2. Theoretical Background

2.1. Plasma state

2.1.1. Introduction

At temperatures around 8000 K the solid and liquid states of matter no longer exist and the materials only exist in the gaseous phase. Above 10,000 K all atomic and molecular particles are ionized and ions are the main constituent particles of matter. This high energy state of the matter is called as the fourth state of matter or the plasma state. The term plasma was firstly used by Irving Langmuir [1] to denote the state of gases in discharge tubes. The plasma state can be considered to be a gaseous mixture of electrons, positively or negatively charged ions and neutral atoms or molecules. Plasma possesses zero net electrical space charge because the numbers of oppositely charged particles in the plasma are equal. Plasma state demonstrates quite different properties compared to those of common substances in the gaseous, liquid or solid states [2]. Figure 2.1 shows schematically the ranges of temperature, or particle energy, in which each of the four forms of matter occur in nature.
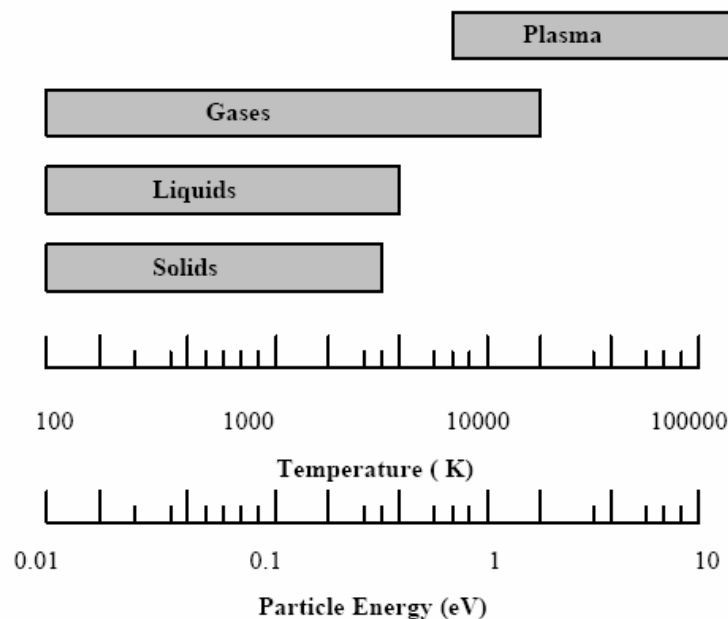

Figure 2.1. States of matter in relation to particle temperature and energy (adapted from Ref. [2]).

The energy required for the formation of plasma state can have very different sources [3]. In order to ignite plasma, an initial ''ionization event'' is essential, i.e., a

molecule or atom loses an electron to create an ion. The ionization process can occur when, for instance, molecules of a gas are subjected to high energy radiation, electric fields or thermal energy. During these processes the energy levels of particles composing the gas increase significantly and as a result electrons are released and charged particles are produced.

It is estimated that more than 99 % of the universe is in the plasma state [4]. The stars of the universe including our sun have extremely high temperatures and they consist entirely of plasmas. It is also suggested that the space between the stars and galaxies are star-origin, radiation induced, rarefied plasmas. Man made plasmas are also commonplace.

2.1.2. Classification of plasmas

Plasma states can be divided into two main categories:

Isothermal plasmas and non-isothermal plasmas.

- Isothermal plasmas can exist either at low pressures of 10^{-5}-10^{-1} Pa when the plasma particles are very energetic, at temperatures of the order of 10^6-10^8 K, or at relatively high pressures, greater than 10^4 Pa, even at temperatures as low as 6×10^3 K. Isothermal plasmas are characterized by high degree of ionization and very high temperatures of electrons and heavy particles, both charged and neutral. The plasma is at thermal equilibrium, so that the temperatures of the plasma particles are equal and all the plasma particles show the same high energy.

- Non-isothermal plasmas are composed of low temperature particles (charged and neutral molecular and atomic species) and electrons of relatively high temperature and they are associated with low degrees of ionization (10^{-4} – 10 %)

Non-isothermal plasmas develop at reduced pressure (ca. 1-10^4 Pa). Here, the mean free path is so large, that, except through electron excitations, no important energy transfer process between the particles can take place, so that no thermal equilibrium can emerge. The electrons can reach temperatures of 10^4 - 10^5 K (1-10 eV), while the temperature of the gas, can be as low as room temperature. Macroscopically viewed, the system is at room temperature.

2.1.3. Forming plasmas in a laboratory (man-made plasmas)

The plasma state can be produced in the laboratory by raising the energy content of matter by combustion, flames, electric discharge, controlled nuclear reactions, shocks, and other means. Plasmas lose energy to their surroundings through collision and radiation

processes. Consequently, energy must be supplied continuously to the system in order to sustain the discharge. Generally, electric energy is used to inject energy to a system in a continuous manner due to convenience of handling [3, 5].

Plasma polymers can be prepared by using low pressure non-equilibrium discharges (non-isothermal plasmas) initiated and sustained by external electrical power transferred to a low pressure gas environment. The power supplies for this type of plasma can be direct current (DC), low frequency (LF), radio frequency (RF) or microwave (MW) frequency devices. All these discharges are initiated and sustained through electron collision process under the action of the electric field. The applied electric field accelerates electrons to energy levels at which ionization and excitation processes occur through inelastic collision mechanisms. Because the ions are heavy, they absorb little energy directly from the electric field.

Sources may be coupled to the plasma apparatus either directly or indirectly. For direct coupling, electrodes that are in contact with the plasma are used. In the case of indirect coupling the electrodes are not in contact with the plasma. Indirect coupling may be either capacitive or inductive.

In this work capacitive direct coupled R.F plasma at 13.56 MHz frequency is employed.

2.1.4. Use of non-isothermal plasmas

Plasma contains activated species able to initiate reactions at the solid surface of samples. Plasma can be used in two ways depending on the gas employed. One use of it is the surface modification of polymers. This process is the alteration of the surface properties and surface morphology of the polymers through etching reactions, implantation of atoms and radical generation. These reactions are achieved by the use of non-polymer forming plasma composed of inorganic gases such as Ar, He, H_2, N_2, and O_2. This process of the surface modification by plasma is called as plasma treatment.

Another use of plasma is the deposition of thin polymeric films on solid substrates. When plasma is generated using organic vapors, plasma polymers are formed and all surfaces of substrates in the plasma zone are coated with the plasma polymers. This process of polymer formation by plasma is called as plasma polymerization.

2.1.5. Internal plasma parameters

2.1.5.1. Plasma density and temperature of the plasma particles

Plasma is a collection of particles, which consists of electrons, ions and excited molecules. Ions density (n_i) and electron density (n_e) are important parameters, which characterize a plasma. For non-isothermal plasmas electron and ion densities are assumed to be equal to each other. This situation can be expressed by the relation $n = n_e = n_i$, where n is called as the plasma density. This relation shows the electrical neutrality of plasmas. Typical n_e values in low pressure non-isothermal plasmas are between 10^9 and 10^{12} cm^{-3}. It is important to note that the degree of ionization in electrical plasmas is usually low, with n_e, $n_i \leq 10^{-4}$ n_g, where n_g is the density of the gas [6].

In a low pressure non-isothermal plasma of a gas, electrons, ions and neutral molecules are not in thermal equilibrium. This non-equilibrium situation is created by different modes of gaining and dissipating energy for electrons, ions and neutral molecules. Electrons and ions absorb energy in an electric field. Since the electron mass (m_e) is much smaller compared to that of the ions (m_i) ($m_e \ll m_i$), electrons experience much more acceleration than ions in the electric field and they gain higher energy expressed in terms of their temperature, electron temperature (T_e) >> ion temperature (T_i). Typical T_e values are ~ 0.5-10 eV (1eV ~ 11600 K), while T_i is ~ room temperature in the bulk plasma [3].

The electrons and ions having kinetic energy transfer all or part of this energy through elastic or inelastic collisions with electrons, ions and neutral molecules. Because the mass of electrons is very small compared to the mass of ions and neutrals, electrons do not transfer kinetic energy by elastic collisions. However, through inelastic collisions they are capable of exciting or ionizing atoms or molecules. Therefore, in low temperature plasmas the most important temperature is the electron temperature. On the other hand, molecules and ions may transfer their entire energy by head on collisions with other molecules or ions. Collisions with the neutral molecules are the major cooling factor for ions because the n_g is much higher than the n_i. So, the particle temperatures obey the restricted range T_e >> T_i ~T_g ~ T_{room} [5].

2.1.5.2. Electron energy distribution

The electron energy distribution function, $f(E_e)$, is an important parameter of the plasma, because the energetic electrons collide with gas molecules, which results in excitation and ionization. Excited molecules and ions produce various kinds of reactions in

the plasma. Formation rates of these excited molecules and ions within the plasma depend on $f(E_e)$ and n_e.

The $f(E_e)$ function is known to approximate to a Maxwellian energy distribution function for a low pressure non-isothermal plasma [6]. Figure 2.2 illustrates Maxwellian electron energy distributions for different average electron energies.

The Maxwellian electron energy distribution function for the electrons is given by

$$f(E_e) = 2.07 E_{av}^{-3/2} E_e^{1/2} \exp\left(\frac{-1.5 E_e}{E_{av}}\right)$$ **Equation 2.1**

In equation 2.1,

E_e is the kinetic energy of electrons which is equal to $\frac{1}{2} m_e V^2$, where m_e is the mass of electron and V is the velocity of the electron,

and E_{av} is the average energy of the electrons. It can be shown that the average kinetic energy of the electrons is related to their temperature by

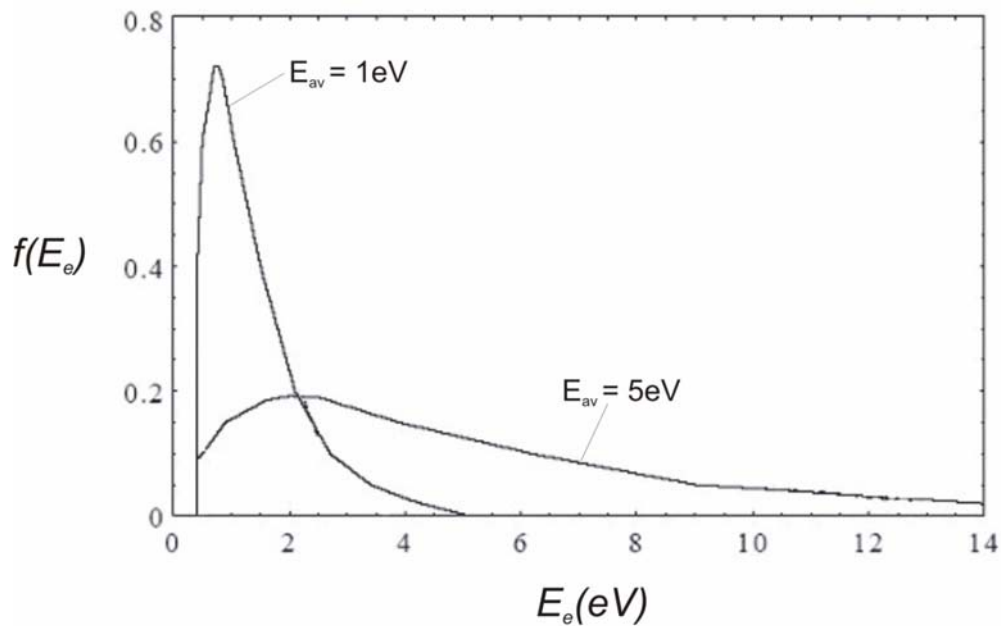$$E_{av} = \frac{3}{2} k T_e$$ **Equation 2.2**

Figure 2.2. The Maxwellian electron energy distribution function. The numbers indicate the average electron energy for each distribution (adapted from Ref. [2]).

An important fact illustrated by Figure 2.2 is that the Maxwellian electron energy distribution function has a high-energy tail. It is extremely important to note that the for an average kinetic energy of the electrons of 5 eV, most of the electrons have kinetic energy high enough to break almost all chemical bonds involved in organic compounds and to create free radical species (c.f. Table 2.1). This is important for the initiation of polymerization but the total energy needed for propagation is very low. This means that the excess energy of electrons results in fragmentation of monomer molecules into small fragments in the plasma. On the other hand, only the high energy tail electrons can contribute to ionization processes, which generally require energies higher than 10 eV. The scission of bonds occurs with a higher frequency than the formation of ions. It was estimated that the concentration of free radicals in plasma is usually five to six orders of magnitude higher than that of ions [7].

Table 2.1. Bond energies and enthalpies of formation of free radicals (adapted from Ref. [4]).

Bond Energies		Enthalpies of formation of free radicals	
Species	Energy (eV)	Species	Energy (eV)
C-H	3.3	CH_2:	4.4
C-N	7.8	$CH_3^\bullet$	1.5
C-Cl	4.0	$HC{\equiv}C^\bullet$	5.8
C-F	5.7	$HC^\bullet{=}CH_2$	3.1
C=O	11.2	NH:	3.6
C-C	6.3		
C=C	7.6		
C≡C	10.0		

2.1.5.3. Ionization cross-section and the mean free path

Collisions between the neutral plasma particles and electrons may cause excitation or ionization. The ionization probability of a neutral plasma particle as a result of collision with an electron can be determined by the ionization cross-section. The ionization cross section is a function of electron energy (E_e). It increases with an increase in E_e above the ionization potential of the atom or molecule (Q) and reaches a maximum when E_e is

several times higher than Q; it decreases with further increase in E_e. This is demonstrated by the electron impact ionization cross-section of benzene vs. E_e (c.f. Figure 2.3). The decrease in ionization cross-section at higher energy of the electrons is explained by the fact that the duration of a collision becomes too short for energy transfer to an atom or a molecule as the velocity of the electron increases with E_e.
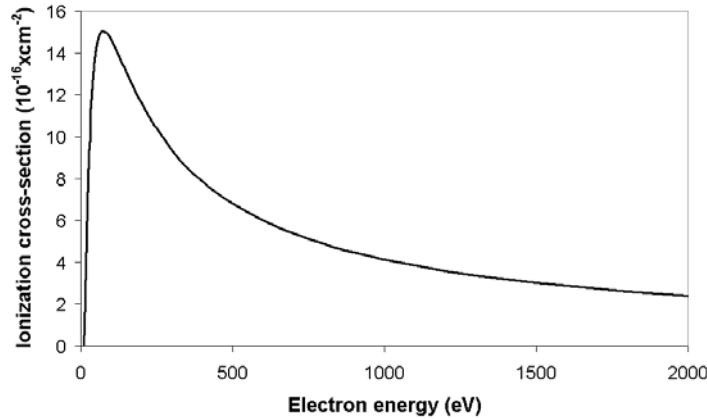

Figure 2.3. Electron impact ionization cross-section for benzene, (adapted from Ref. [8])

Ionization can also occur through a stepwise process, in which impact by lower energy electrons cause first the excitation of an atom or a molecule to a metastable state. Subsequent impact of the metastable with an electron can cause its ionization.

Collisions between the plasma particles can be characterized by their collision rate and by the mean free path, which is the mean distance traveled by a particle between successive collisions. As the collision rate of the plasma particles increases, their mean free path decreases.

Plasma is a mixture of neutral gas molecules or atoms, ions and electrons. However, the collision rate of one particular gas molecule or atom with another gas molecule or atom is much higher than the collision rate of one particular gas molecule or atom with an electron or an ion, because in a plasma n_g is much higher than n_i and n_e. Similarly, the collision rate of one particular ion or electron with a gas molecule or an atom is much higher than the collision rate of one particular ion or electron with another ion or electron. According to classical kinetic theory of gases, with these assumptions, the mean free path of a neutral gas molecule or an atom (λ_g) is given as

$$\lambda_g = \left(\frac{1}{4\sqrt{2}\pi n_g r_g^{\;2}} \right)$$
Equation 2.3

where r_g is the radius of the neutral gas molecule or atom.

On the other hand, the mean free path of an electron (λ_e) can be described by a similar equation

$$\lambda_e = \left(\frac{1}{\pi n_g r_g^2} \right)$$
<div align="right">**Equation 2.4**</div>

It is clear that the electron has $4\sqrt{2}$ times larger mean free path than the neutral gas molecule or atom.

It should be noted that both λ_g and λ_e depend on the number of neutral gas molecules or atoms in a system. Because the number of neutral molecules or atoms is proportional to the pressure of the system, λ_g and λ_e are inversely proportional to the pressure of the system. For example, the mean free path of an Argon atom decreases from $4.6\ 10^{-5}$ m to $6.7\ 10^{-8}$ m when the pressure is increased from 1 Torr to 760 Torr [6].

2.1.5.4. Debye shielding and Debye length

Plasma is electrically neutral only in a macroscopic sense. The velocity of electrons is much higher than the velocity of ions and any displacement of fast moving electrons generates a local electric field that acts on both electrons and ions. When such an electric field is created in the plasma the charged particles will respond to restore the overall electrical neutrality of the plasma. This response of charged particles to compensate for the effect of local electric fields is called Debye Shielding [2].

For estimation purposes and taking into account that $T_e(eV) \sim 11{,}600$ K, the Debye length can be approximated by the following equation

$$\lambda_D\ (cm) = 743 \sqrt{\frac{T_e(eV)}{n_e(cm^{-3})}}$$
<div align="right">**Equation 2.5**</div>

An ionized gas can be considered as plasma only if the Debye length is much smaller than the physical dimensions of the plasma region. An example of typical values found in a non-isothermal plasma at $T_e = 1$ eV, and $n_e = 10^{10}$ cm^{-3} is $\lambda_D = 74$ µm.

2.1.5.5. Plasma Potential

Due to the higher electron mobility in plasma, the electrons will tend to reach the borders of the plasma at a faster rate than the ions. The electrons would leave the plasma at a faster rate than ions, ending up at the chamber walls. The result for the plasma would be a slow increase in the net positive charge. As the plasma charges positively, it becomes less energetically possible for the electrons to leave, because now the walls of the chamber

are more negative than the plasma. On the contrary, the ions that reach the edge of the plasma are accelerated to the chamber wall. Eventually, a steady state condition would be reached in which the plasma potential is high enough that the loss rate of electrons is reduced to the same level as the loss rate of ions. In this way the plasma will retain its overall neutrality. The plasma potential (V_p), which is now the average potential of the bulk plasma with respect to the chamber, will be several volts more positive than the chamber potential [6].

2.1.5.6. Floating potential

If an electrically floating surface, for instance a substrate, is placed in contact with the plasma, it will rapidly charge negatively because of a higher flux of fast electrons compared to slow ions. As the substrate charges negatively, electrons are repelled and ions are attracted. The electron flux decreases, until a steady state is reached. At this state the electron flux balances that of the ion flux. Hence, the surface acquires a negative potential or negative self-bias with respect to the plasma potential. The plasma is therefore always at a positive potential relative to any surface in contact with it. Because of the Debye shielding effect (see section 2.1.5.4), the potential developed between the surface and the plasma bulk is confined to a layer of thickness of several Debye lengths. This layer of positive space charge that exists around all surfaces in contact with the plasma is called the plasma sheath [2].

The sheath potential, V_s, is the electrical potential developed across the plasma sheath. The value of the sheath potential adjusts itself in such a way that the flux of electrons is equal to the flux of ions reaching the surface. Its value is given for a planar surface by

$$V_s = \left(\frac{kT_e}{2e} \right) \ln \left(\frac{m_e}{2.3m_i} \right)$$

Equation 2.6

Since the ion mass is 3-4 orders of magnitude higher than that of an electron, the floating potential will have a (negative) value which is several times that of the electron temperature in volts.

2.2. Plasma Polymerization

2.2.1. Basics of plasma polymerization

Plasma polymerization is a thin film forming process, where thin films deposit directly on surfaces of substrates. In this process, low molecular weight molecules, e.g., monomers, are converted into high molecular weight molecules, called as plasma polymers, with the assistance of energetic plasma particles, which are electrons, ions and radicals. In a chemical sense, plasma polymerization is different from conventional polymerization such as radical or ionic polymerization mechanisms [5]. In any case, polymers formed by plasma polymerization show a distinguished chemical composition, as well as chemical and physical properties from those formed by conventional polymerization, even if the same monomer is used. Plasma derived polymers are irregular, generally unsaturated, and branched and/or cross-linked due to high electron temperatures (T_e) and UV radiation. This is illustrated by the structure of an ethylene plasma polymer shown in Figure 2.4. The high degree of cross-linking causes plasma polymers to be insoluble in most organic solvents. Also functional groups that are not present in monomers and low molecular weight products often exist in plasma polymer structures. In addition, they may contain a large number of radicals available for post plasma reactions [3].
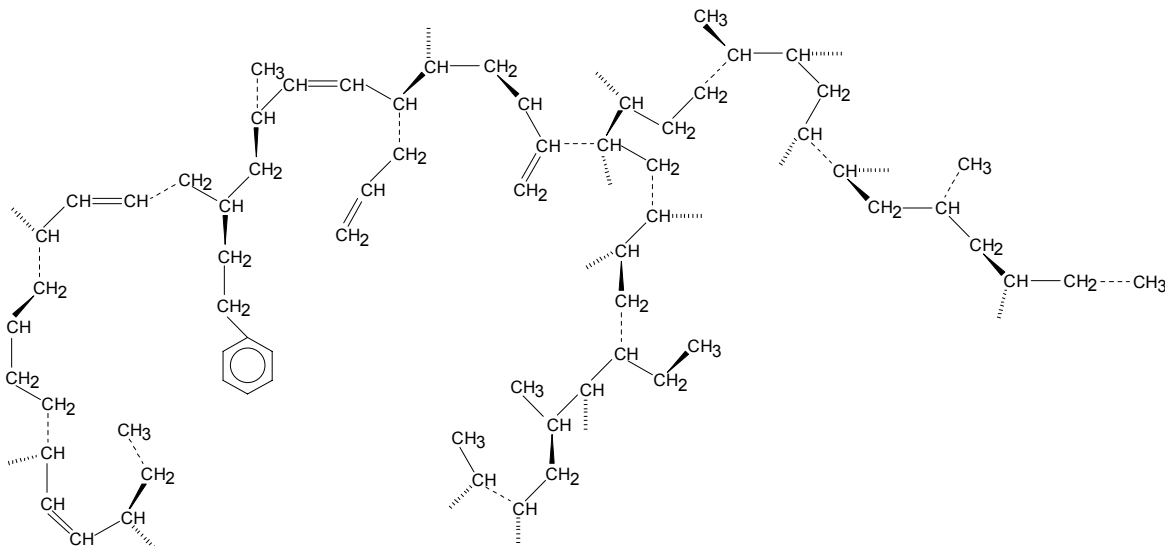

Figure 2.4. Model of a plasma deposited ethylene film, as proposed by Tibbitt et al. [9] according to Infrared (IR) and Nuclear Magnetic Resonance (NMR) spectroscopy data.

Plasma polymerization technique became a popular approach for synthesis of functional polymers. Plasma polymers with desired structures and controlled density of a specific chemical group found many applications in different fields like adhesion and biomaterial science [10, 11]. However, control of the chemical composition of plasma polymers is not straightforward.

2.2.2. External plasma parameters

Activation and fragmentation of the monomer molecules in plasma are the first steps of the plasma polymerization process. Recombination of these fragments and subsequently re-activation and re-fragmentation of the recombined molecules by the plasma are other important reactions taking place. All these reactions, which affect the structure of the deposited films, depend on the internal plasma parameters that are described in section 2.1.5, e.g., n, T_e, and T_i. Control of the internal plasma parameters is complex. However, variations of external parameters will influence the internal parameters of the plasma. Therefore, it is possible to alter and control some chemical aspects of the plasma polymerized films by an appropriate choice of the external plasma parameters. These are the magnitude of the plasma input power, the flow rate of the monomers introduced into the plasma and the pressure in the reaction chamber [12]. Additionally, hydrodynamic factors e.g., reactor type [13], reactor size [14], the location of the electric energy input, the inlet and the outlet of the monomer flow [3] have a great influence on the product of plasma polymerization. Because all the hydrodynamic factors were kept constant in this work, their effect will not be further discussed.

Plasma power is a parameter, which directly affects the important internal plasma parameters. When the plasma power is increased the energy of the electrons (E_e) is increased. This results in an increase in the plasma density (n), and temperature of electrons (T_e) and ions (T_i). Additionally, the mean free path of the plasma particles decreases and their collision cross-section increases. All these variations cause more energetic plasma, where the fragmentation and re-arrangement of the monomer molecules is pronounced. This generally results in a more irregular, unsaturated, and branched and/or cross-linked plasma polymers.

When the monomer flow rate is decreased, the retention time of the monomer molecules in the plasma chamber increased. Thus monomer molecules are subjected to more collisions, which results in more fragmentation and re-arrangement in the plasma.

Yasuda combined these two parameters and proposed a controlling parameter, W/FM, where W is the plasma power [J/s], F is the monomer flow rate [mol/s], and M is the molecular weight of the monomer [kg/mol] [3]. The W/FM parameter is an apparent input energy per monomer molecule [J/kg]. The magnitude of the W/FM parameter is considered to be proportional to the concentration of activated species in plasma. The relevance of this parameter in plasma polymerization is shown in Figure 2.5. These variations in the polymer deposition rate with the W/FM parameter show that plasma initiates polymer forming and polymer degrading processes.

In the monomer-sufficient region where the activated species have a lower concentration than the monomer molecules the polymer forming process dominates and the polymer deposition rate increases with increasing W/FM parameter. The power supplied to monomer molecules is relatively low, so that the monomer molecules are subjected to less fragmentation. Plasma polymers with less rearrangement and loss of functional groups i.e., with a certain level of structural retention, are formed.
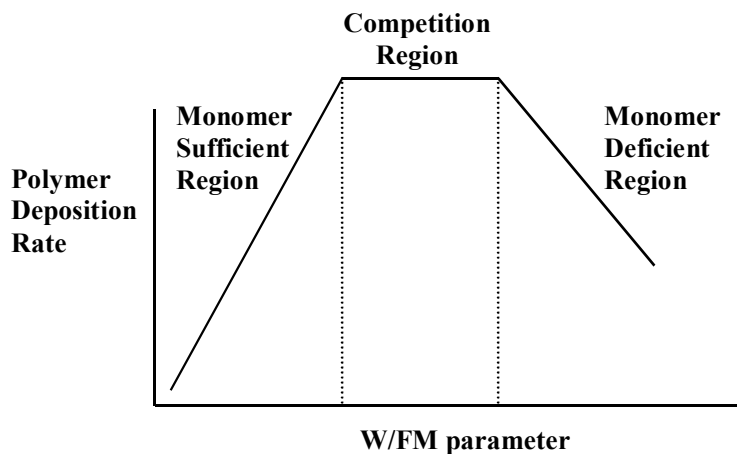

Figure 2.5. Domain of plasma polymer deposition (adapted from Ref. [3]).

On the other hand, in the monomer-deficient region, the ablation process dominates and the polymer deposition rate decreases with increasing W/FM parameter due to low concentration of monomer molecules. The power given to monomer molecules is rather high and the monomer molecules are subjected to heavy fragmentation. Irregular plasma polymers with high rearrangement and low structural retention are formed.

Usually plasma polymerization is operated in the monomer-sufficient region [3]. It should be recognized that the chemical composition of the formed plasma polymers is strongly influenced by the magnitude of the plasma power and the monomer flow rate.

The monomer pressure in the reaction chamber is a rather complex external plasma parameter. Variations in the reaction pressure cause several effects to happen simultaneously. For instance, when the reaction pressure is increased the mean free path of the plasma particles decreases and their collision rate increases (c.f. 2.1.5.3). This increases the fragmentation and re-arrangement of the monomer molecules. However, when the mean free path of the electron decreases, they gain less energy from the electric field and their collision rate with the neutral molecules increases. This results in a decrease in T_e, which should decrease the fragmentation and re-arrangement of the monomer molecules. Because of such competing processes, the reaction pressure is a rather complex external plasma parameter when the chemistry of the plasma polymers should be controlled.

2.2.3. Continuous wave (CW) and pulsed plasma polymerization

Continuous wave plasma polymerization is the traditional technique for the deposition of thin films. As shown in Figure 2.6, in this mode power is supplied to the system continuously. Plasma polymers produced by CW plasmas are characterized by a considerable loss of functional groups preformed in the monomer, as well as irregular and cross-linked structures [15]. This is due to continuous fragmentation of monomers in the plasma and a random polyrecombination of the fragments and atoms. With a CW system, some controllability on the chemistry of plasma polymers has been demonstrated via changes in plasma variables such as plasma power and monomer flow rates [3, 11, 16-20], substrate temperatures [21-23] and substrate positioning relative to the plasma discharge zone [3].

Different from CW plasma, in pulsed plasma the power is given to the system only for a certain period of time (pulse) and then it is switched off (c.f. Figure 2.6).

The main parameters that characterize pulsed plasmas are the pulse period and the duty cycle. The duty cycle values are calculated from the following equation

$$Duty\ cycle\ value = \frac{t_{on}}{(t_{on} + t_{off})}$$

Equation 2.7

Figure 2.7 represents the 0.1 duty cycle value, where the pulse frequency is 1 kHz and the pulse period is 1 ms. A duty cycle value = 1.0 represents the CW plasma case.

Additionally, the duty cycle is an effective external plasma parameter to control the power given to the plasma. The effective energy input provided by pulsed plasma can be estimated from the duty cycle values by using the following formula.

Effective power = Plasma power during the pulse x duty cycle value **Equation 2.8**

For example, for an experiment at a plasma power 20 W and a duty cycle of 0.1, the effective power given to the system is 2 W.
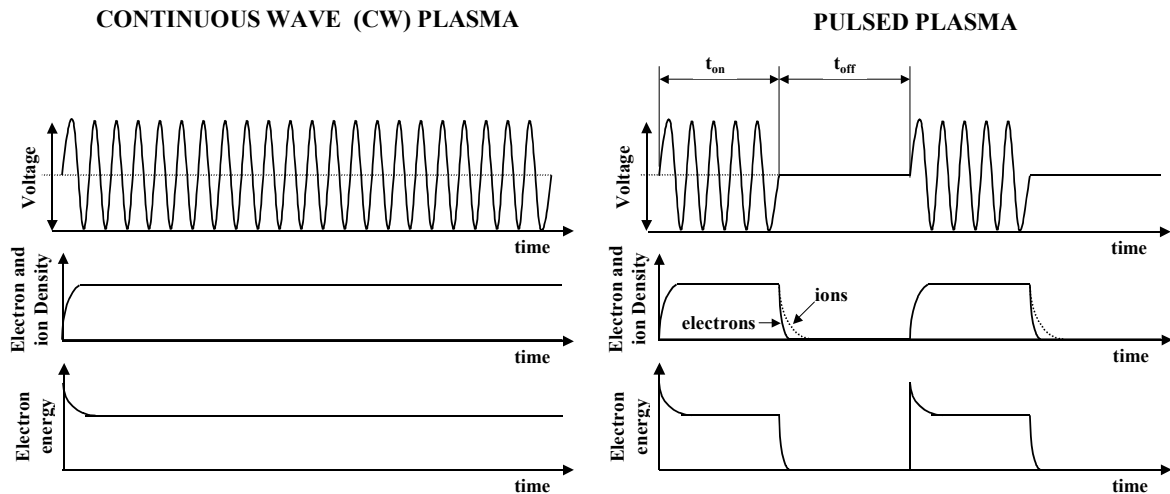

Figure 2.6. Schematic presentation of a continuous wave (CW) and pulsed plasma.

It has been often reported that pulsed plasma polymerization offers a good compromise to efficiently produce polymer structures with a minimum of irregularities and maximum retention of the functional groups preformed in the monomer [15, 24-28]. The differences between the CW and the pulsed plasma deposited films were attributed to partially different reaction mechanisms when one or the other regime is used. During a CW plasma deposition, the competing deposition and etching reactions of the excited species in the plasma lead to a different polymer structure when pulsed plasma is used. It appears that the "plasma off" periods in the pulsed experiments play a very important role in the deposition process, allowing polymerization reactions to take place, which could not normally occur under CW conditions. During the "plasma off" phase it is believed that some of the longer living radicals will continuously enable polymerization reactions, leading finally to a more conventional polymer structure.
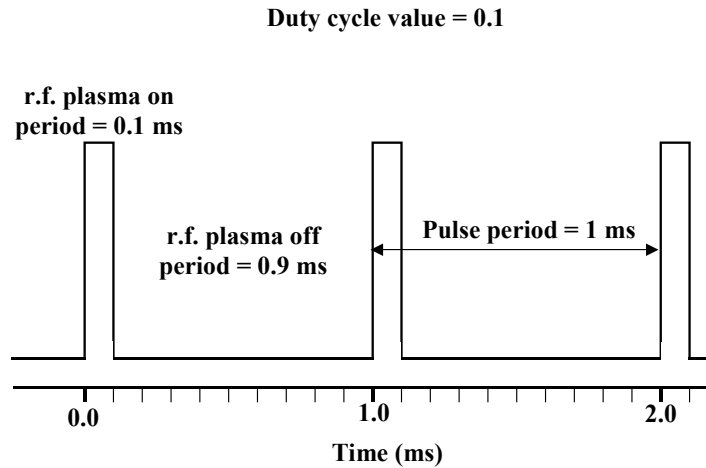
Duty cycle value = 0.1

Figure 2.7. Schematic representation of the duty cycle used for the pulsed 13.56 MHz r.f. plasma film deposition.

2.2.4. Mechanism of plasma polymerization

Plasma polymerization is an entirely different type of a polymer forming process in comparison to the conventional polymerization reaction. The polymer forming process in plasma polymerization is much more complicated and may comprise different and competing reaction schemes.

Yasuda [3] proposed a mechanism, termed rapid step growth polymerization (RSGP), for polymer forming reactions in plasma. Although, it does not cover the entire range of conditions for the deposition of plasma polymers, the RSGP mechanism is commonly well accepted. The RSPG mechanism is schematically shown in Figure 2.8.

According to Figure 2.8 the RSGP can proceed through two parallel cycles. Cycle I consists of the reaction of monofunctional activated species (M·) e.g., free radicals. Cycle II is based on difunctionally activated species (·M·). Cycle I requires the re-excitation of the product species, whereas cycle II can proceed without re-excitation as long as difunctionally reactive species are available. In this RSGP mechanism the addition of the radicals to monomer molecules and the polyrecombination between two radicals proceed to form macromolecules with or without a radical.

The reactive species in RSGP are represented by radicals because these are considered to be the most important species in the formation of the deposits. However, any other reactive species can contribute to any of the steps. More recent works carried out by

Beck et al. [29, 30] and O'Toole et al. [31, 32] advocates that ions also play an important role for the deposition of polymeric materials from low power plasmas.
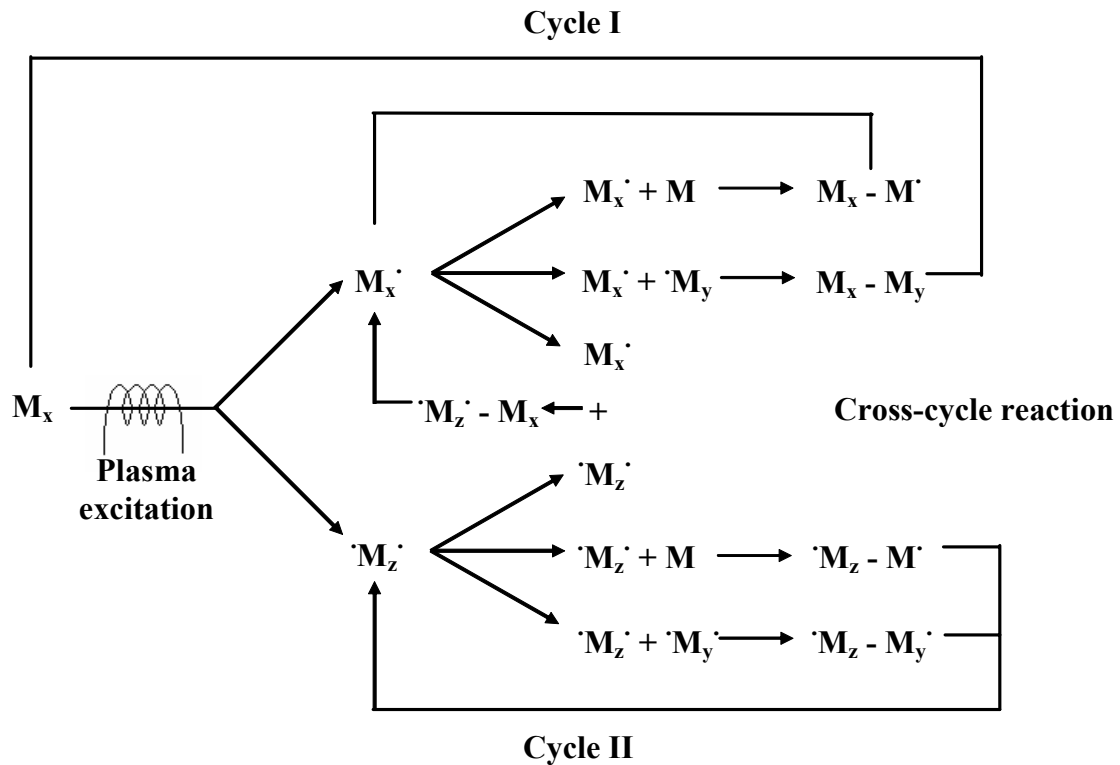
Cycle I

$$M_x^{\cdot} + M \longrightarrow M_x - M^{\cdot}$$

$$M_x^{\cdot} \qquad M_x^{\cdot} + {}^{\cdot}M_y \longrightarrow M_x - M_y$$

$$M_x^{\cdot}$$

$$M_x \underbrace{\qquad}_{\substack{\textbf{Plasma} \\ \textbf{excitation}}} \qquad {}^{\cdot}M_z^{\cdot} - M_x \longleftarrow + \qquad \textbf{Cross-cycle reaction}$$

$$\qquad {}^{\cdot}M_z^{\cdot}$$

$$\qquad {}^{\cdot}M_z^{\cdot} \qquad {}^{\cdot}M_z^{\cdot} + M \longrightarrow {}^{\cdot}M_z - M^{\cdot}$$

$$\qquad {}^{\cdot}M_z^{\cdot} + {}^{\cdot}M_y^{\cdot} \longrightarrow {}^{\cdot}M_z - M_y^{\cdot}$$

Cycle II

Figure 2.8. Schematic representation of the rapid step growth polymerization (RSGP) mechanism in plasma polymerization (adapted from Ref. [3]).

It must be noted that in plasma polymerization, polymerization and deposition are inseparable components of the overall mechanism. None of the steps considered in RSGP is a polymerization itself. While repeating the steps via cycle I or cycle II, the species involved will be deposited on the substrate surface forming macromolecules.

2.2.5. Radicals in plasma polymers

The freshly deposited plasma polymers typically contain radicals. This is because the radicals are the most relevant species in growth mechanism of plasma polymerization, which is productive for the formation of deposits. Additionally, ultraviolet light generated from the plasma and ion as well as electron bombardment are also sources for formation of radicals in the deposits.

The quantity of these radicals depends on the chemical nature of the monomer as well as the external plasma parameters [3].

The most obvious effect of radicals is that the freshly deposited plasma polymers rapidly react with in-diffusing oxygen when they are exposed to ambient air. The addition of oxygen to radicals produces peroxy radicals that are converted to peroxides and hydroperoxides. These peroxides and hydroperoxides are metastable and may decay into various reactive products and secondary radicals, which is well-known as "auto-oxidation" process [33, 34]. In terms of plasma technology the effect of air exposure is denominated as the "ageing" of the plasma deposited films in air.

2.3. Potential applications of plasma polymers

Applications of plasma polymer films may conveniently be divided into two classes. Firstly an alteration of the surface properties of a substrate is the goal. Secondly, the application may capitalize on the bulk properties of a plasma polymer films. Some examples will be given below.

The surface chemistry of a solid material can be easily modified by plasma treatment or by deposition of a very thin plasma polymer film. An example of such application includes modification of the surface of a polymer to promote the adhesion at the interface. Published applications include modifications of the surface of polyamide fibers and weaves to increase adhesion to the epoxy matrix in a composite [35, 36]. Another example dealt with the improvement of the adhesion of epoxy resins to films of polyethylene, poly(tetrafluoro ethylene) and poly(vinyl chloride) by coating them with an acetylene plasma polymer [37].

The plasma modification of the surface chemistry of conventional polymers has been applied to create blood compatible and biocompatible surfaces. Plasma-polymerized films were formed using acrolein, methacrolein, allyl alcohol and allylamine as monomers to increase the adsorption of the F(ab')2 anti-human IgG antibody to the solid-phase surface (flat glass plate) [38]. F(ab')2 anti-human IgG antibody was coated onto these materials, and the dose response of 125I-protein A uptake to human IgG was investigated. Large dose responses were obtained when plasma-polymerized films of acrolein, methacrolein, allyl alcohol and allylamine were used to coat the glass substrates. In particular, aldehyde or OH group-containing films show good responses of 125I-protein A uptake to hIgG.

In order to introduce amino groups, plasma deposition of ethylene diamine was successfully carried out on gold surfaces. These plasma deposited films were used in surface plasmon resonance immunosensing [39].

Reducing protein adsorption on plastics via direct plasma deposition of tri(ethylene glycol) monoallyl ether was reported by Beyer et al. [40]. The major focus of their work was optimization of the degree of retention of the C-O-C bonds of the starting monomer during the deposition progress. Overall, the results obtained from their work provide additional support for the utility of one-step plasma processes to reduce biological fouling of surfaces via deposition of poly(ethylene oxide) surface units.

Plasma polymers can be prepared as protective coatings by using suitable plasma conditions (generally high plasma power) that lead to the formation of highly cross-linked, pinhole free films. For example, plasma polymerization of ethane has been used to prepare protective coatings for NaCl optical components in CO_2 lasers [41]. Plasma polymerization has also been used to prepare films for improving the corrosion performance of metal. Corrosion protection of cold-rolled steel using plasma polymerized films of hexamethyldisiloxane has been reported by Conners et al. [42].

McCulloch et al. [43] prepared plasma polymer films from hexamethyldisiloxane that were a few hundred Angstrom thick. These were used as barrier layers on nonlinear optical devices. They found that a plasma polymer layer deposited on the film surface was successful as a barrier layer preventing solvent penetration and crack formation.

2.4. Characterization techniques for plasma polymers

There is a considerable interest in the structure of plasma polymers. The analytical methods used for characterization of plasma polymers, however, are limited, since the amount of plasma polymer obtained is very small and plasma polymers are of limited solubility in many solvents due to their high degree of cross-linking. These restrictions limit the use of characterization techniques like Nuclear Magnetic Resonance (NMR) spectroscopy in the analysis of plasma polymers. This section will introduce the most frequently applied techniques to investigate the chemical structure of plasma polymer films. These are X-ray photoelectron spectroscopy (XPS), infrared (IR) spectroscopy and Near Edge X-Ray Fine Spectroscopy (NEXAFS). Static secondary ion mass spectrometry (SIMS) has also proved to be a powerful technique for characterization of such films although it is a rather new technique in this field in comparison to others.

XPS, which is also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a powerful technique for surface characterization. XPS is well suited for the characterization of plasma deposited films providing elemental and some functional group analysis. XPS elemental analysis is capable of detecting all elements expect hydrogen and

helium. In addition, information about functional group species can also be provided by XPS.

IR spectroscopy is another most widely used technique for exploring the chemistry and structure of plasma-deposited films. It can be used for either bulk or surface analysis. The IR sampling depth is greater than other techniques mentioned above but it can provide complementary information [44]. Fourier transform infrared (FTIR) has been used successfully to monitor the effects on the chemistry of plasma polymers of factors such as plasma power, deposition time [45-48] and sample position within the reactor [45].

NEXAFS can be used as a spectral "fingerprint" technique to identify the local bonding environment. The spectra exhibit chemical shifts within each group similar to XPS spectra but more importantly considerably different fine structure for carbon in different molecular groups. This clearly illustrates the power of NEXAFS to distinguish chemical bonds and local bonding. In many ways it is superior to XPS, which does not provide local structural information. The biggest advantage of the NEXAFS is that it can provide semi quantitative information about the amount of unsaturation present in the plasma deposited films.

The use of static secondary ion mass spectrometry in characterization of surfaces is also well established. The advantages of using static SIMS for polymeric surface analysis are its surface sensitivity (outermost 15 Å), its analytical sensitivity, and the direct relationship between surface structure and the SIMS fragmentation pattern [49-53]. Those properties make SIMS a very attractive tool to investigate the surface of plasma deposited films. It can provide information about the unsaturation, branching and/or cross-linking, and aromatic and/or aliphatic content of the plasma deposited film [54-59]. SIMS is probably the only surface analytical method, which may provide information on branching, and cross-linking that cannot be done by the competing or complimentary methods of surface analysis.

Different from the surface characterization techniques described above mass spectrometry has been used to probe both neutral and charged species present in the plasma-phase. In gas phase mass spectrometry, plasma species (ions, neutrals and radicals) are sampled through a small aperture, which leads to the mass spectrometer. Neutral species from the plasma passes through an ionization chamber and are ionized by electron impact prior to analysis in the spectrometer. Charged species are mass analyzed without any further ionization. Mass spectrometric studies on gas phase plasma reactions provide valuable information to understand the polymer formation mechanism, which is not fully

covered. MS has been applied to the analysis of methacrylates [31], carboxylic acids [29, 30, 32], allyl alcohol [60], styrene and acrylic acid [30].

It must be noted that each (surface) analysis method discussed here can provide some information about the structure of the plasma polymers. However, to have a complete picture of the structure of plasma polymers, multi method approaches are necessary.

2.5. Review of literature related to SSIMS analysis of plasma polymers

There are number of studies in the literature on plasma polymers and their characterization (c.f. Ref. [3]). In this section, characterization of plasma deposited films by static secondary ion mass spectrometry will be reviewed. Special attention will be given to studies, which derive information about composition, unsaturation, branching and/or cross-linking of plasma deposited films from their respective SSIMS data.

Legget et al. [56] investigated the structure of a plasma deposited styrene film by comparing its SIMS spectrum with the polystyrene reference sample spectrum. They concluded that static SIMS was highly sensitive to subtle changes in surface chemistry. The static SIMS spectra exhibited features due to cross-linking and unsaturation of the plasma deposited styrene film.

Plasma polymers from ethane, ethylene and acetylene were investigated by XPS, IR, SIMS and Auger electron spectroscopy (AES) [61]. It was concluded that structural differences between plasma deposited films could be derived from their respective SIMS spectra. While the plasma deposited acetylene film was the most unsaturated one, the plasma deposited ethane film was the most saturated one. Some spectral features, which were attributed to the branching of the plasma polymers, were observed in the spectra of plasma deposited ethylene and acetylene films. However, Tsai et al. [61] could not conclude on the degree of cross-linking of the different plasma polymers. Additionally, they analyzed the oxygen uptake of the films after exposure to air by using the oxygen containing hydrocarbon secondary ions in the positive SSIMS spectra.

A series of SSIMS studies was undertaken by Chilkoti et al. [62-65] to investigate the plasma polymers prepared from carbonyl containing volatile organic compounds, such as acetaldehyde, acetone and 2-butanone. The use of deuterated compounds was necessary for structural assignments in the case of quadrupole SIMS, in particular to distinguish oxygen containing secondary ions from the pure hydrocarbon ones. It was found that the C/O ratio in the monomer had only little effect on the chemical composition of the plasma polymers, which primarily corresponded to a hydrocarbon type surface. The identified

secondary ions and spectral features were compared with the spectra of conventional hydrocarbon and oxygen containing polymers to deduce information on the surface composition of the respective plasma polymers. Unsaturation, branching and/or cross-linking was observed in all plasma deposited films. Moreover, some indications of the presence of a broad range of different structural units, e.g., ethers, acrylates, and methyacrylates on the surface of these plasma polymers were observed.

Ward and Short [16] showed that the SSIMS spectra of plasma polymers prepared from methyl acrylates under low power conditions, were largely reminiscent to conventionally prepared poly(methyl methacrylate) (PMMA). They found by SIMS data that the monomer structure had been retained in the plasma polymers. A number of negative secondary ions have structures, which contain a complete monomer unit. However, the formation of short chains and cross-linking was also concluded.

Ward and Short [17] also investigated the structure of plasma polymers prepared from a series of vinyl sulphones with respect to plasma power. The negative SSIMS spectra of plasma polymers prepared at high and low power were examined. Differences between relative intensities of the prominent ions showed that there had been a greater retention of structures from the monomer in the plasma polymers that were prepared at low plasma power.

Later, Ward and Short [18] investigated the functional group and structural retention of the plasma deposited films from a series of methyl acrylates monomers as a function of plasma power and monomer flow rate. High functional group and structural retention could be achieved in the plasma polymerization of monomers at low plasma power and high monomer flow rate. Additionally, they could derive information on the possible plasma polymerization mechanism from the respective SSIMS data.

A similar study was carried out by Ameen et al. [19]. Plasma polymers of allyl alcohol were prepared under a range of different monomer flow rate conditions. The plasma polymer prepared using the higher flow rate showed a good retention of hydroxyl groups. This was attributed to a mechanism of incorporation of the monomer into the plasma polymerized film through an opening up of the carbon-carbon double bond. With decreasing flow rate of the monomer the hydroxyl group retention decreased and most oxygen atoms were incorporated into the polymer network, e.g., ether bridges. Lower flow rates also resulted in plasma polymers with higher degrees of cross-linking and irregularity.

Static SIMS and XPS were applied for a characterization of deposits formed from acrylic acid plasmas on aluminium foils [66]. At low power, the plasma deposited acrylic acid film showed conservation of the COOH functionality and secondary ions containing five repeat units were detected. At high power, fewer COOH functions and only monomeric secondary ions were observed, reflecting the tendency of ester formation and cross linking under higher power conditions.

Eufinger et al. [67] demonstrated the feasibility to link structural features reflected by the SSIMS spectra to given external plasma parameters. Specifically, the positive ion mass spectra of plasma deposited films from hexamethyldisiloxane produced in the low plasma power and high reaction pressure regime revealed more structural retention. The relative intensities of the secondary ions, especially for the cluster peaks between m/z 175 and 221, in the positive SSIMS spectra of plasma polymers became more similar to those observed in SSIMS of conventionally prepared poly(dimethylsiloxane), when the external plasma parameters were changed from hard to mild.

SSIMS was also used to examine structural differences between the plasma polymers prepared from 2-hydroxyethyl methacrylate, acrylic acid and acetone. They were prepared with and without substrate cooling by dry ice/methanol and liquid nitrogen [23]. Comparison of SSIMS spectra of films deposited at different substrate temperatures indicated that a reduction in substrate temperature generally resulted in higher yields of oxygen containing secondary ions. SSIMS data also suggest that the reduction of substrate temperature results in less polymer unsaturation and cross-linking. This showed that the lower temperature favors the retention of monomer structures without fragmentation. They explained their results by increased adsorption or condensation of monomer molecules on the substrate surface at low temperatures.