, as well as carbides and silicides [24, 25]. The sputtering rate for the compound material that forms on the target is significantly less than the rate for the elemental target material. As the degree of target compound coverage increases, the deposition rate decreases. The reactive sputtering process can be divided into three modes: metallic, transition and reactive [25]. For a deposition process to be stable, it is beneficial to operate the magnetron cathode with its surface either fully or partially metallic, while maintaining an adequately high partial pressure of the reactive gas to form the desired compound film. When the entire target surface is covered with the compound material the target is said to be reactive [24]. There are three major limitations of reactive sputtering: (a) hysteresis effect, (b) jump transition from the metallic to the reactive mode, and (c) arcing. The hysteresis effect arises in consequences of two competitive processes: the sputtering of the target surface and the covering of its surface by reaction products. At low values of the reactive gas flow rate, all reactive gas is gettered by the sputtered metal. This is valid till the flow rate is equal to the gettering rate of sputtered metal. This regime corresponds to the metallic mode of the target surface. When the flow rate is gradually increased above this level, the partial pressure of the reactive gas in the chamber increases and the deposition rate decreases. A further increase of the flow rate results in linear increase of the partial pressure and the sputtered target is transitioned into the reactive mode. The deposition rate attains a constant value which is typical for reactive mode of sputtering. A decrease of flow rate at this stage is accompanied by decrease of partial pressure of the reactive gas, but a return to the metallic mode is delayed. This is because the partial pressure of the reactive gas remains high until a compound layer on the surface of the target is fully removed and the metal is again exposed to be sputtered. As a result, the consumption of reactive gas increases and its partial pressure decreases to the background level. Hence a
closed hysteresis loop is formed. The hysteresis is an undesirable phenomenon because it prevents to form compound films with stoichiometry and is responsible for unstable sputtering in the transition mode. The experiments [24,25] show that a stable deposition of compound films in the transition mode can be realized when the pumping speed of the pumping system exceeds the critical value of the pumping speed. However, in most sputtering systems, particularly in industrial ones this condition is not satisfied and so the hysteresis effect takes place. Experiments, however, also reveal that just in the transition mode not only stoichiometric films but also sub-stoichiometric films with new interesting properties can be formed [25]. Moreover, these stoichiometric films are deposited at a considerably higher deposition rate compared with that under the reactive mode of the sputtering. When an insulating layer forms on the target surface, it can charge up. If the charge reaches the breakdown voltage for the insulating layer an arc will occur. Arcing can be suppressed by eliminating uneroded areas and removing the accumulated charge from insulated surfaces on the uneroded areas. The existence of uneroded areas is an inherent property of the planar magnetrons. They are formed everywhere outside the magnetron racetrack, strongly decrease the efficiency of the target utilization and thus decide on the target lifetime. The hysteresis effect and arcing can be avoided only in the case when the whole surface of the sputtered target is uninterruptedly exposed to the magnetron discharge and the compound layer is continuously removed. One immediate solution to these problems is to use RF power. But RF power is more expensive to use than the DC power. Moreover, a matching network is required in an RF system further adding to the overall cost. For an equivalent amount of power, the deposition rate with RF power is about the half the rate for DC power. Despite certain limitations, the reactive sputtering is a viable method for depositing compound films from an elemental target, but the method to control the reactive gas has a strong influence on the reactive deposition rate and the film properties. Flow control of the reactive gas, although simpler to implement, invariably produces low deposition rates compared with the deposition rate from the metallic mode. Partial pressure control of the reactive gas allows the deposition of films in the transition region between the metallic and reactive mode of the target which leads to higher deposition rate compared to flow control and better film properties.
1.3 Plasma Polymerization and Conjugated Polymers

In the plasma assisted sputtering deposition processes discussed in the previous section, the deposited layer is built up by the accumulation of atoms sputtered from a target by energetic ions. Another important thin film deposition method is plasma enhanced chemical vapour deposition (PECVD), in which a film is deposited by polymerization of monomers produced in the plasma, or by other heterogeneous chemical reactions on the surface being coated. It has been known since the late 19th century that glow discharge plasmas that contain reactive or polymerizable chemicals would deposit thin films on the inner wall of vacuum systems [11]. These films were long regarded as a nuisance because they were unwanted and difficult to remove. It was not until the late 1960s that the potential value of these films to microelectronic circuit fabrication was appreciated. In the period from 1960 to 1975 research and development in this field flourished, and the technical approaches developed during this period established a basis for the thin film PECVD techniques [26,27]. PECVD is possible because energetic electrons produce molecular fragments and other active species that form thin films superior to those produced by purely chemical or electrochemical processes [11]. Such active species are created in significant concentrations by purely chemical processes only with difficulty. Even when this is possible, CVD processes may produce significant quantities of toxic or unwanted by-products. PECVD systems can be divided into two broad areas of application. The first of these is the deposition of non-polymeric thin films which result from surface chemical reactions and do not result from polymerization. These non-polymeric PECVD coatings are frequently oxides that are used as insulating layers, optical coatings, and oxygen barriers for food packaging. The second and largest area of application is the deposition of polymer-like thin films formed by the polymerization of monomers generated as active species in the plasma. Such films are useful as semiconducting and insulating layers in microelectronic chips, as protective coatings, and as reflective or anti-reflective optical coatings [26].

Polymers (or macromolecules) are molecules of high molecular mass composed of many small structural units connected by strong covalent bonds [28]. Natural polymers are proteins, cellulose, and rubber. Polymers composed by identical structural
units are called *homopolymers*. *Copolymers* contain more than one unit along the chain. The geometry of the macromolecule depends on the valency structure of the structural units. In the simplest case of linear polymers, each unit is connected to precisely two neighbours, such as in the linear polyethylene. In branched macromolecules, a number of structural units show a valency greater than two and connect to three or more neighbouring units. Finally, some polymers show three dimensional interconnected units and are called either cross-linked polymers or network structures. Vulcanization of rubber is an example of a linear polymer cross-linked into a network. Organic materials have been traditionally considered as an insulator until a feeble electrical conductivity was reported in the late 1950s [29]. An epoch of using organics for electrical applications has begun since 1977, when Chiang et al. [30] discovered a gigantic increase of eleven orders of magnitude of electrical conductivity of a polyacetylene when doped with halogen. A new term of *organic semiconductor*, which is commonly used today, was therefore coined specifically for this new class of conducting materials [31]. This term refers to the use of organic materials as active layers in a variety of semiconductor devices. The rapid interest in this field has been mainly due to the fact that this class of materials allows devices to obtain a unique trade off between electrical conductivity, light emission/absorption and mechanical flexibility. This discovery, unveiling the mystery of plastic electronics, led to the award of a Nobel Prize in Chemistry in 2000 to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa for their contributions in the field of conjugated polymers. An organic polymer that possesses the electrical, electronic, optical and magnetic properties of a metal while retaining the mechanical properties, processibility etc. commonly associated with a conventional polymer is termed an intrinsically conducting polymer or synthetic metal [32]. Such polymers offer a unique combination of properties not available from any other known materials and express a promise for utility in a wide variety of applications. In his lecture at the Nobel Symposium in 1991 Professor Bengt Rånby designated electrically conducting polymers as the *fourth generation of polymeric materials*. In saturated polymers, all of the four valence electrons of carbon are used up in covalent bonds and hence they are insulators. However, the electronic configuration of conjugated polymer is fundamentally different. In conjugated polymers, the chemical
bonding leads to one unpaired electron (π-electron) per carbon atom. The orbitals of successive carbon atoms overlap, leading to electron delocalization along the backbone of the polymer. The electronic delocalization provides the highway for charge mobility along the polymer chain [33]. Intrinsically conducting polymers are based on the presence of conjugated structural systems. Conjugated polymers exhibit insulating or semiconducting properties in their virgin states and become conducting upon doping [32]. In contrast to the well characterized inorganic semiconductor systems where the doping process is practically the replacement of atoms of the semiconductor with other atoms which narrow the energy gap between the valence and the conduction bands, doping of conjugated polymers involves oxidation or reduction of the π-electronic systems. Conjugated polymers were initially attractive because of the principal interest in the doping and the doping induced metal-insulator transition. Also the chemistry and physics of these polymers in their virgin semiconducting state are of great interest because they provide a route to plastic electronic devices. There is currently an intense endeavour to exploit the unique properties of conjugated polymers for the development of optoelectronic devices like organic light emitting diodes (OLED), photovoltaic cells and field effect transistors (FETs) [34]. The discovery of OLED by J. H. Burroughes et al. [35] provided the motivation for a major push in this direction.

The advantage of a chemically produced polymer compared with a plasma-chemically synthesized material is the defined structure, exact stoichiometry, often the presence of a super molecular structure (crystallinity), defined properties and significantly better ageing stability. The subject of PECVD produced polymer-like thin films includes a wide variety of morphological structures, including classical linear polymers, in which monomers are linked in long repeating linear chains [11]. In polymeric solids, these long chains are arranged in parallel array or with some other highly ordered (crystalline) structure. PECVD may also produce quasi-polymeric structures with linear branches in two and three dimensions that have no consistent repeating pattern [26]. In addition, polymer-like films may contain macromolecular structures formed by monomers and/or molecular fragments with a complex three-dimensional morphology and few or no repeating units in linear arrays. Plasma polymerization is a widely used deposition method in which monomers supplied to, or
produced within a deposition chamber by plasma-chemical reactions, polymerize on contact with the substrate to build up a polymer-like coating [26,27]. Glow discharge polymerization processes lead to more complex structures than those associated with the chemical vapour deposition (CVD). In PECVD, the feed material may consist either of a monomer, which is capable of forming a polymer in conventional sense or a polymerizable material. The latter will not form polymeric structures when subject to conventional CVD, but its plasma-generated molecular fragments will do so. Plasma polymerization is the chemical reactions triggered by the dissociation of molecule of which reactive species are mainly free radicals [10]. Ions play little role, if any, because the neutral species out numbers ions in order of $10^6$ to 1 in the glow discharge of organic molecules [26]. The general concept for the plasma polymerization is to approximate the structure of plasma polymers to that of classic polymers as much as possible. Therefore, low power input to the plasma is necessary because the average energy input per monomer molecule has to be $<0.01$ eV for a classic (pure chemical) radical polymerization. The constant energy flux in continuous wave (CW) plasma is too high. Pulsed plasma with long off-time offers an alternative and possibly a tool to initiate pure chemical chain propagations. During the plasma-off period reactive monomer molecules strike the radical sites at the polymer surface, graft and thus form the growing macromolecular chain. Ultraviolet and some visible photons may be energetic enough to break atomic or molecular bonds on a surface, and to produce polymeric free radicals and/or monomers. Electrons, plasma generated active species, and sufficiently energetic UV photons from the plasma can modify the molecular state of the surface by the following processes [11]:

a) **dissociation**, the production of an individual atom or small molecular fragment from a larger molecule,
b) **scissioning**, breaking the molecular chain of a polymer or producing two large molecular fragments from a parent molecule,
c) **branching**, the production of side chains on a large molecule or polymer, and
d) **cross-linking**, which produces a two or three dimensional molecular matrix by forming bonds between adjacent molecules or polymers.
Industrial use of PECVD for the formation of polymer-like thin films employs DC, RF, or microwave plasmas to achieve glow discharge polymerization. In plasma polymerization, the starting material can have a more complex structure, or even be unpolymerizable by conventional CVD, because of the ability of a glow discharge to scission and fragment the input molecular species. The morphological and chemical nature of plasma generated polymer-like material may, and usually does, differ from that produced by conventional CVD processes. A plasma polymerized coating may exhibit a more complex three dimensional structure, cross-linking, an absence of exactly repeating units, and a higher density of free radicals and polar attachment sites. These features are a strong function of the chemical nature of the starting material. Plasma polymerization has gained importance because of its ability to modify material surfaces. Plasma polymerization is a versatile technology that has a number of inherent advantages such as possibility of use of wide range of monomers, synthesis does not require the use of solvents and oxidants and thus gives a product with less contamination and superb stability towards high temperature, intensive light and strong electric fields [26,36–38]. Moreover, plasma polymerization is a simpler synthesis process than conventional methods since fewer fabrication steps are necessary. In addition, through these processes thin film with good controllability and reproducibility of the surface composition can easily be formed. By contrast, the depositions by chemical methods involve complicated processing. For example, the classical chemical synthesis of polyaniline uses aniline, an oxidant and a strong mineral acid as a dopant. Therefore, the synthesis conditions have to be carefully designed to accommodate the use of oxidants and solvents and to remove them after synthesis to obtain pure polyaniline films. It is now recognized that under low input energy conditions the polymer-like films prepared by plasma polymerization resemble conventional polymers [27,36–39]. During the last 30 years, plasma polymerization has been recognized as an established field. A number of applications have been proposed and realized [26,37–39].
1.4 Scope of the Thesis

The earliest use of thin films by mankind is probably in the application of glazes to brickwork and pottery [40]. Thin films are fabricated by the deposition of individual atoms, molecules and ionic species on a substrate. A thin film is defined as a low dimensional material created by condensing, one-by-one, atomic/molecular/ionic species of matter. Plasma processes such as magnetron sputtering and plasma polymerization provide a relatively new route for the functionalization of thin film devices. Plasma polymerization and magnetron sputtering are two highly competent techniques for the deposition of uniform thin films. This thesis presents studies on the deposition, characterization and properties of polyaniline-like, titanium dioxide (TiO$_2$) and TiO$_2$/polyaniline-like films prepared by plasma processes. Polyaniline-like films are deposited by radio frequency plasma polymerization at 13.56 MHz excitation frequency and titanium oxide films are prepared by direct current reactive magnetron sputtering. Further, it has been attempted to couple both the processes of magnetron sputtering and plasma polymerization to deposit TiO$_2$/polyaniline-like nanocomposite and bilayer films by using the same plasma reactor.

Polyaniline [IUPAC: poly (imino-1, 4-phenylene)] is an electronic polymer with very great scientific and technological importance due to exceptional electronic, optical, and structural properties. Also known as aniline black (undesirable black deposit formed on the anode during electrolysis involving aniline) was first synthesized by Runge in 1834 and used as textile dye. The pioneering work of Green and Woodhead presents the first successful attempt in the controlled chemical synthesis and physiochemical characterization of polyaniline [41]. Unlike most of the conjugated polymers, it has non-conjugated carbon backbone due to the presence of nitrogen atom between two phenyl rings and in base form it exists at different oxidation levels [42],

\[
\text{benzenoid diamine} \quad \text{quinoid diimine}
\]

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where \( y \) can be varied continuously from 1 (completely reduced) to 0 (completely oxidized). Polymerized from the aniline monomer, polyaniline in base form can be found in one of three idealized oxidation states:

- \( y = 1 \), completely reduced leucoemeraldine base (LB) – colourless
- \( y = 0.5 \), half oxidized emeraldine base (EB) – blue
- \( y = 0 \), fully oxidized pernigraniline (PNB) – blue/violet

The colour change associated with polyaniline in different oxidation states can be used in sensors and electrochromic devices. Though colour is useful, the best method for making a polyaniline sensor is arguably to take advantage of the dramatic conductivity changes between the different oxidation states or doping levels. The conductive form of polyaniline is the protonated emeraldine or emeraldine salt whose colour is green and the conductivity is around 15 S.cm\(^{-1}\) [43]. The conductivity of a metal is around 10\(^3\) S.cm\(^{-1}\). Polyaniline has been investigated extensively over a century and attracted interest for several important reasons; the monomer is inexpensive, polymerization reactions are straightforward and proceed with high yields, and exhibits excellent stability. The excellent processibility and the presence of a number of intrinsic redox states have substantially enhanced the potential applications of polyaniline for use in practical devices. Moreover, polyaniline has gained widespread use in novel organic electronic applications such as, electroluminescence, corrosion resistance, organic rechargeable batteries, biological and environmental sensors, composite structures, static dissipation, membrane gas phase separation, actuators, organic semiconductor devices for circuit applications, bioelectronics and variety of other applications [43–45].

The objectives of plasma polymerization include the production of a uniform, adherent, solid film with additional characteristics for particular applications. The chemical and physical properties of plasma polymer-like films derived from a monomer are dependent on many factors of overall conditions of plasma polymerization. In other words, a monomer does not yield a well-defined polymer in plasma polymerization. The variation of properties is largely influenced by the energy input parameter of plasma polymerization. There are three immediate directions of study of plasma polymerization: new materials including hard coatings and composite films under high
energy flux, plasma polymers resembling conventional polymers under energy deficient conditions and plasma polymers under intermediate energetic conditions. Plasma polymerization depends on the mode of operation, monomer flow rate, input power, reactor pressure, geometry of the reactor, reactivity of the starting monomer, temperature of the substrate etc. The deposition of polyaniline-like films are carried out by RF plasma polymerization of aniline and the impact of input parameters such as RF power, system pressure, and reaction time on the structural and optoelectronic properties of the deposited films have been examined. We call these films as plasma polymerized aniline (PPA). The structural, morphological, and optoelectronic properties of PPA are included in Chapter 3.

Titania (TiO$_2$) has become the material of choice for self-cleaning windows and as protective coatings, because of its favourable physical and chemical properties [46]. Fujishima and Honda (1972) discovered the photocatalytic splitting of water on TiO$_2$ electrodes [47]. This event marked the beginning of a new era of research in TiO$_2$ and as a whole, in the field of heterogeneous photocatalysis. Not only titania is highly efficient at photocatalysing dirt in sunlight and reaching the super-hydrophilic state, it is also non-toxic, inexpensive, chemically inert in the absence of light, relatively easy to handle and deposit into thin films and is an established household chemical – it is used as pigment in cosmetics and paint and as food additive. In addition to self-cleaning properties, TiO$_2$ coatings are promising as anti-microbial coatings [48] and find applications in photochromic devices [49], dye-sensitized solar cells [50] and gas sensors [51]. Because of favourable optical properties, it is also involved in the development of optical waveguides [52] and multilayer antireflection coatings [53]. Semiconductors with physical dimensions of the order of wavelengths of the electrons exhibit properties which are not usually observed in the bulk solid. Such materials are often referred to as nanoparticles, nanocrystals or quantum dots. Bulk or macroscale powder titania is a brilliant white solid, non-toxic and widely used as a pigment in paint, cosmetics and food, while nanoscale titania particles are used in sunscreens and their absorption properties, surface properties and band gap vary with their size and shape [54]. Due to the wide range of applications, the depositions of nanocrystalline TiO$_2$
films have been of much interest [55]. Moreover, nanostructured TiO\(_2\) with controlled phase offers a new dimension in the engineering of tailored surfaces. Yeh et al. [56] reported the deposition of one dimensional well-aligned rutile nanocrystals by RF magnetron sputtering where the growth behaviour was related to the pressure, power, substrate temperature and orientations of the substrate. Also, the growth of TiO\(_2\) nanowire could be greatly enhanced by using the catalytic material, tuning the growth temperature as well as growth duration [57].

![Bulk structures of (a) rutile and (b) anatase crystals. In both structures, slightly distorted octahedra are the basic building units.](image)

TiO\(_2\) crystallizes in three distinct structures [54]: two tetragonal phases of anatase \((a = 3.785 \text{ Å}, c = 9.513 \text{ Å})\) and rutile \((a = 4.5933 \text{ Å}, c = 2.9592 \text{ Å})\), and an orthorhombic phase, brookite \((a = 5.4558 \text{ Å}, b = 9.1819 \text{ Å}, c = 5.1429 \text{ Å})\). The most abundant crystalline phases of TiO\(_2\) are anatase and rutile whereas brookite is formed in thin films under special conditions [58]. The structure of rutile and anatase can be described in terms of chains of TiO\(_6\) octahedra [59]. The two crystal structures differ by the distortion of each octahedron and by the assembly pattern of the octahedra chains. Figure 1.3 shows the unit cell structures of anatase and rutile crystals. Each Ti\(^{4+}\) ion is
surrounded by an octahedron of six $O^2-$ ions. The octahedron in rutile is not regular, showing a slight orthorhombic distortion. The octahedron in anatase is significantly distorted so that its symmetry is lower than orthorhombic. The Ti–Ti distances in anatase are longer whereas Ti–O distances are shorter than in rutile. In the rutile structure each octahedron is in contact with ten neighbour octahedrons while in the anatase structure each octahedron is in contact with eight neighbours. These differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO$_2$. The lower packing fraction of crystal lattice, explains why anatase crystal exhibits both a lower hardness and refractive indices than rutile. Rutile is the thermodynamically stable phase, while anatase and brookite exist as metastable phases at temperatures below $\sim$600 °C depending on the various factors such as defects, grain sizes and impurities [60]. The size dependence of the stability of various TiO$_2$ phases has recently been reported [61]. Rutile is the most stable phase for particles above 35 nm in size. Anatase is the most stable phase for nanoparticles below 11 nm. Brookite has been found to be most stable for nanoparticles in the 11–35 nm range. Moreover, both anatase and rutile phases are well distinguishable in terms of their structural, physical and chemical properties. The anatase phase finds applications in, among others, photocatalysis and nanostructured solar cells. The rutile form is widely used as a white pigment and opacifier. The rarer mineral brookite is not used commercially; this coupled with its relatively complicated structure, has led to few studies of its properties. At elevated pressures, TiO$_2$ has a rich phase diagram with series of structural phase transformations to viz. columbite, baddeleyite, fluorite, pyrite and cotunnite [58]. Cotunnite is the hardest known oxide. Magnetron sputter deposition is a promising technique for uniform coatings over a large area and has high potential for film growth with precise control on the crystallographic structure and orientation of the deposited films. Reactive sputtering from metallic target for compound film deposition has been known for long time [62]. The DC reactive magnetron sputtering of TiO$_2$ films is of great importance as it permits desirable and reproducible properties of the deposited films with high deposition rate at ambient substrate temperature. The structural and physical properties of TiO$_2$ prepared by magnetron sputtering can be controlled and modified by varying process parameters such as sputtering pressure and
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power, target-to-substrate distance, reactive gas partial pressure, substrate temperature and DC and RF substrate bias. Chapter 4 describes the depositions and characterizations of nanocrystalline TiO₂ films by DC reactive magnetron sputtering under various plasma conditions. The microstructure, optical, and dielectric properties are investigated and the effect of input plasma parameters is examined. Moreover, it has been observed that ion energy plays crucial role in the growth behaviour of reactively sputtered TiO₂ films. The elastic compliance coefficients relate mechanical strain to mechanical stress. The elastic properties of anatase and rutile phases are estimated from X-ray line profile analysis by considering the broadening of X-ray diffraction peaks due to the stress-strain anisotropy of the material.

The concept of enhancing properties and improving characteristics of materials through the creation of multi-phase nanocomposites and multilayers is not recent [63]. The idea has been practiced ever since civilization started and humanity began producing more efficient materials for functional purposes. In addition, a large variety of nanocomposites exist in nature and in living beings (such as bone). Hybrid materials typically consist of an organic (host) solid containing an inorganic component or vice versa. Or they can consist of two or more inorganic/organic phases in some combinatorial form with the constraint that at least one of the phases or features is in the nanosize. Hybrid organic-inorganic materials constitute a remarkable and growing category within the world of materials science. The multifunctional behaviour for any specific property of the material is often more than the sum of the individual components. Both simple and complex approaches to creating such structures exist. The methods used in the preparation of nanocomposites range from chemical means [64–67] to vapor phase deposition [68–70]. Conjugated polymer based nanocomposite materials have received growing interest due to their exceptional electrical, optical and optoelectronic properties. Dhawale et al. [65] reported diffusion free interface between TiO₂ prepared by chemical bath deposition and electrodeposited polyaniline for gas sensing applications. Detection of ultraviolet (UV) radiation is becoming increasingly important in a number of areas, such as environmental monitoring, irradiation measurement and UV communication. TiO₂ is an n-type wide band gap semiconductor.
and has been applied successfully in organic electronics. A considerable interest in the fabrication of the TiO$_2$/organic p–n junction structure has also been developed for photovoltaic and photodiode applications. Recently, solution processed composites of semiconducting anatase TiO$_2$ and poly (9,9-dihexylfluorene) have been reported for efficient UV photo-detector fabrications [64]. The wide band gap of TiO$_2$ ($\sim$3.2 eV) only allows it to absorb UV light that occupies only a small fraction (3–5%) of the solar photons, which limits its wide use. Hence it is of paramount importance to shift the optical response of TiO$_2$ to visible light without compromising its photoactivity. Li et al. [67] reported the improved photosensitizing action of polyaniline modified TiO$_2$ nanoparticles. Over the past two decades, considerable effort also has been devoted to the development of low cost, flexible, large area organic electronics for consumer products. Compared with wet chemical processes [64–67], little attention has been paid to the fabrication of hybrid heterojunction by plasma based techniques [68–70]. This is possibly due to the expensive manufacturing processes and limitations for large area applications. However, inorganic/organic composite films have been successfully prepared by DC or RF magnetron sputtering and plasma polymerization. Because nanocrystalline TiO$_2$ and PPA can work as the constituents of a nanocomposite film or a heterojunction it might be challenging to examine the possibilities of nanocomposite and bilayer heterostructure for various functions. **Chapter 5** highlights the possibilities of depositions and optimizations of TiO$_2$/PPA nanocomposite films and fabrication of hybrid heterojunction interface for specific applications. **Chapter 6** presents overall summary of the work and future scope of study in this exciting field.

### 1.5 References


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