CHAPTER 2
PREPARATION OF R.F. PLASMA POLYMERIZED THIN FILMS AND FTIR ANALYSIS

2.1 Introduction

The concept of plasma dates back to Irving Langmuir, who in 1928 introduced the term plasma in his studies of electrified gases in vacuum tubes. Plasmas are quasi-neutral particle systems in the form of gaseous or fluid-like mixtures of free electrons and ions, frequently also containing neutral particles (atoms, molecules), with a large mean kinetic energy of the components. In addition, there are a large amount of excited molecular conditions, which by emitting electromagnetic radiation turns back to the ground state and this gives the characteristic luminance of the plasma. Plasma occurs in the sun, in lightnings and flames. Plasmas are frequently subdivided into low and high-temperature plasmas. Arc Plasma at normal pressure and low-pressure glow discharge are low-temperature plasmas, while fusion plasmas are high-temperature plasmas [1-6]. Plasmas are used in fluorescent tubes and in recent times, in the surface technique.

Plasma polymerization is a new material preparation process. It refers to formation of polymeric materials under the influence of plasma, which is generated by some kind of electric discharge. Here gaseous monomers, stimulated through a plasma, condense on freely selectable substrates, as high cross-linked layers. Plasma polymerization covers a wide interdisciplinary area of physics, chemistry, interfaces, materials and so on [1]. Because the most practical means of carrying out plasma polymerization involves the use of an electric glow discharge in a vacuum, the term glow discharge polymerization has been used synonymously with plasma polymerization. The well-recognized concept of polymerization today is based on the molecular processes by which the size of the molecules increases. In contrast to such
molecular processes, polymer formation in plasma has been recognized as an atomic (non molecular) process [7]. If one wants to coat a certain substrate with a conventional polymer, several steps are required. In coating by plasma polymerization, in contrast, all these functional steps are replaced by an essentially one-step process to produce a good polymer coating. Initially polymers formed under the plasma condition were recognized as an insoluble deposit that provided only difficulty in cleaning and nothing else. The two most important characteristics of this undesirable deposit, which are the most sought later, in modern technology of coatings are excellent adhesion to substrate materials and strong resistance to most chemicals. Plasma polymerization is an inexpensive tool for fabricating organic thin films. This technique results in homogeneous, highly cross-linked and thermally stable polymer thin films. Fig. 1 gives a comparison of the structures of plasma polymers and conventional polymers.

![Comparison between the plasma polymer and the conventional polymer of the same monomer](image)

Fig. 1. Comparison between the plasma polymer and the conventional polymer of the same monomer
Chapter 2

The dielectric properties of the plasma polymerized thin films have potential applications in microelectronics. These films are used in the production of microcapacitors and in the deposition of passivation layers onto semiconductor devices [1]. A good passivation layer must fulfill two requirements; it has to shield the device from outside influence but at the same time should not interrupt its operations [8]. Plasma polymerized thin films are finding use in fabricating storage batteries, LEDs, sensors, super capacitors, etc. Films with low dielectric permittivity are potential candidates as intermetallic dielectrics in microelectronics [9]. Nowadays multilayer optical interference films have been developed [10, 11] out of plasma polymerization techniques.

2.2 Mechanism of Plasma Polymerization

The mechanism by which plasma polymerization occurs is complex. Before discussing in detail the mechanisms of formation of polymeric materials in plasma, it is necessary to review some fundamental aspects of polymerization. Polymerization reaction can be classified into two major groups on the basis of the mechanism of growth reactions. These are step-growth polymerization and chain-growth polymerization [1]. In step-growth polymerization, a polymer is formed by stepwise repetition of the same reaction over and over again. If the monomer is represented by \( M \) and the growing molecule by \( M_i \) (where \( i = 1, 2, \text{etc.} \)), step-growth polymerization can be represented by

\[
\begin{align*}
M_1 + M & \rightarrow M_2 + H_2O \\
M_2 + M & \rightarrow M_3 + H_2O \\
M_n + M_m & \rightarrow M_{n+m} + H_2O
\end{align*}
\]

Here all the reactions at each step is identical to the first reaction.

In chain growth polymerization, a long-chain molecule is formed by a series of consecutive steps that is completed in a very short time. In this case, the products are only final polymers. Unlike the case of step-growth polymerization, intermediate-size molecules cannot be isolated. Consequently, the entire polymer formation can be
considered an essentially one-step process, as long as the concept of chemical reactions that relies on the identification of the reactants and the products is concerned. When the chain-carrying species is indicated by $M\cdot$ and the monomer by $M$, the chain-growth mechanism can be shown by

$$
\begin{align*}
M\cdot + M &= M_2\cdot \\
M_2\cdot + M &= M_3\cdot \\
M_n\cdot + M &= M_{n+1}\cdot
\end{align*}
$$

and

$$M_m\cdot \rightarrow M_m \text{ (polymer)}$$

The first three reactions represent the propagation reaction and the last reaction in which the chain-carrying species is lost is the termination reaction.

In the elucidation of mechanisms of plasma polymerization a brief review of radiation polymerization and parylene polymerization is extremely helpful since they are closest to plasma polymerization. Polymerization initiated by ionizing radiation such as $\gamma$ rays from $^{60}\text{Co}$ or high energy beams is radiation polymerization. Here the formation of the chain-carrying species such as the cation, anion, or free radical is a consecutive process to the ionization of a monomer. But in plasma polymerization, the reactive species are not necessarily formed as the consequence of ionization. The study of parylene polymerization also provides information needed for the elucidation of plasma polymerization mechanism. This is a rare example of polymerization that occurs with high efficiency in vacuum. This kind of polymerization can be more adequately described as a rapid step-growth polymerization by polycombination of difunctional active species. Here reactive species do not add onto monomer; instead, they react with each other to form a polymer. The radiation polymerization is similar to plasma polymerization since the primary step in both is ionization of monomers. However, radiation polymerization does not yield polymers in vacuum. The similarity between plasma polymerization and parylene polymerization is in the formation of polymer deposits in vacuum and differ in that parylene polymerization does not involve the ionization process. In short, plasma polymerization can be viewed as a
hybrid of these two polymerization mechanisms.

The overall plasma polymerization mechanism proposed by Yasuda is based on the rapid Step-growth mechanism [1]. The deposition of a plasma polymer can be envisaged as occurring by rapid step-growth polymerization (RSGP)

\[(M_m \cdot + M_n \cdot \rightarrow M_{m+n}) \times N\]

where \(N\) represents the number of repetitions of similar reactions. In 1973 Yasuda and Lamaze pointed out that an elementary reaction product was not immune to reactivation in plasma polymerization [12]. Therefore the combination of two monofunctional reactive species, such as a radical or cation \((M_m \cdot + M_n \cdot \rightarrow M_{m+n})\) is not necessarily a termination step as it is in conventional polymerization. Instead, plasma polymerization, proceeds via the stepwise fragmentation and recombination of molecules and/or oligomers to form macromolecules [1,13]. In Fig. 2, \(M_x\) refers to a neutral species that can be the original monomer molecule or any of the dissociation products, where \(x = i, j, k, \text{ etc.}\) indicates a size difference between species.

Fig. 2. Schematic representation of the bicyclic rapid step-growth polymerization mechanism proposed by Yasuda
The overall reaction cycle of plasma polymerization occurs via two major routes of rapid step growth. The first route or cycle I is the repeated activation of reaction products derived from monofunctional activated species. The second route or cycle II occurs through the formation of bifunctional or multifunctional activated species, similar to what is found in parylene polymerization. Reactions A and D in Fig. 2 are the same as the first step of propagation by the addition mechanism. Therefore these reactions require a chemical structure that allows for the addition of $M\cdot$. Reaction D is essentially the same as reaction A, with the monofunctional reactant replaced by a bifunctional reactant. Reaction B is essentially a termination by the recombination mechanism and reaction C is similar to reaction B, with one of the reactants being bifunctional. Reaction E is a combination reaction between bifunctional intermediates. Plasma polymers are formed through any combination of the different routes, as a result of the RSGP mechanism. Anyway, the chain growth mechanism is absent here. The reaction between a cation and an anion ($M_{i}^{+} + M_{k}^{-} \rightarrow M_{i+k}^{0}$) is the only combination of ionic species that can contribute to the reaction scheme in Fig. 2 as $M\cdot$. Plasma polymerization is mainly dominated by free radical chemistry. It seems quite probable that plasma polymerization proceeds mainly via reactions of neutral species, although ions do indeed exist in plasma.

2.3 Preparation of Plasma Polymerized Thin Films

In plasma polymerization, plasma of the monomer vapour is generated by employing d.c., a.c. (50Hz.), radio frequency (MHz) or microwave (GHz) techniques. At frequencies above 1MHz, no direct contact between electrodes and plasma is necessary. Hence in r.f. plasma polymerization, the energy can be fed to plasma by inductive or capacitative coupling. Hence r.f. plasma can be initiated and sustained by external electrodes at a much lower voltage than it is required for maintaining d.c. glow discharge.

The schematic of the plasma polymerization unit is shown in Fig. 3. The system comprises of an r.f. generator source that uses four 807 RCA tetrode valves.
To pressure gauge

Aluminium foil

To rotary pump

Monomer

Sample

Fig. 3. Schematic of the plasma polymerization unit.

The r.f. source oscillates in the frequency range 5 – 13MHz and has an output power of ≈ 35 watts. The deposition chamber is a long glass tube of length 35 cm and diameter of 3.5 cm. For maintaining plasma the energy is fed to the deposition chamber by capacitative coupling using aluminium foils. The tube is connected to a rotary pump and is evacuated to a pressure of $10^{-2}$ Torr. The monomer flow in the tube is regulated using a manually operated needle valve.

In order to prepare the polymer films flat glass slides (5 x 2 cm) are used. These glass substrates are first cleaned in running water and are immersed in chromic acid for 1-2 hours.
in order to remove alkaline impurities. The slides are then washed in distilled water and are cleaned ultrasonically. The microscopic impurities are striped off by ultrasonic agitation in water. The glass slides are then dried and placed inside the deposition chamber in between the aluminum foil electrodes, which are wrapped around the glass tube and are capacitatively coupled. First, the chamber is evacuated to a pressure of $10^{-2}$ Torr, keeping the monomer needle valve closed. The r.f. power is switched on and bluish glow appears in between the electrodes. The monomer needle valve is opened gradually and a glow discharge is obtained in between the electrodes by applying a current in the range 60-80 mA. After a time interval of 30 minutes to 1 hour, a thin film of the corresponding polymer is coated on the glass substrate. Three different polymers namely poly 2,6-dimethylaniline, poly diethylamine and poly dimethylamine are prepared in the above described set up.

2.4 FTIR Analysis

Functional groups present in the plasma polymerized films can be identified through Fourier Transform Infrared Analysis (FTIR). New bond formations to any significant degree can be determined by this method. Even though the complex nature of plasma polymers makes the precise interpretation of their IR spectra difficult, much useful information concerning the general nature of polymers can be obtained [1,14]. Before analysing the FTIR spectra of plasma polymers let us have a brief discussion of the method.

FTIR method: In almost all spectrometers the recorded spectrum has a background fluctuation called noise. In order for the real spectral peak to be well distinguished, the signal to noise ratio (s/n) of atleast 3 or 4 is necessary. In the regions of the electromagnetic spectrum where sources are weak and detectors are less sensitive it is always advantageous to use Fourier Transform Spectroscopy. Another major disadvantage of the conventional dispersive method of recording a spectrum is its slowness. Here the frequency is swept smoothly across the whole span of the spectrum by rotating the monochromator. This method is very inefficient in some cases. For example, suppose a spectrum with one or two lines in it is needed. Here we have to sweep from one end to the other in order to find the lines, but most of the time is spent recording nothing but the background noise. An FTIR instrument gives the same information as a simple infrared spectrophotometer, however, the
performance of the former overweighs with respect to speed, sensitivity and much smaller requirements of the sample [15].

Fourier Transform Spectroscopy provides almost instantaneous recording of the whole spectrum with the help of computers [16, 17]. In the IR region FT method is the transfer of the information from time (t) domain to frequency (v) domain by a mathematical analysis known as Fourier transformation, which is performed with the help of computers. A function f(y) in the time domain is related to a function f(x) in the frequency domain by the relation.

\[
f(x) = \int_{-\infty}^{\infty} f(y) \exp(-iy) \, dy
\]

Here f(x) is said to be the Fourier transform of f(y). Or the intensity in the frequency domain is given as

\[
I(v) = \int_{-\infty}^{\infty} f(t) \exp(-ivt) \, dt
\]

In the frequency domain spectrum intensity variation with frequency is shown while in time domain spectrum intensity variation with time is shown. All FT spectrometers consist of an interferometer unit [18, 19]. Michelson's interferometer invented by Albert Abraham Michelson in 1880 forms the basis for the development of FTIR. The interferometer unit is for obtaining the time domain spectrum. Performing the Fourier transform on this signal will give the original frequencies and intensities emitted by the source. But this process is time consuming. The invention of computers and the advances of computers to perform mathematical operations made FTIR a reality. A great advantage of the FTIR method is that the radiation of all wavenumbers from the source falls on the detector all the time. This is called multiplex advantage, which gives a gain of \( \sqrt{n} \) in signal-to-noise ratio for an FTIR spectrum over the same total time on a dispersive spectrum [20, 21]. Here n is the number of resolution elements. Besides multiplex advantage, rapid scanning and constant resolving power over the entire spectrum are added advantages of the FTIR method over the ordinary IR method where dispersive measurements are made.

Sampling techniques for FTIR spectroscopy depend on the nature of the sample
In the case of liquid samples, the easiest way is to place one drop of sample between two IR transparent plates of rock salt (NaCl) or potassium bromide. Solid samples can be milled with KBr to form a very fine powder. This powder is then compressed into a thin pellet, which can be analyzed.

**Analysis of monomer and polymer spectra**: In the present work, the FTIR spectra of the monomer samples namely, 2,6-dimethylaniline, diethylamine and dimethylamine (structures in Fig. 4) and the corresponding polymers are recorded in the range 400 cm\(^{-1}\) - 4000 cm\(^{-1}\).

![Diagram of monomers](image)

**Fig. 4. Structure of the monomers**

The FTIR spectra of the 2,6 dimethylaniline monomer and polymer are shown in Figs. 5 and 6 respectively. The introduction of two ortho methyl groups into aniline brings 2,6-dimethylaniline. In the monomer spectrum 3078, 3025 and 2965 cm\(^{-1}\) correspond to the three ring CH or aromatic CH stretch frequencies corresponding to the three ring CH bonds of the benzene ring. The frequency at 2965 cm\(^{-1}\) is present in the polymer spectrum also, which implies that the benzene ring is retained in the polymer. The presence of group frequencies 2925 and 2866 cm\(^{-1}\) in the polymer spectrum indicates the presence of the methylene group in the polymer [23, 24]. These are frequencies corresponding to asymmetric and symmetric stretch of CH\(_2\). This implies that the methyl group of the monomer is changed to methylene group. The most important observation made by comparing the two spectra is that pertaining to NH stretching frequencies. 2,6-dimethylaniline being a primary amine, there are two bands in the monomer spectrum in the NH stretch region corresponding to asymmetric (3462 cm\(^{-1}\)) and symmetric (3383 cm\(^{-1}\)) stretch. But in the polymer spectrum only a single frequency (3343 cm\(^{-1}\)) is there.
presence of this single frequency is characteristic of a secondary amine, which has only one NH bond. Hence it can be inferred that NH$_2$ group in the monomer is changed to NH group in the polymer. Thus the possible linkage is through the hydrogen abstraction of the NH$_2$ group in the monomer. This is the linkage reported for poly aniline [25]. Hence by comparing the FTIR spectra of monomer and polymer samples of 2,6 dimethylaniline, we can come to the conclusion that there are two linkages, one of which is from the amino group and the other from the methyl group. This substantiates the highly branched and cross-linked nature of the r.f plasma polymers.

Figs. 7 and 8 show the FTIR spectra of diethylamine monomer and polymer samples. Diethylamine is an aliphatic secondary amine and shows only one NH stretch (3409 cm$^{-1}$) in the monomer spectrum. In the polymer spectrum the broad NH stretch at 3337 cm$^{-1}$ rather than at $\approx$ 3400 cm$^{-1}$ implies intermolecular hydrogen bonding, as might be expected in a highly branched polymer [1]. The four peaks within 2800 – 3000 cm$^{-1}$ in the monomer spectrum correspond to CH stretching frequencies of methyl and methylene groups. Of these 2965 and 2839 cm$^{-1}$ are associated with the asymmetric and symmetric stretch of methyl group while 2919 and 2806 cm$^{-1}$ are those of methylene group. In the polymer spectrum only two frequencies are there in this region. Or those two frequencies corresponding to the symmetrical stretching of methyl and methylene groups are absent. This suggests that the possible linkage has taken place through both methyl and methylene groups of diethylamine.

The FTIR Spectra of the dimethylamine monomer and polymer are shown is Figs. 9 and 10. Being a secondary amine, dimethylamine also shows only one NH Stretch (3443 cm$^{-1}$) in the monomer spectrum. Just as in diethylamine here also in the polymer spectrum we have the broad NH Stretch at a lower value of 3290 cm$^{-1}$ due to the intermolecular hydrogen bonding expected in a highly branched polymer [1].
Fig. 5. FTIR spectrum of 2,6-dimethylaniline monomer
Fig. 6. FTIR spectrum of 2,6- dimethylaniline polymer
Fig. 7. FTIR spectrum of diethylamine monomer
Fig. 8. FTIR spectrum of diethylamine polymer
Fig. 9. FTIR spectrum of dimethylamine monomer
Fig. 10. FTIR spectrum of dimethylamine polymer
REFERENCES


