

2. Theoretical Background

2.1. Basic Plasma literature

2.1.1. Plasma State

'Plasma' sometimes also referred to as the fourth state of matter, is an electrically conducting medium in which there are roughly equal numbers of positively and negatively charged particles, produced when the atoms in a gas become ionized (Encyclopedia Britannica online).

The term 'Plasma' was first introduced by Irving Langmuir (1881-1957) [22] to explain the behavior of gases in an electrical discharge. The plasma state can be considered to be a gaseous mixture of neutral and oppositely charged particles with a roughly zero net electrical charge. The required energy to produce a plasma can have very different sources [3]. In order to ignite a plasma, an initial "ionization event" is essential. Ionization processes can occur when for instance molecules of a gas are subjected to high-energy radiation, electric fields or high caloric energy. During these processes the energies of particles composing the gas increase significantly and as a result electrons are released and charged heavy particles are produced. At atmospheric pressures and temperatures around 5000 K materials only exist in the gaseous phase. Above 10000 K ions are the main constituent particles of matter. Under these conditions and at even higher temperatures, matter is considered to be in the Plasma State. More elevated temperatures induce a very high degree of ionization, and temperatures of 10^8 K and higher lead to mixtures of bare nuclei and electrons.

2.1.2. Classification of plasmas

Plasma states can be divided in two main categories: hot or thermal plasmas (near equilibrium plasmas) and cold or electrical plasmas (non-equilibrium plasmas).

Hot plasmas are characterized by very high temperatures of electrons and heavy particles, both charged and neutral and they are close to maximal degrees of ionization (100%). All species are in thermal equilibrium with each other. The electron and ion densities (n_e and n_i respectively) can, if the temperature is high enough, be comparable with or even exceed the neutral gas density, n_g . Cold plasmas are characterized by a low temperature of particles (charged and neutral molecular and atomic species), a relatively

high temperature of electrons and very low degrees of ionization (10^{-4} -10%). Some examples of hot plasmas include electrical arcs, plasma jets of rocket engines, thermonuclear reaction generated plasmas, etc., while cold plasmas include low pressure, direct current (DC) and radio frequency (RF) discharges as well as discharges from fluorescent illuminating tubes.

2.1.3. Plasma in the laboratory

The Plasma state can be produced in the laboratory by raising the energy content of matter by mechanical (close to adiabatic compression), thermal (electrically heated furnaces), chemical (exothermic reactions, e.g., flames), radiant (high energy electromagnetic and particle radiation, e.g., electron beams), nuclear (controlled nuclear reactions), and electrical (arcs, coronas, DC and RF discharges) means, and by the combination of them as in the combination of mechanical and thermal energies (e.g., explosions). Plasmas lose energy to their surroundings through collisions and radiation processes; consequently energy must be supplied continuously to the system in order to sustain the discharge. Hence, the most common method of sustaining a plasma is by continuously supplying energy to the system through an electrical discharge as in the case of plasma polymerization, where a low pressure non-equilibrium discharge through capacitively or inductively coupled electrodes is used to initiate and sustain the plasma [3, 4, 23].

Owing to the high reactivity and energy of plasma species, a number of specialized chemical applications of the plasma state have been developed in the following directions: plasma polymerization and plasma enhanced grafting of thin layer macromolecular structures and etching of inorganic or polymeric substrate surfaces. Plasma polymerization involves the dissociation of starting materials and reorganization of the resulting neutral or charged molecular fragments into macromolecular structures located inside or outside of the plasma zone. This will be discussed in detail in section 2.2. Macromolecular thin layers can also be synthesized by the plasma-generation of active species on substrate surfaces, followed by graft polymerization reactions in the absence of the plasma and in the presence of non-excited and non-fragmented monomer molecules. Inert gas sputtering procedures can be developed that can allow the creation of specific surface morphologies by selective ablation for instance, of amorphous and crystalline surfaces.

2.1.4. Internal plasma parameters

Plasmas are characterized by the following main parameters: plasma density, plasma temperature, electron energy distribution, mean free path, Debye length and sheath potential.

Plasma density: Plasma consists of charged and neutral particles. In the case of cold plasmas the electron and ion densities, n_e and n_i are assumed to be equal to each other. Typically n_e values in low-pressure cold plasmas are between 10^9 and 10^{12} cm^{-3} . In electrical cold plasmas the degree of ionization is usually low, with $n_e, n_i \leq 10^{-4} n_g$.

Plasma temperature: The plasma temperature represents the mean translational energy of the particles in the discharge. In the case of cold plasmas there is a lack of thermal equilibrium. Most notably, because of their lower mass, electrons are easily accelerated to energies which are sufficient to ionize the gas particles, with typical values of electron temperature, T_e , in the range of 10^4 to 10^5 K. These values correspond to ~ 0.5 - 10 eV. The ions on the other hand undergo a significant amount of cooling due to head on collisions with other molecules or ions. Collisions with neutral molecules is a major cooling factor for ions because the n_g is much higher than the n_i . The ion temperature, T_i , is approximately the same as the room temperature (T_{room}) as well as the neutral particle temperature (T_g). So the particle temperatures obey the relation $T_e \gg T_i \sim T_g \sim T_{\text{room}}$ [4].

Electron energy distribution: The electron energy distribution of non-equilibrium low-pressure plasmas can be often described by a Druvesteyn approximation (Figure 2.1), where the temperature of the electron is considered to be much higher than that of the ions, and where it is assumed that the energy transfer of electrons is by elastic collisions. It can be observed that a small number of electrons have relatively high energies (5-15 eV) while the bulk of the electrons belong to the low energy electron range (0.5-5 eV). Since the ionization potentials of the atoms of common organic compounds (e.g. $\text{C}^+ = 11.26$ eV, $\text{H}^+ = 13.6$ eV, $\text{O}^+ = 13.6$ eV, $\text{N}^+ = 14.53$ eV) belong to the tail region of the electron energy distribution, there is a low degree of ionization in the cold plasmas.

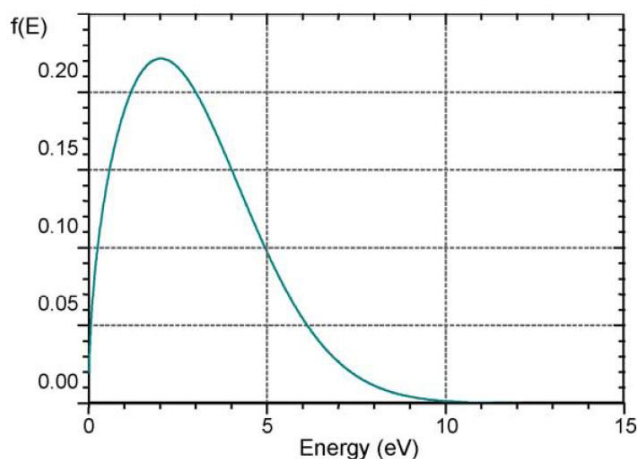


Figure 2.1: Druvesteyn electron energy distribution of a cold plasma (average electron energy 3 eV) [23].

Table 2.1: Bond energies and enthalpies of formation of free radicals [23].

Bond energies		Enthalpies of formation of free radicals	
Species	Energy (eV)	Species	Energy (eV)
C-H	3.3	$\cdot\text{CH}\cdot$	6.1
C-N	7.8	$\text{CH}_2\cdot$	4.4
C-Cl	4.0	$\text{CH}_3\cdot$	1.5
C-F	5.7	$\text{HC}=\text{C}\cdot$	5.8
C=O	11.2	$\text{HC}=\text{CH}_2\cdot$	3.1
C-C	6.3	$\text{NH}\cdot$	3.6
C=C	7.6	$\text{NH}_2\cdot$	1.9
$\text{C}\equiv\text{C}$	10.0	$\cdot\text{Si}\cdot$	4.7
$\text{CH}_3\text{-H}$	4.5	$\text{C}_6\text{H}_5\cdot$	3.4

It is important to note that the range of energy of most of the electrons (2-5 eV) is high enough to dissociate almost all the chemical bonds involved in organic compounds (Table 2.1), and to create free radical species capable of reorganizing into macromolecular structures. Higher energies are usually required for the dissociation of unsaturated bonds and the formation of multiple free radicals. Accordingly, original or plasma-generated unsaturated bonds will have a better ‘survival rate’ under plasma conditions, in comparison to σ bonds.

2. Theoretical Background

Mean free path: Plasma particles can be characterized by their mean free path, which is the mean distance a particle traverses between two successive collisions. However, the collision rate of a particle with another one is much higher than the collision rate of a gas particle with an electron or an ion, because in a cold plasma $n_g \gg n_i, n_e$. According to the kinetic theory of gases, with these assumptions, the mean free path of neutral gas particle λ_g is given as [23]

$$\lambda_g = \left(\frac{1}{4\sqrt{2}\pi n_g r_g^2} \right) \quad \text{(Equation 2.1)}$$

where r_g is the radius of the neutral gas particle. Similarly the mean free path of an electron (λ_e) can be described by a similar equation

$$\lambda_e = \left(\frac{1}{\pi n_g r_g^2} \right) \quad \text{(Equation 2.2)}$$

Debye length: The electrical neutrality of a plasma is true only in the macroscopic sense. The electric field of each particle interacts with the electric charges of the surrounding particles. Neutrality of the plasma is achieved when the field of each particle is compensated outside the zone where shielding occurs. The characteristic parameter that describes the electrical shielding (when the potential of each particle is shielded by charges of the surrounding particles) is called the Debye length (λ_D), and it defines the volume (Debye sphere) within which the neutrality rule can be violated. This parameter can be approximated by the following equation

$$\lambda_D = \sqrt{\frac{\epsilon_0 k T_e}{n_e e^2}} \quad \text{(Equation 2.3)}$$

where ϵ_0 is the permittivity of free space; e is the charge of the electron; k is the Boltzmann constant; T_e is the temperature of electrons, and n_e is the electron density. An ionized gas is considered as a plasma only if the Debye length is much smaller than the physical dimensions of the plasma region.

Sheath potential: Charged and neutral particles collide in the plasma phase and with surfaces, which confine the discharge. Due to a higher flux of electrons the surface would

gain a negative potential. This results in a positively charged plasma layer of a thickness of several Debye lengths in the vicinity of the surface. This positively charged plasma layer is recognized as the plasma sheath.

Across the sheath potential the flux of the electrons equals the flux of ions reaching the surface; the net current through the sheath is zero. The thickness of the plasma sheath confines a region where the electron density is negligible, and its value depends on the frequency of the electromagnetic field and the pressure in the system. The electric potential, V_s , developed across the plasma sheath is called the sheath potential and is given for planar surfaces by [24]

$$V_s = \frac{kT_e}{2e} \ln\left(\frac{m_e}{2.3m_i}\right) \quad \text{(Equation 2.4)}$$

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

2.2. Plasma polymerization

2.2.1. Introduction to plasma polymerization

Plasma polymerization refers to the formation of materials on the surface of a substrate under the influence of a plasma. In this process, the growth of low-molecular weight molecules (monomers) into high-molecular weight molecules (polymers) occurs with the assistance of the plasma energy. There is a significant difference in the mechanisms of polymerization between the conventional methods of polymerization and plasma polymerization. Chemical reactions which occur in the conventional polymerization such as radical or ionic polymerization are highly specific and in most cases predictable, while in the case of plasma polymerization the chemical reactions are generally very complex and involve multiple reaction pathways ending up in the formation of a broad range of species. In any case, even if the same monomer is used in conventional and plasma polymerization, there is a significant difference in the chemical and physical properties between the products. Plasma polymerization has an additional advantage of being able to use compounds for polymerization which are not polymerizable by conventional methods. The capability of plasma polymerization to form ultra-thin films is a unique and valuable asset. However, plasma polymers are generally chemically

2. Theoretical Background

inhomogeneous, branched and cross-linked as it can be observed from the model of plasma polymerized ethylene films [Figure 2.2.][6]. Generally some functional groups (and radicals) which were not present in the monomers are formed by subsequent reactions on the surface of the deposited polymer. Radicals play a significant role in the post plasma reactions of the polymer [3]. These properties of the plasma polymerized films make plasma polymerization a tool for the synthesis of polymers with desired structures and controlled density of a specific chemical group. These polymers have found application in various technologies [25-28].

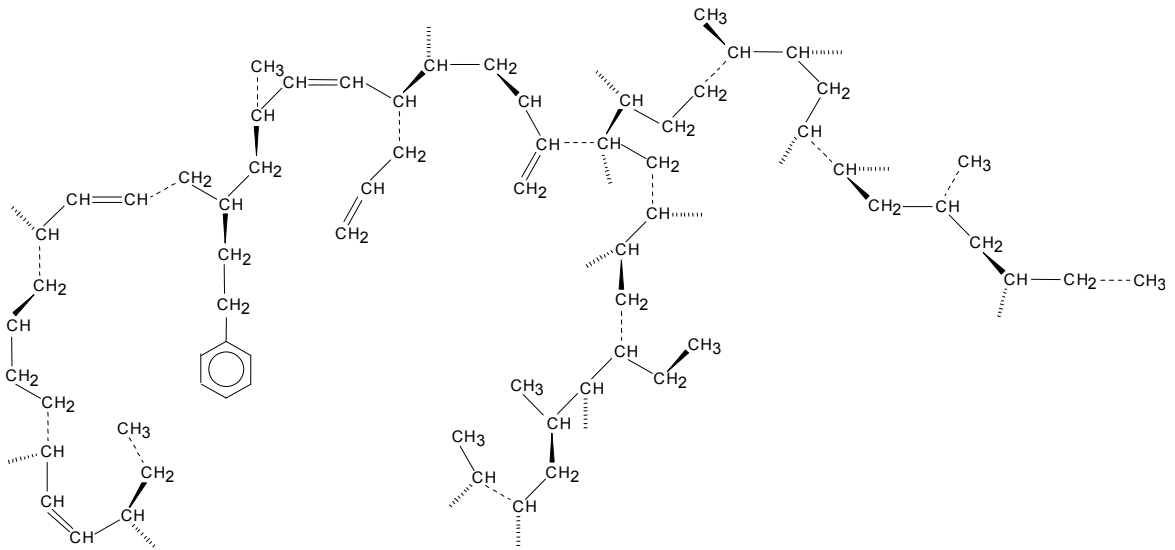


Figure 2.2: Model of a plasma deposited ethylene film, as proposed by Tibbitt et al. [6] according to Infrared (IR) and Nuclear Magnetic Resonance (NMR) spectroscopy data.

The nature of the deposited film depends on the internal (as discussed in section 2.1.4.) and external (reactor geometry [29], type of excitation, applied power, monomer pressure, gas flow rate, duty cycle or pulsing) plasma parameters. The effects of these parameters have been studied by several researchers over the past years [e.g. 16, 30-33]. Although it is possible to directly control the internal plasma parameters, it is a highly complex and cumbersome task. However, as shown in the following chapters, it is possible to exercise an indirect control on these internal plasma parameters by the control of a few selected external plasma parameters. These parameters were plasma power, duty cycle and the monomer pressure during plasma polymerization.

2. Theoretical Background

An increase in plasma power, whether directly or by increase of the duty cycle (cf. section 2.2.1.), increases the electron energy. This subsequently leads to increasing plasma density as well as electron and ion temperatures. The mean free path of the plasma particles decrease as there is an increase in plasma density and an increase in collision rate of particles (Equations 2.1, 2.2). As a result a more energetic plasma is formed which subsequently results in a higher rate of fragmentation and re-arrangement of monomer molecules. This parameter along with the flow rate of the monomer were combined by Yasuda, to give the Yasuda factor W/FM , where W is the discharge power in Watts, F is the monomer flow rate in cubic centimeters per minute and M is the molecular weight of the monomer in grams per mole [34]. This factor is a measure of the energy input per unit mass of the monomer in Joules/kg; therefore, the magnitude of the W/FM parameter is considered to be proportional to the concentration of activated species in a plasma.

A plot of the general dependence of the plasma polymer deposition rate for a monomer on the W/FM parameter is shown in Figure 2.3 at three different flow rates at a constant effective plasma power (Equation 2.6). At a low W/FM values (region I), the deposition rate is linearly dependent on W/FM , as shown by the straight line. On the right side of the dashed line the deposition rate is independent of W/FM . This region (III) is the monomer-deficient region, where sufficient discharge power is available but the monomer feed-in rate is the deposition rate determining factor. To the left of the dashed line (region II) is the power-deficient transient region, where ample monomer is available but the power input rate is not sufficient. Generally plasma polymerization is operated in the monomer-sufficient region, which is the region I.

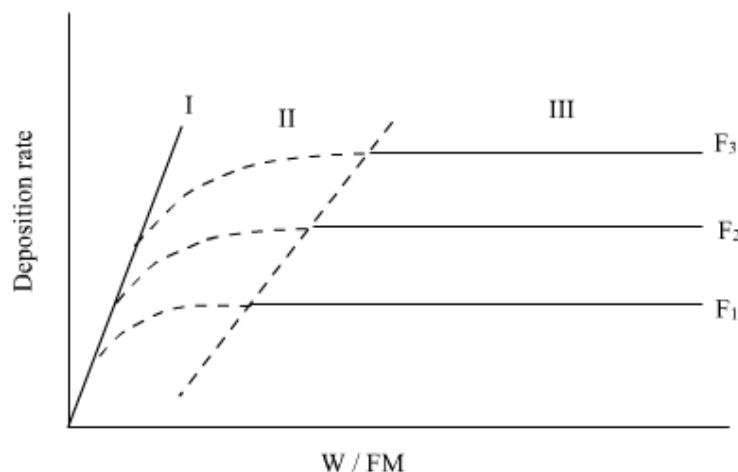


Figure 2.3: Dependence of plasma polymerization regions (I, II & III) on deposition rate and W/FM at various flow rates [3].

The monomer pressure during polymerization is another important parameter. An increase in pressure results in an increase in particle density that subsequently leads to a decrease in the mean free path of the plasma particles (Equation 2.1, 2.2). The collision rates increases and results in higher fragmentation and rearrangement rates of the monomer molecules. However, a decrease in mean free path of the electrons leads to a decrease in the electron energy. This subsequently decreases the fragmentation and rearrangement rate of the monomer molecules. Because of such competing processes, the reaction pressure becomes a rather complex external parameter. However, some amount of control can still be exercised on the chemistry of the plasma polymers using the monomer pressure as a parameter.

2.2.2. Continuous wave and pulse plasma polymerization

Past studies on plasma polymerization focused on continuous-wave (CW) discharge plasmas. In this mode lots of active species are created by high-energy electrons and ions. There is a high degree of fragmentation of the monomer molecule because of excess energy consumed per monomer. Plasma polymers produced by CW plasmas are characterized by a considerable loss of functional groups of the monomers, as well as irregular and cross-linked structures. Some control on the chemistry of plasma polymers has been demonstrated via changes in selected external plasma parameters like plasma power and monomer flow rate [3, 5, 17, 25, 31, 32, 35], substrate temperature [36-38] and substrate positioning relative to the plasma discharge zone [3].

To retain higher degrees of functionality in the films and films with well defined chemical structure the pulsed discharge technique was introduced in the field of plasma polymerization. Introduced by Tiller [7] in 1971, Yasuda [11] in 1977 and Vinzant et al. [39] in 1978, the advantages of using r.f. pulsed plasmas over continuous wave plasmas have been discussed in various studies [8-10]. In this method power is given to the plasma in pulses. The parameter which characterizes a pulse plasma is the pulse period and the duty cycle. The duty cycle is given as the ratio of the pulse ON time to the total pulse time period.

$$\text{Duty cycle} = \left(\frac{t_{\text{on}}}{t_{\text{on}} + t_{\text{off}}} \right) \quad \text{(Equation 2.5)}$$

A schematic representation of a pulse plasma is seen in Figure 2.4. The variation in the duty cycle results in a change in effective power supplied to the system according to the equation,

$$\text{Effective power} = \text{Plasma power} \times \text{Duty cycle} \quad \text{(Equation 2.6)}$$

In various studies, it has been reported that the pulse plasma polymerization does offer a better option to produce plasma polymers with minimum irregularities [18, 30, 40-43]. In the case of pulse plasma it is expected that the plasma polymerization could proceed during the “ON” period and depending upon the length of “OFF” time, also during the “OFF” period. Conventional polymerization such as radical chain propagation could take place during the “OFF” period of the discharge hereby increasing the retention of the functional group of the monomer in the deposited films. The use of low power additionally prevents excessive monomer fragmentation and reduces the plasma-induced damage to the depositing polymer.

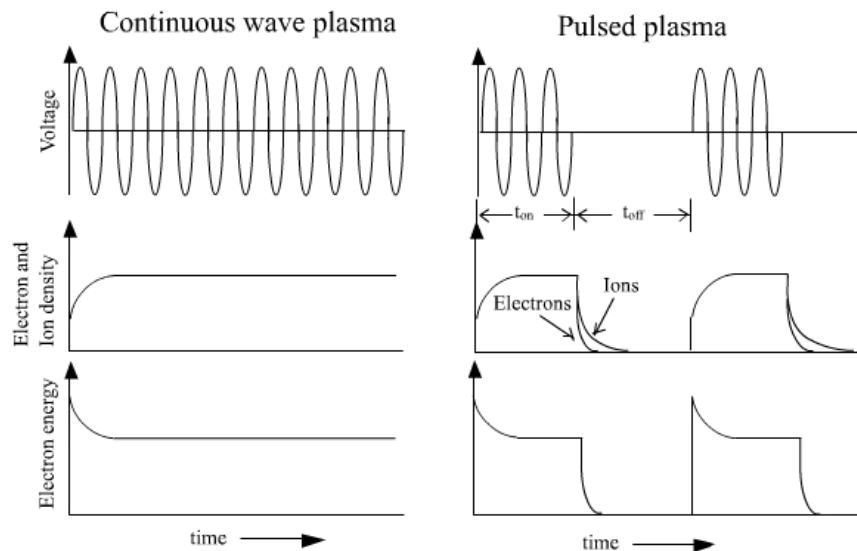


Figure 2.4: Schematic representation of continuous wave (CW) and pulsed plasmas.

2.2.3. Growth mechanism of plasma polymerization

The mechanism of plasma polymerization differs significantly from the mechanisms involved in conventional polymerization methods. Conventional

2. Theoretical Background

polymerization mechanisms such as Step-growth polymerization and Chain-growth polymerization are very unlikely to play a significant role in plasma polymerization [3].

An overall mechanism, Rapid Step Growth Polymerization (RSGP), also called “activation-growth model”, was proposed by Yasuda [3]. This mechanism is schematically shown in Figure 2.5. Here $[M]$ refers to a neutral species that can be the original monomer molecule or any of its dissociation products. The activated species that are capable of participating in the chemical reaction to create a covalent bond are given by $[M\cdot]$. Difunctional activated species are shown by $[\cdot M\cdot]$. The subscripts i, j and k merely indicate the difference in the size of species involved.

As shown in the Figure 2.5 the overall reaction contains two major routes of rapid step growth. Cycle I is via the repeated activation of the reaction products from the monofunctional activated species, and cycle II is via difunctional or multifunctional activated species. The cycle I and cycle II play equally significant roles. In both cases the growth mechanism of polymerization is a rapid step growth polymerization.

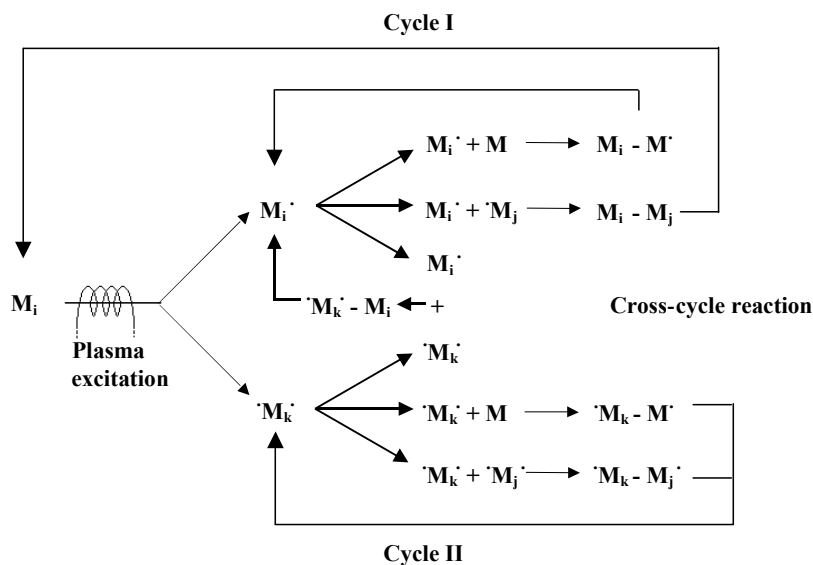


Figure 2.5: Schematic representation of the rapid step growth polymerization (RSGP) mechanism in plasma polymerization (adapted from Ref. [3]).

Among the possible neutral activated species that can participate in the RSGP mechanism, the free radical is the most probable and important species. This can be supported by the fact that most polymers formed in a plasma contain a high concentration of free radicals (10^{17} to 10^{20} spins per cubic cm). The formation of free radicals has been

ascribed by Hansen and Schonhorn [44] to the impingement of energetic particles on the surface, and by Hudis [45] to ultraviolet (UV) radiation from the plasma. The quantity of these trapped radicals depends also on the chemical nature of the monomer as well as the external plasma parameters [3]. The most obvious effect of radicals can be seen during the aging (exposure to ambient air) of the freshly deposited plasma polymers. The addition of oxygen from the ambient air to the radicals on the surface of the plasma polymers produces peroxy radicals that are converted to peroxides and hydroperoxides, which are metastable and may decay into various reactive products and secondary radicals [46, 47]. Attempts to suppress these radicals, known as quenching, are also described in the literature [28] for plasma deposited films.

2.3. Applications of plasma polymers

Plasma polymer films have found certain applications in a broad range of fields including electronics, optics and life sciences. Despite the difficulties in understanding the complex multi-mechanism nature of the formation of plasma polymerized films, literature data indicate that these films find potential applications in the area of thin layer biomaterials, adhesives, low-dielectric constant films, generation of super-hydrophobic coatings and many more. [48-51].

It has been demonstrated that efficient surface modification reactions can be carried out with cold plasmas even on very inert substrate surfaces [23]. These have led to developments in enhancing the compatibility of dissimilar polymer surfaces such as preparation of biobased composites from natural fibers and polyolefin-based materials.

The advantages of cold-plasma techniques have also offered efficient routes for the generation of biocompatible surfaces. It has been shown that oxygen-, air-, and water-vapor plasma atmospheres implant hydroxyl, carbonyl, carboxyl and ether functionalities onto various substrate surfaces that play a significant role in cell adhesion and cell-growth mechanisms [52]. Cell adhesion and growth studies indicated that the concentration of adhering cells on plasma-treated polyethylene surfaces corresponds to the content of OH-groups present on the substrate surfaces [53]. Artificial corneas based on polyvinylalcohol copolymers, have been modified under acetone/oxygen, ammonia, and argon plasma atmospheres for enhancing epithelization [54]. Enhanced attachment and growth of human endothelial cells were observed on surfaces exposed to ammonia-plasma. Immobilization of active enzymes has been accomplished in the absence and presence of spacer molecular

chains intercalated between the polymeric substrates using continuous wave and pulsed RF plasmas for functionalization of natural and synthetic polymer surfaces [55, 56].

Other applications include modifications of the surface of polyamide fibers and weaves to increase adhesion to the epoxy matrix in a composite [57, 58]. Depositions of electrically conductive structures have also been intensively studied [48, 59, 60]. Plasma deposited films on gold surfaces with amino groups were used in surface plasmon resonance immunosensing applications [61].

Several applications have also emerged in the field of protective coating of materials ranging from ordinary plastics [62] to optical components in lasers [63]. Plasma polymerization has also been used to prepare films for improving the corrosion performance of metals. Corrosion protection of cold-rolled steel using plasma polymerized films of hexamethyldisiloxane has been reported by Connors et al. [64].

Plasma assisted etching of surfaces (e.g. Silver nitride) is also of great importance for the development of sub-micron-dimensions-based technologies (microelectronics, biotechnology, molecular recognitions processes etc) where the characteristics of patterned arrays, passivation layers, conductors, and functionalized array areas, define device performances [65].

2.4. Chemical characterization of plasma polymers

The chemical character of plasma polymer films has been studied by a range of modern analytical techniques. However, in most plasma polymerization experiments only very small quantities of solid plasma polymer products can be produced, typically only milligrams. Moreover, these plasma polymer films are generally insoluble in organic solvents because of their high degree of cross-linking. These factors generally complicate the characterization of plasma polymers. Therefore, more sophisticated tools must be used instead of several analytical methods generally used in the analysis for conventional polymers. Infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), static secondary ion mass spectroscopy (SIMS), solid state nuclear magnetic resonance (NMR) spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and near-edge X-ray absorption spectroscopy (NEXAFS) are by far the most utilized techniques to investigate the chemical structure of such films.

IR spectroscopy can be used for the bulk chemical analysis of plasma polymer films. Although a primarily qualitative analytical tool, it has been used to quantitatively

measure the concentrations of functional groups and the cross-linking density of plasma polymer films [66, 67]. IR spectroscopy can also be used to increase the utility of ESCA by obtaining complementary information [5]. Fourier transformed infrared (FTIR) spectroscopy has been successfully used to monitor the effects of plasma parameters on the chemistry of plasma polymers [68-71].

XPS or ESCA is a powerful technique for analysis of the surface of plasma polymer films. Since the plasma polymers are generally extremely thin film, ESCA is ideally suited for determination of the chemical properties of these films, i.e. quantitative elemental analysis, functional group identification dependent on the electronegativity of nearest neighbor atoms, and depth profiling.

The use of static secondary ion mass spectrometry in characterization of surfaces is also well established. The advantages of using static SIMS for surface analysis of polymers are its surface sensitivity (outermost 15 Å), its analytical sensitivity, and the direct relationship between surface structure and the SIMS fragmentation pattern [72-76]. It can provide information about the unsaturation, branching and/or cross-linking, and aromatic and/or aliphatic content of the plasma deposited film [77-81].

Solid state NMR characterization of plasma polymers have also been reported in literature. Kaplan et al. studied the chemical characteristics of plasma polymerized ethane, ethylene, acetylene and toluene using NMR [82-84].

Electron microscopy, TEM and SEM, are two techniques which are widely used to obtain morphological information on plasma polymer thin films [85-88].

In recent times, NEXAFS has also proved to be an effective tool for the analysis of plasma polymer films. It is used to identify local structural information such as chemical bonds. It can also provide semi-quantitative information about the amount of unsaturation of the films.

Additionally mass spectroscopic (MS) techniques have been used to study the gas phase plasma reactions to understand the polymer forming mechanisms. The MS technique has been applied to the analysis of plasma of methacrylates [89], carboxylic acids [90-92], allyl alcohol [93], styrene and acrylic acid [91].

Although the number of techniques available for the characterization of plasma polymers is large, none of the methods individually is capable of giving a complete picture of the structure of plasma polymers. Hence, a multi-method approach that includes several of the techniques mentioned above is necessary.