Synthesis and Characterization of Parylene Based Composite for Bio Medical Application

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This report is submitted as a FYP thesis in partial fulfillment of the requirement for the degree of

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Certificate

This is to certify that work in this thesis has been carried out by Mr. Ali Abbas, Mr. Ali Raza and Mr. M. Arslan Aslam and completed under my supervision in laboratories of School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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Dedication

We dedicate our dissertation work to our beloved parents, and to all the fellows and lab attendants who supported us in our work.

Acknowledgements

Firstly, we are grateful to Almighty Allah for good health and wellbeing that were necessary for the successful completion of the research as well as thesis. We would like to appreciate the people who assisted us during an intensive period of eight months of conducting our research work.

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Last but not the least; we are thankful to our family members for their spiritual support throughout research work and writing this thesis. Thank you very much, everyone!

Abstract

Bone fracture is very common problem now a day. Implant materials used in this regard are usually 316-L or titanium alloys that provide mechanical support to the fractured area but have no or little contribution in the biological process of bone healing. Parylene has been increasingly use for medical applications such as insulation of Electrochemical Impedance Spectroscopy and Microelectrode Array. Parylene has unique mechanical and surface properties along with corrosion resistance that has also made it a potential candidate to be used as a scaffold. Surface modified parylene films have been recently use as a scaffold for bone healing process and gave very promising results. The purpose of this study is to synthesize surface modified parylene base composites for bone implants and performed the surface and biological characterization.

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Chapter 01

INTRODUCTION

With inventions of new materials and disruptive techniques, medical science has been revolutionized. In this revolution, materials science is playing instrumental role. Different materials are available which are better in properties and have good compatibility with body tissues as compared to old-fangled materials. In medical science, bone fracture is very common problem now a day. Implant materials used in this regard are usually 316-L or titanium alloys that provide mechanical support to the fractured area but have no or little contribution in the biological process of bone healing. Parylene has been increasingly use for medical applications. The usage of Parylene is high because of its biocompatibility, conformant nature and ease of utilization.

The purpose of this project is to synthesize a coating of Parylene over a substrate by using “Pulsed laser deposition” rather than “chemical vapor deposition” which is commonly being used for such coatings. After synthesis, we characterize these coatings by using FTIR and XRD characterization techniques to conform that whether the coatings have been established over the substrate or not. After getting positive results, we moved on to apply same technique for synthesis of composites wherein we used pellets containing 90-95% Parylene and 5-10% boron nitride, and then subjected them to same PLD process for synthesis of Parylene based boron nitride composites films.

The sole orientation of this project is to contrive a new approach, as a replacement to chemical vapor deposition, with more ease, efficiency and cost-effectiveness. Another factor of novelty is that used power of boron nitride rather than its nanotubes and Nano-sheets which makes it attractive choice over other approaches. The direct usage of boron nitride power can be vindicated by a patent.

1.1 Polymers

Most common material that is used in production of biomaterials is polymer. Many implants and parts are making with polymeric materials now days. For example, epoxies and acrylics are used to coat the implants to improve their compatibility and to make the implants corrosion free. A bioengineer always looks at that material which fulfills the required medical applications with reduced cost and weight. Polymeric material along with metals and ceramics is used to make biomaterials. Most common parts made with the help of polymers are pacemakers, encapsulations, soft-tissue replacements, heart valves, cardiac assist devices, artificial blood vessels and skin etc.

The properties which make the polymeric materials superior to other materials in making biomaterials are barrier to chemical attack, corrosion resistance, flexibility, better bio compatibility and light weight. Now, the polymeric materials are used to coat the implants such as bone fixation plates and joints implants to make them corrosion free and more biocompatible. Now researchers are working on these coatings to use as healing of fractured part improvers.

Applications	**Polymer**
Heart Pacemaker	Silicones tubes, acrylic, nylon, polyurethane
Blood Vessels	Polyester, Polytetrafluoroethylene
Hip, knee and Shoulder Joint	High M.W Polyethylene
Finger Joints & silicon sutures	Nylon, polyglucolic acid and Polylactic acid
Coated implants (Bone fixation)	Parylene, Epoxies, Acrylics

1.2 Composites

The best example of naturally occurred composite bio material is bone. 70% of our bone is constructed of Hydroxyl appetites. Now a day artificial bones are made through combine different material as composite. Examples of naturally occurred composites are bone, skin, cartilage, lungs and dentin etc. The structure of naturally occurred composite is of hierarchical structures [15]. Now different types of composite materials are used to coat the implant to make it more biocompatible and strengthen such as HA composite and Parylene composite coating etc. Below is the comparison table of different biomaterials such as metals, polymers, ceramics and composites [16].

Materials	Advantages	Disadvantages	Examples
Polymers (nylon, silicon, polyester)	Resilient Easy to fabricate	Not strong Deform with time May degradable	Suture, blood vessels, hip sockets
Metals (Ti and its alloys, Ag, Au, stainless steels)	Strong, tough, Ductile	May corrode Dense Difficult to prepare	Joint replacement, dental root implant, pacers, bone plates and screws
Ceramics (alumina, zirconia, hydroxyapetite)	Very Biocompatible	Brittle Not resilient	Dental and orthopaedic implants
Composites (carbon-carbon, bone cement)	Strong Tailor made	Difficult to prepare	Dental resin, bone cement

Figure 1: Different Materials with advantages, disadvantages & examples

1.3 Selection of Biomaterials

Selection of materials always carries through many processes to find out the materials with similar properties as original part has in it. We must make a proper plan to choose the exact required material.

1) Problem Analysis
2) Requirement Consideration
3) Availability of materials and their properties
4) Choice of material with similar properties

Some considerations should keep in mind while choosing material:

- What is the role or functions of that material in body?

- What is the environment in which it will work and effects of the environment on the properties of that material?
- What is the period for which it is implanted in body?
- Is it safe for human health?

Some important feature/characteristics of biomaterials are described below:

1.3.1 Biocompatibility

Material used in implants should be compatible regarding to body. It should not create problems like blood clotting, inflammation around implanted part, heating the part during function etc. It should not be harmful or toxic to human body.

1.3.2 Toxicology

Biomaterial which is used as implant in body should not be toxic. Implanted biomaterials should not release out anything from its mass into body fluid which may case harmful diseases like cancer, inflammation etc. in the body. For example, bone fixation implants release toxic corrosive material into fluid flowing around with the passage of time.

1.3.3 Healing

The main purpose of implanted biomaterial should be to improve healing power of that destroyed or infected site. When we implant biomaterial in infected site then reaction will call “foreign body reaction” with different intensity and duration depending on anatomical site? For example, if we insert the coted bone fixation plated at fractured then increase the healing power on that point.

1.3.4 Pathobiology and Functional Tissue Structure

Coated medical devices inserted into tissues and organ. We study that what is the structure and functionality of normal and abnormal tissues to check the effects of implants on surrounding tissues and organs.

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Chapter 02

LITERATURE REVIEW

We can use multiple materials for biomedical applications. In our project we used Parylene, polymer, as biomedical material and reinforced it with Boron nitride to make composite.

2.1 Parylene

Parylene first was discovered by “Michael Szwarc” in 1947.Now it has become an attractive material in biomedical, aerospace and electronics industries. Parylene is basically a trade name of unique polymer “poly (p-xylene)” which is used as deposited films or coatings in electrical circuits, transistors, medical instruments and in aerospace industry. There are many derivatives of Parylene available in market. The substitution of functional group, at different orientations, segregates the Parylene derivatives from each other i.e. Parylene N, C.

2.2 Structure of Parylene

Parylene has a sustainable chemistry in which no by/side products produce with reduced usage of hazardous material. In case of N-type Parylene, precursor [2.2] Para cyclophane which converts into 100% monomer with no by-product above 500c. In this process no initiator and terminator group is needed. So, it is also called a green polymer chemistry [1].

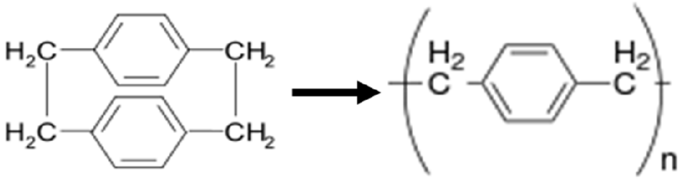
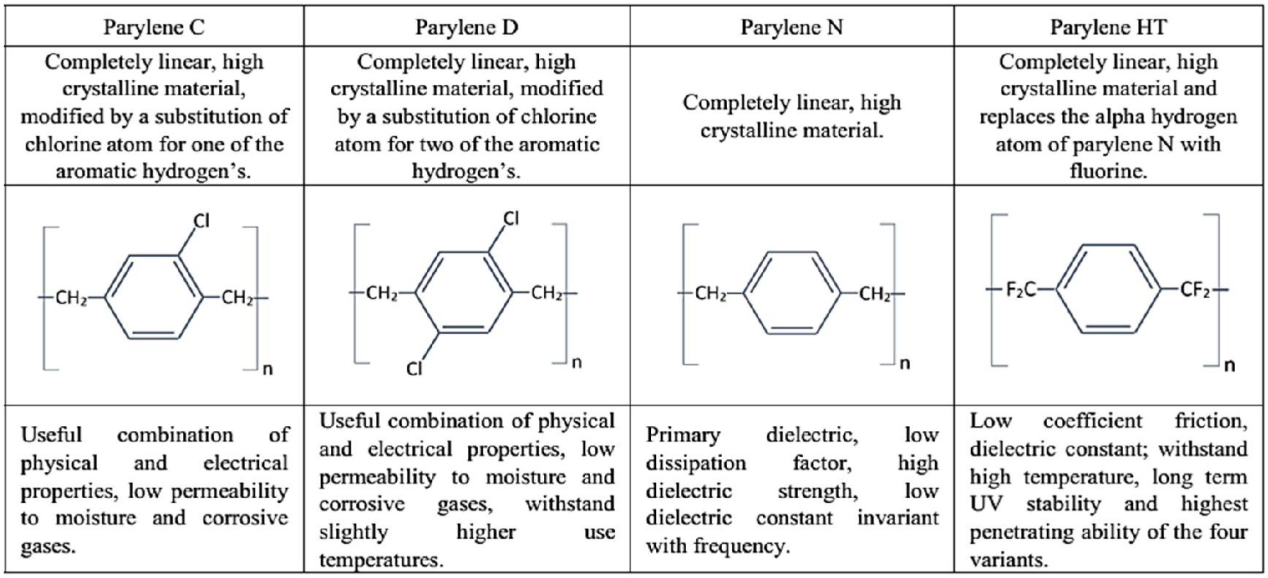


Figure 2: Parylene Structure

Most commonly used parylene in industry is C-type, in which one chlorine atom is used as substitute of aromatic hydrogen at para-position at benzene ring. It gives conformal coating due to vapor deposition method which gives deposition of monomer in all direction. In D-type parylene, two chlorine atoms are substituted by aromatic hydrocarbons of benzene ring.

Table 1 Parylene classifications & their properties



Parylene C	Parylene D	Parylene N	Parylene HT
Completely linear, high crystalline material, modified by a substitution of chlorine atom for one of the aromatic hydrogen's.	Completely linear, high crystalline material, modified by a substitution of chlorine atom for two of the aromatic hydrogen's.	Completely linear, high crystalline material.	Completely linear, high crystalline material and replaces the alpha hydrogen atom of parylene N with fluorine.
Useful combination of physical and electrical properties, low permeability to moisture and corrosive gases.	Useful combination of physical and electrical properties, low permeability to moisture and corrosive gases, withstand slightly higher use temperatures.	Primary dielectric, low dissipation factor, high dielectric strength, low dielectric constant invariant with frequency.	Low coefficient friction, dielectric constant; withstand high temperature, long term UV stability and highest penetrating ability of the four variants.

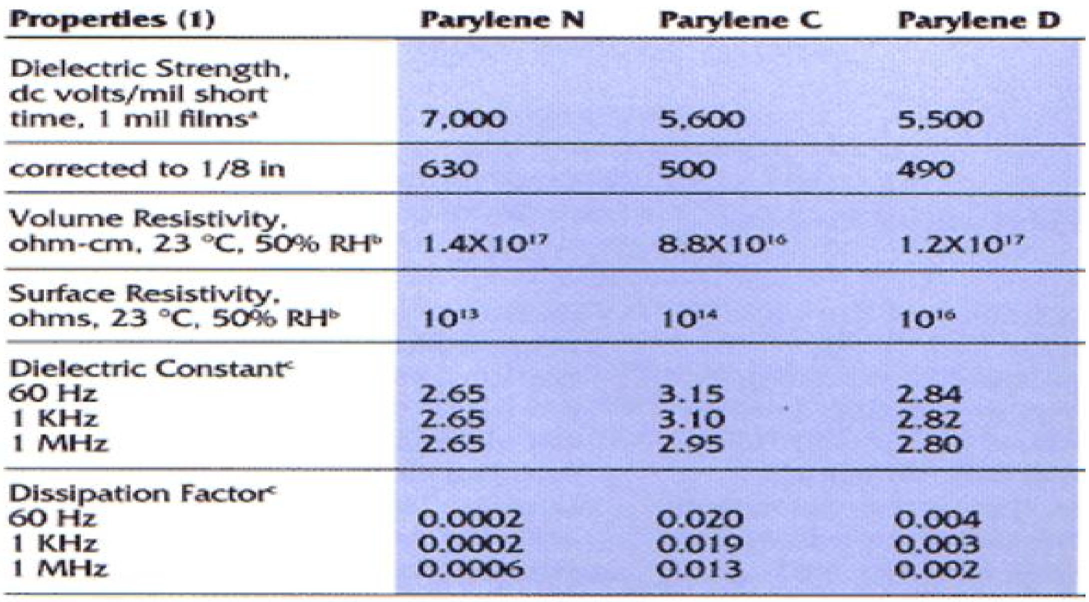
2.3 Properties of Parylene

The Parylene shows some important properties such as electrical, barrier, thermal and mechanical.

2.3.1 Electrical Properties

Due to atypical electrical insulation property, Parylene is used as a dielectric layer in most electrical applications. As compared to epoxies and silicones, it has a high dielectric strength. If we compare C and N type Parylene then N-type has a low dissipation factor than C-type. Because in c-type, chlorine atom is present which increases dielectric constant and dissipation factor. So, N-type has best electrical properties in this regard.

Table 2 Parylene Electrical Properties [22]



Properties (1)	Parylene N	Parylene C	Parylene D
Dielectric Strength, dc volts/mil short time, 1 mil films[a]	7,000	5,600	5,500
corrected to 1/8 in	630	500	490
Volume Resistivity, ohm-cm, 23 °C, 50% RH[b]	1.4X10^{17}	8.8X10^{16}	1.2X10^{17}
Surface Resistivity, ohms, 23 °C, 50% RH[b]	10^{13}	10^{14}	10^{16}
Dielectric Constant[c]			
60 Hz	2.65	3.15	2.84
1 KHz	2.65	3.10	2.82
1 MHz	2.65	2.95	2.80
Dissipation Factor[c]			
60 Hz	0.0002	0.020	0.004
1 KHz	0.0002	0.019	0.003
1 MHz	0.0006	0.013	0.002

2.3.2 Barrier Properties

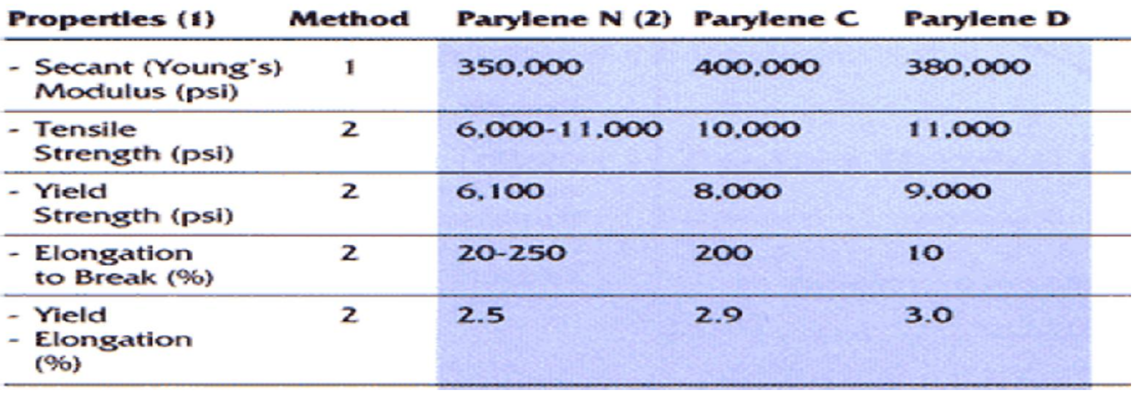
Parylene is used as protective layer for material using in incompatible and hazardous environment because it shows resistance against moister and chemical vapors transmission through it. Parylene C-type has best barrier properties due to its structure and conformal coating. Gas permeability of C-type is also very low as compared to other types of parylene and polymers such as epoxies and silicones.

All types of parylene are insoluble in all type of solvents up to 150°C and shows resistance against chemical attack at room temperature. N-type parylene becomes soluble in solvent at its boiling point (265C). Stress-cracking agents cannot affect the performance of these coatings.

2.3.3 Physical and Mechanical Properties

Parylene has high tensile and yield strength than other polymers due to its higher molecular weight. Benzene ring contributes a major part in molecular weight. Hardness of parylene is approximately equal to the hardness of skin. Conventional methods such as extrusion, molding and casting can’t be used to form parylene. Melting point of parylene is also is very high due to higher molecular weight. C-type parylene is best choice to improve mechanical properties of substrate.

Table 3 Parylene Physical &Mechanical Properties [2]

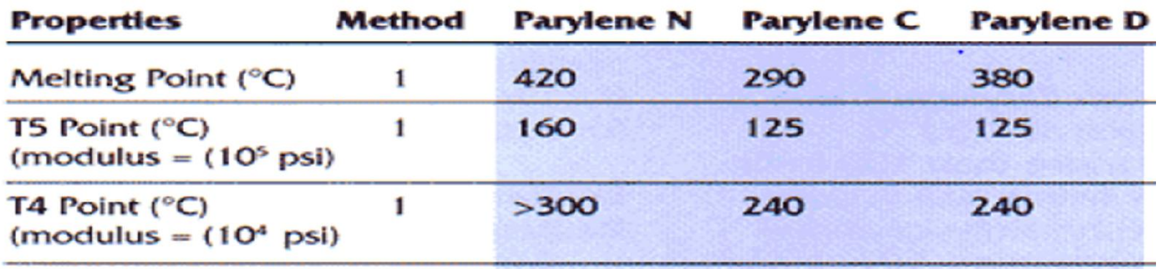


Properties (1)	Method	Parylene N (2)	Parylene C	Parylene D
- Secant (Young's) Modulus (psi)	1	350,000	400,000	380,000
- Tensile Strength (psi)	2	6,000-11,000	10,000	11,000
- Yield Strength (psi)	2	6,100	8,000	9,000
- Elongation to Break (%)	2	20-250	200	10
- Yield - Elongation (%)	2	2.5	2.9	3.0

2.3.4 Thermal Properties

Like other polymers parylene has its own temperature range which depends on their usage and environmental conditions. Above this operating range, it becomes brittle and yellowish. According to Arrhenius extrapolation test data, C-type parylene can serve for 10 years at 100 C. If we use this same sample in oxygen free atmosphere then it can serve for more time at same temperature. We can apply annealing process on it to increase hardness, cut-through resistance and wear resistance due to increase in density and crystallinity.

Table 4 Thermal Properties [2]



Properties	Method	Parylene N	Parylene C	Parylene D
Melting Point (°C)	1	420	290	380
T5 Point (°C) (modulus = (10^5 psi)	1	160	125	125
T4 Point (°C) (modulus = (10^4 psi)	1	>300	240	240

2.3.5 Vacuum and Optical Properties

Vacuum stability of C-type is higher than N-type due to less weight loss under vacuum testing (0.12% loss at 121 F). Parylene only can absorb light in visible region when thickness of sample coating is less than 300nm.

2.4 Applications

There are many uses of parylene in different industries like automotive, aerospace, electronics and medical devices.

2.4.1 Automotive

To prevent the parts from moister, chemical, dust, fumes and corrosion, industry uses parylene coatings due to its barrier properties (chemical and moister). A thin layer coating with superior crevice and 3D penetration gives strong barrier properties. In sensors, parylene coated gold wires are used to enhance performance.

2.4.2 Microelectronics

To prevent the printed circuit boards from moister and harsh environmental conditions, thin and uniform adherent layer coatings of parylene are used. It also gives dielectric protection to circuits due to its fine insulation electrical properties. Coating process of parylene does not affect the properties of substrate due to its vapor deposition method at room temperature.

2.4.3 Bio-Medical Applications

Parylene conformal coatings are using in bone fixation plates, neurosensory and in pace-makers due to its biocompatibility. Parylene is used to protect medical devices from surface damage due to corrosion through bio-fluid, chemicals and moister.

2.4.4 Bladder Volume Sensor

These sensors are used to record the change in volume of bladder of patient. So these real-time sensors which are implanted in bladder require a conformal, bio-compatible coating. This coating should also not be harmful to surrounding tissue. These coated sensors don’t form new blood vessels around implantation [2].

2.4.5 In Bone Fixation

A stainless-steel alloy plate is used to fix the fractured bone. These plates are biocompatible and give strong mechanical sport to bone. But there are some disadvantages of the plates. 1) If these plates remain in body for a long time, they go under corrosion due to saline conditions and elevated temperature. By products of corrosion are produced and caused major diseases like cancer. 2) During implantation of these plates micro motions occur along plate-bone interface which produce wear formation. Cyclic forces on these points act and cause inflammatory reaction. To overcome this problem, polymer (Parylene- organic saline) coated plates are using in biomedical industry now days. Parylene coating gives high mechanical strength, wear resistance during implantation and corrosion protection due to low permeability to water. Industry prefers Parylene-C over N-type due to its higher thermal stability and barrier properties (chemical/moister) [3]

2.5 Boron Nitride

Boron nitride is an important material which is used in diverse applications due to its disruptive properties. It is formed by combination of Nitrogen with Boron which renders ‘BN’. Multiple variants of BN are available in markets which have altogether different properties due their structural disparities. We can cherry-pick from soft to highly hard BN according our need and applications. Beside that it has best possible properties in context of nanotechnology. It challenges the usage of carbon nanotube due to its compatibility in some applications. In context of mechanical properties, it has seized the lion share of reinforcements in those composites wherein we use nanotubes to beef up the properties of subjected materials. We can thus conclude that BN is an important material, and has great potential to revolutionize applications.

2.6 Pulsed laser deposition (PLD)

In analytical chemistry and solid-state physics, PLD is a useful process of deposition of solid material occurs through photons of laser. A high-power beam of laser of short pulsed is targeted upon the surface of material which sublimates it into vapor phase particles. Because of this exposure, vapors of material formed which deposits on the substrate like glass or silica and make thin films of matter.

The thickness of film deposition on substrate in Pulsed laser deposition (PLD) depends on two factors one is the pulse duration and second is the wavelength of laser which is targeted on the material [4]. Consequently, sublimation occurs which depends on capability of target that how much it absorbs photons of laser. Below is the principle of Pulsed laser deposition PLD:

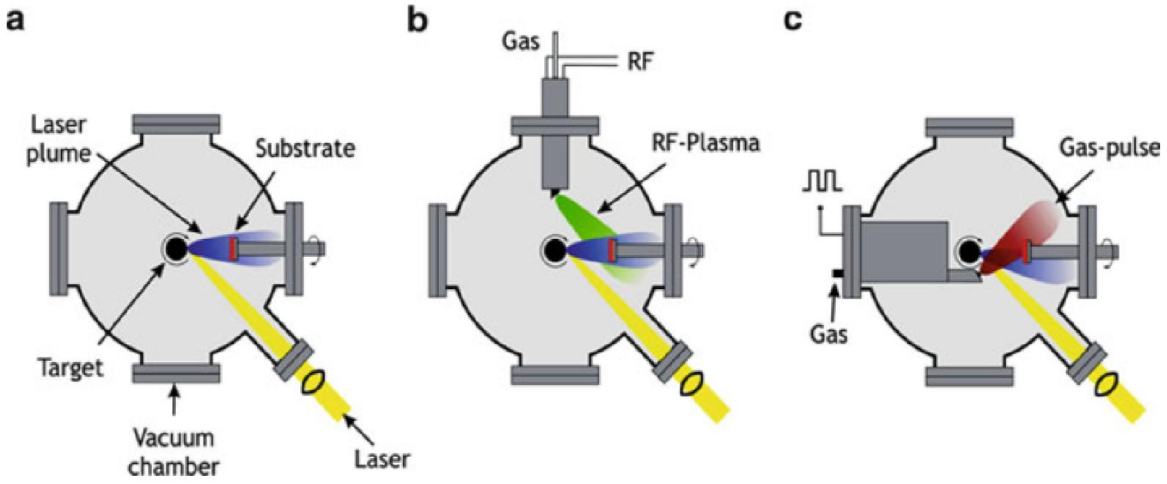
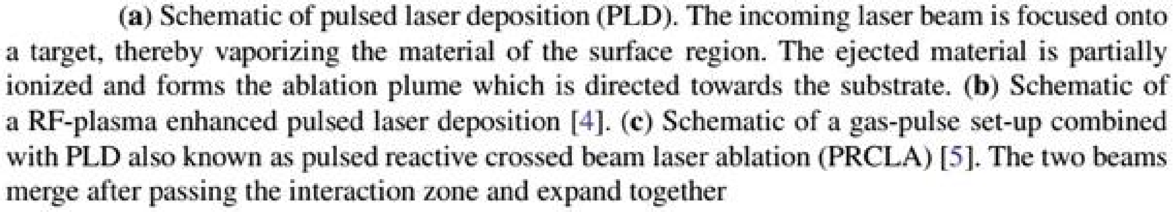


Figure 3 Pulsed Laser Deposition [5]



(a) Schematic of pulsed laser deposition (PLD). The incoming laser beam is focused onto a target, thereby vaporizing the material of the surface region. The ejected material is partially ionized and forms the ablation plume which is directed towards the substrate. **(b)** Schematic of a RF-plasma enhanced pulsed laser deposition [4]. **(c)** Schematic of a gas-pulse set-up combined with PLD also known as pulsed reactive crossed beam laser ablation (PRCLA) [5]. The two beams merge after passing the interaction zone and expand together

A vacuum chamber must be necessary for the removal of material when a pulse of laser is absorbed onto the target surface. There is a certain limitation of power density which must be crossed for the significant removal of matter in the form of plume which is ionized material. For the formation of plume, the minimum power density needed depends on laser wavelength, duration of pulse and the capability of material laser absorption. Conventionally, the length of laser pulse is 10ns whereas for femtosecond laser length is 500fs. The plasma plume is moving from target material towards the glass or silica substrate where it is deposited as film. The factors which determines the films thickness or its growth are vacuum pressure, target material, background gas, growth temperature, material flux and repetition rate. Background gas reactivity can be increased by using either gas pulse configuration [5] or a RF plasma source [6].

2.7 Advantages

PLD has following advantages for thin film growth:

- The flexibility in power density and in wavelength permits to deposit any materials.
- A vacuum system is necessary for the pure deposition of target material otherwise gas impurities also deposit along with the target material and it is not part of the laser in PLD.
- The growth rate of film can be accurately controlled through Pulsed laser beam.
- Most of the materials and their combination films can be obtained by the transfer of material continuously.
- Plume Kinetic energy control the growth properties and film growth modes.

2.8 Disadvantages

PLD also has few disadvantages. Few disadvantages are essential for electromagnetic interaction and for the ablation process between matter and photons:

- Some plume species have large kinetic energy which is the cause of defects in material surface, growing film and sputtering.
- Nonuniform energy profile occurs due to using a laser beam of nonuniform energy distribution which also gives rise inhomogeneous energy gradient present in plume.
- Various expansion velocities are present in low atomic weight elements like lithium or oxygen and inhomogeneous energy plume is present. hence elements have uniform energy distribution and hence to get the desired film composition required we need heavier elements.
- Since for the operation of PLD high power is required, microscopic and macroscopic particles from the matter is released. These particles are dangerous for the film to achieve required properties.

The drawback of last point can be reduced if we use pure crystal or if polycrystalline is used then it must be dense. The other factors are for this drawback are mechanical properties and capability of absorbing laser beam by target material.

2.9 Lasers used for laser ablation

There are two kinds of lasers which can successfully be utilized to serve the purpose of ablation. The two types are predominantly being used in this regard. The first one is Nd: YAG and the second one is Excimer; both are equally important but Nd: YAG has some leverage over Excimer. Nd: YAG is economical, divergence is minimal, could easily be installed in small ablation setups; Moreover, the maintenance is low. Although Excimer has better beam profile but some limitations make it a less preferable choice. In Excimer the halogen gas is used instead of crystal; therefore, the setup is bulky and requires high care.

The actual reason for beam profile is that: YAG beam profile is not identical to Gaussian shape; but, Excimer has flat energy distribution. That’s why the Excimer beam profile is homogenous and better.

The wavelength of laser beam is very important parameter in the whole process. Mostly, the degree of ablation is inversely proportional to wavelength. The wavelength of Nd: YAG is about 1064nm which lies in infrared region. Double, triple, quadrant and quintupling frequency of the Nd: YAG lasers can be obtained. In Excimer laser, wavelength of laser is dependent on the gas being used.

Shorter wavelength is better for perfect ionization and vaporization of target material. The energy of photon of laser wavelength at 266, 213, and 157nm is 4.66, 5.83 and 7.90 eV respectively. Absorption capacity of target material is also an important factor which decides about the frequency of laser. Furthermore, pulse length (ns or fs) and wavelength jointly affect the plasma. In case of ‘fs’, there will be no interaction between plasma and laser due to short pulse time.

2.10 Ablation Process and plume formation

Photons when hit the target material, it delivered its energy to the material lattice via electronic phenomena. Generally, photons enter the material to a depth of many nm in material where it directly conveyed its energy to the electronic system of material. Electronic relaxation process is very fast with a time range of 10^-4 to 10^-3 s. In metals, the transfer of energy of photons to the material lattice is nearly 1.5ps and depends strongly on the specific heat, thermal conductivity and phonon electron coupling [9]. In case of nonmetallic materials electronic relaxation time varies largely from metals lies in the range of 10^-12 to 10^-13 s. In nonmetallic materials the process of absorption held for a smaller time span relative to the process of thermal diffusion in which vapors are formed and formation of plasma occurs during the time when the pulse of laser is used. The process of vaporization can be explained through the theory of heat flow in which the temperature of surface of target material can be measured through thermal diffusivity and light absorption. Hence the laser ablation process for femtosecond and nanosecond ablation are totally different from each other.

High vacuum pressure is needed in pulsed laser deposition for the formation of purified thin film growth. Conventional thermal evaporation mechanism or sputtering process are unlike from PLD. Two points are present in PLD process which makes it suitable for thin film deposition:

1. Larger vapor fluxes of pulses i.e. ~1ms are distinguished through time scale of no vapor flux ~100ms.
2. Comparatively high energies vapor fluxes arrive at the deposition point. Few ions have energy in kiloelectron volt while neutral atoms have various energies in electron volt range.

In the presence of Background gas in pulsed laser deposition mechanism 2 points are observed during the deposition process:

1. Vapor flux has reduced kinetic energy.
2. Presence of background gas of high flux like oxygen gas hitting the target during deposition process.

The presence of large flux background could alter the film growth rate and may alter the energies of surface of target and increases the amount of oxygen in thin films. If background gas is changed like NH3 is used then it provides reactive nitrogen, and hence the composition of newly films forms can be considerably changed [9].

Chapter 03

EXPERIMENTAL METHODOLOGY

In this project, as we have mentioned above, we use pulsed laser deposition for synthesis of Parylene films over the substrate. The whole synthesis can be bifurcated into two parts. These are given below.

- Synthesis of Parylene thin films
- Synthesis of Parylene based composites

3.1 Synthesis of Parylene thin films

In synthesis of Parylene thin films, we used powder of Parylene as a precursor. The Parylene powder was targeted by a beam of laser for sublimation, and then deposited the vaporized material over the substrate. In this process, we must keep in mind that by using laser bean we can only sublimate the targeted materials, the assurance of dimer breakage is not there. To assure to breakage of dimer, which inevitable for polymerization, the substrate must be heated to 750 degrees before targeting with sublimated material.

3.2 Schematic Diagram of PLD

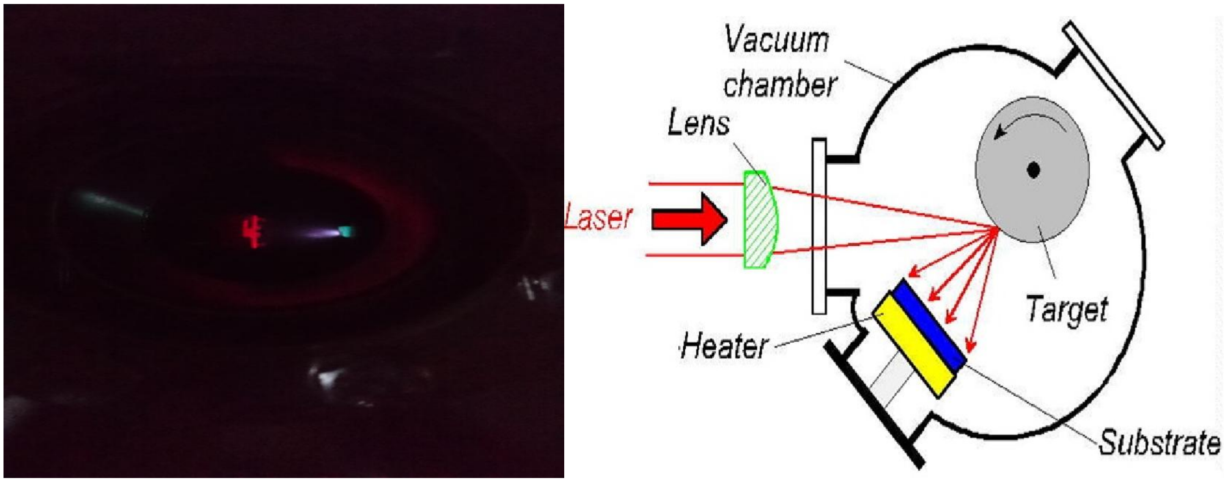


Figure 4 PLD Schematic Diagram

The laser source ejects the laser beam straight in direction of target, which is Parylene powder in our case, to sublimate the material up and resultantly formation of plume takes place. The vaporized material in form of plume travels towards substrate and deposits on it.

3.3 Actual apparatus of PLD

This apparatus is available at University of Sargodha.

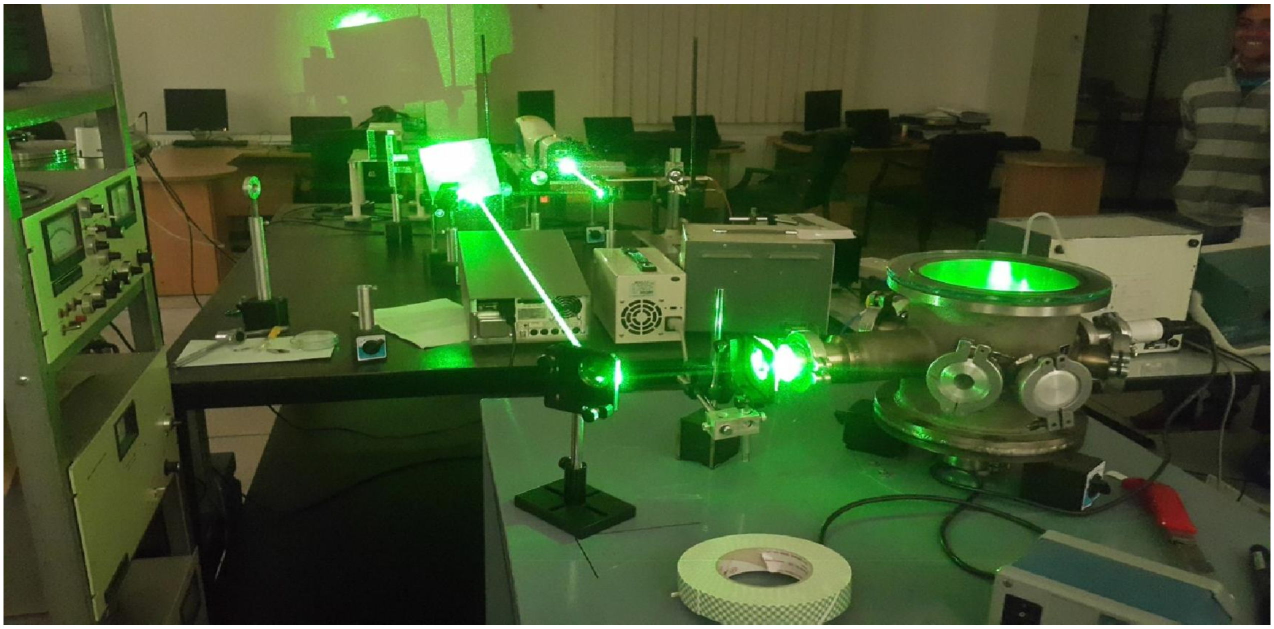


Figure 5 Actual Apparatus of PLD

3.4 Principle behind process

When laser beam hits the target, it sublimates it and the formation of plume occurs. This target moves directly into plasma state without passing through liquid state because the energy of laser is so much high that super heating occurs and atoms can't maintain their positions and move into random state in the form of plasma plume. Plasma plume contains ions, electrons, atoms, molecules in vapor state which move in the forward direction towards substrate followed by straight path and finally it deposits on substrate and where it condensed to solid state. This process takes place in nanoseconds. The reason of the movement of plasma is the columbic repulsion between ions. High pressure vacuum is applied in this process so that no impurity gets deposited on substrate along with target. In PLD we don't use inert gas like argon because may be due to high energy laser used it ionize argon gas and it also deposits on quartz substrate.

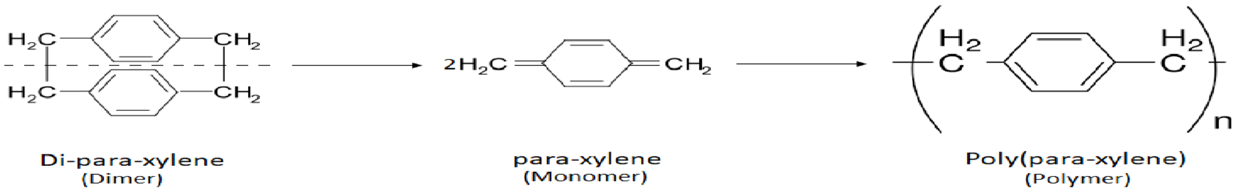


Figure 6 Pyrolysis Reaction

3.5 Synthesis of Parylene based composites

After characterization of thin films produced by PLD, we found that this technique can be successfully used to synthesize Parylene thin films. After that confirmation we proceeded towards formation of Composite of Parylene and Boron nitride. Again we can divide synthesis of composites into two parts. At first place, we prepared pellets comprising Parylene and Boron nitride. After preparation of pellets, we subjected them to same process of PLD which was followed in synthesis of Parylene thin films at first place.

3.6 Pellets formation

We make the pellets of Parylene through hydraulic press. Firstly, we analyze the size and weight which we needed for pellets so that it can be fixed in PLD. So, we took mixture of Parylene and Boron nitride at different proportions then used hydraulic press for making of pellets. Since the maximum pressure limit of hydraulic press is 15 ton but we used 10 ton and after applying 10 ton we wait 10 seconds so that pellets become completely compacted and the chances of breakdown of pellets is minimum.

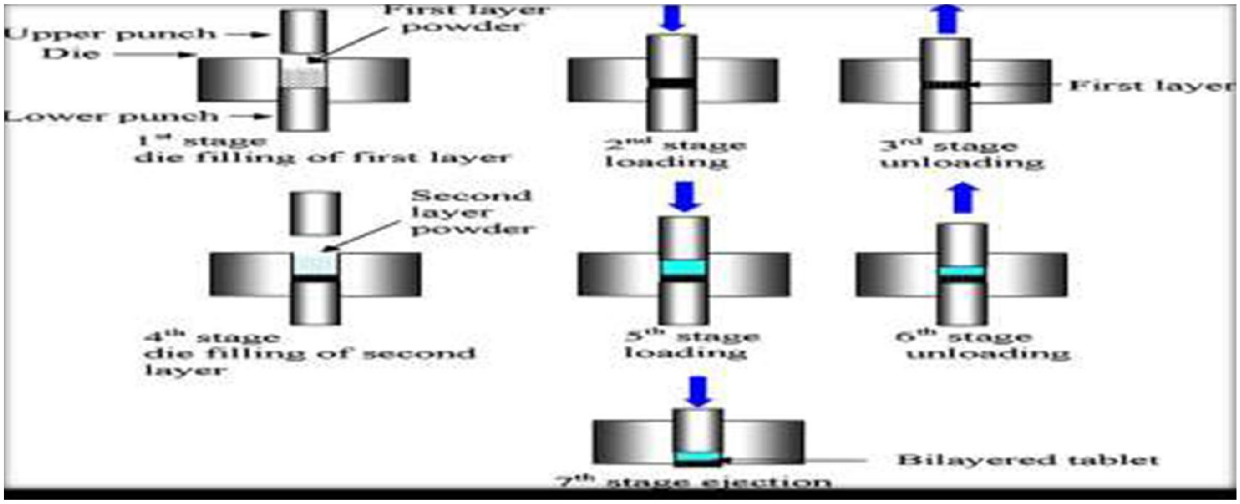


Figure 7 Schematic diagram of Hydraulic Press

By using hydraulic process, we prepared two pellets with different mixing proportions of Parylene and Boron nitride. In first pellet the mixing ratio of Parylene and boron nitride was 19: 1, and in second pellet the ratio was 18: 2.

Composition of Pellets: Total weight = 1 gram

Table 5 Composition of Pellets

SR #	Type	Parylene %	Boron Nitride %	Weightage (grams) P + BN
1	Pure	100	0	(1g + 0g)
2	Mixed (5%)	95	5	(.95g + .05g)
3	Mixed (10%)	90	10	(.90g + .1g)

3.7 Synthesis of thin films of Parylene based composites

The process in case of composite thin films is identical to the process which was used in Synthesis of Parylene thin films earlier. Two pellets which were prepared by using hydraulic press used as a target in PLD. Since the Parylene was in the form of dimer which is its commercial form. So, our aim was to break down the dimer into monomer and multiple monomers when combine then polymerization occurs. To ensure the occurrence of dimer breakage and Polymerization, following parameters were used:

Parameters	**Parylene**	**Parylene with 5% Boron nitride**	**Parylene with 10% Boron nitride**
Base pressure	3.6x 10^{-6}*mbar*	3.6x 10^{-6}*mbar*	4x 10^{-6} *mbar*
Substrate Temperature	750 °C	750 °C	750 °C
Laser Energy	10 MJ	10 MJ	10 MJ
Quartz lens Focal length	50cm	50cm	50cm
Distance between target and substrate	4cm	4cm	4cm
Temperature after Deposition	800°C	800°C	800°C
Wavelength of laser	355nm	355nm	355nm

Table 6 Parylene Parameters

Chapter 04

RESULTS AND DISCUSSION

4.1 Fourier Transform Infrared Spectroscopy-FTIR

The FTIR is characterization technique which is used to identify the functional groups in polymeric materials. The spectrograph renders information about energy absorbed by each functional group. By this information, we can pinpoint the point correctly.

4.1.1 Schematic Diagram

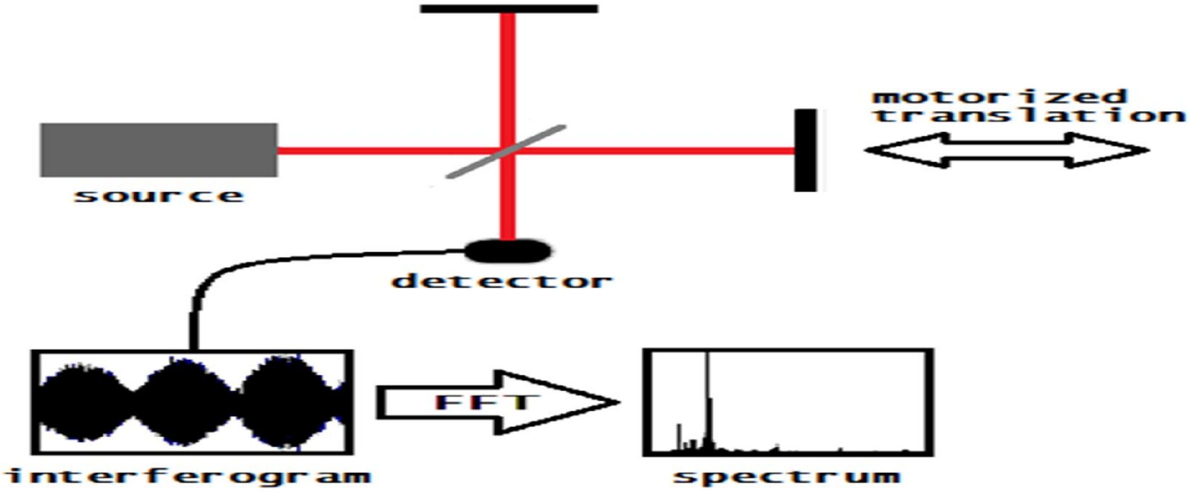


Figure 8 FTIR Schematic Diagram

4.1.2 Discussion and comparison about FTIR of Parylene

After coating the Parylene on surface of substrate, it is indispensable to do confirmation testing to authenticate the coated materials whether it is required one or not. It also helps in identification of contamination and phase transformations. FTIR is an important technique to get information about coated material. The result in the form of spectrograph compared with standard spectrograph to deduce conclusion about subjected material.

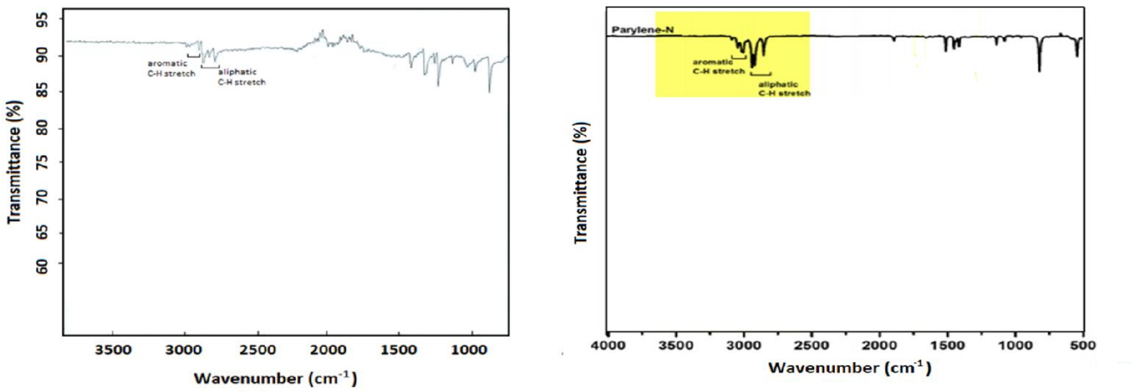
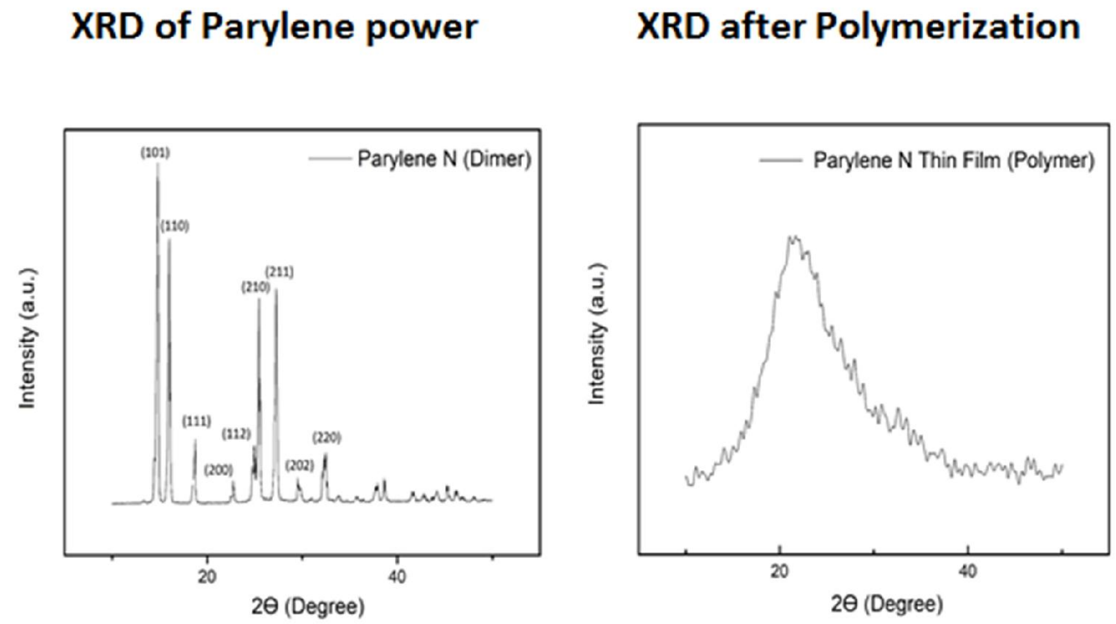


Figure 9 Comparison b/w Sample vs Reference FTIR

Maxima peaks in the graph are actual clues to make conclusion about sample. The sample coating is of Parylene-N.

4.2 X-Ray Diffraction Technique

X-Ray Diffraction is a non-destructive technique which was used to know the crystal structure of our sample. As material properties are linked to the atomic arrangement in crystals hence to study the crystallographic structure and parameter of lattice XRD is used. Crystalline structure compromise of planes of atoms which reflect the X rays at an angle, this technique is used to detect the structure of material. When in cathode ray tube X rays are generated by copper are filtered and incident on the film, their interaction generates constructive and destructive interference which when detected through detector if satisfies Braggs law are processed and analyzed.


XRD of Parylene power

XRD after Polymerization

Figure 10 Comparison b/w Parylene Powder XRD vs Thin film XRD

4.2.1 Parylene Powder XRD

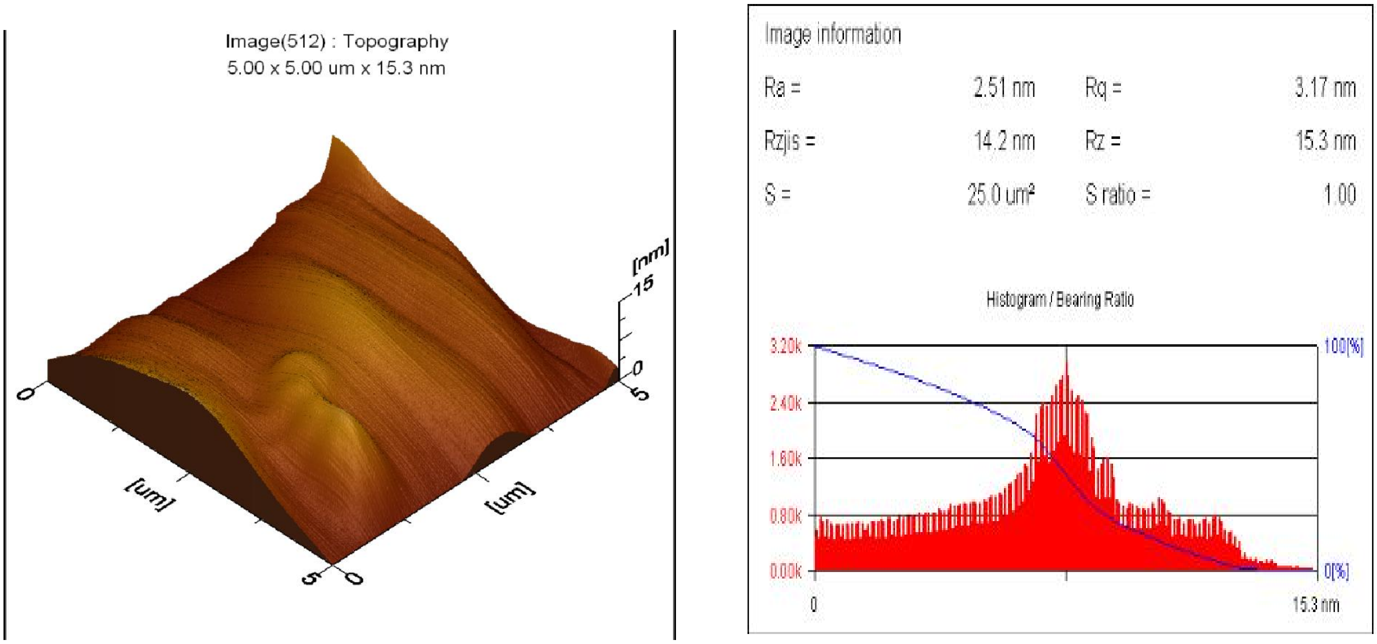
The XRD of parylene N dimer was carried out using Cu Ka Radiations. Characteristics peaks were observed at 2Θ = [15, 17, 19, 23,25,27,30 and 32.5] indicated that powder is crystalline in nature. The planes corresponded to the aforesaid peaks are (101), (110), (111), (200), (112), (210), (211) and (220) respectively were confirmed from literature.

4.2.2 Parylene Thin Film XRD

The XRD of parylene (polymer) deposited film was carried out under the same conditions as above. A broad peak is observed at 20˚ indicated that deposited parylene film is semi crystalline in nature. The nature of peak shows that parylene deposited in form of polymer not in form of a dimer**.**

4.3 AFM of Pure Parylene thin film

AFM is used to check the topography of the thin film and by comparing the thin films we found that its Ra and Rq both are higher than CVD produced thin films which shows that thin films of parylene which are produced through PLD is much better than CVD technique.

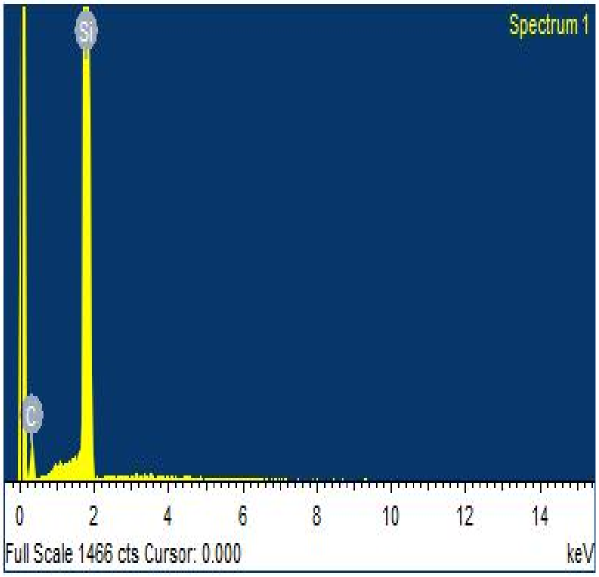


Ra =	2.51 nm	Rq =	3.17 nm
Rzjis =	14.2 nm	Rz =	15.3 nm
S =	25.0 um²	S ratio =	1.00

Figure 11 AFM of Pure Parylene & Image Information

4.4 EDX of Pure Parylene thin film

EDX stands for energy dispersive x-ray spectroscopy which measures the composition and their weight percent of elements present in the material. The purpose of our doing EDX is to check the composition of thin films whether the respective elements are deposited on substrate or not so by doing it we found that parylene has been deposited on it. C element showing the parylene while Si element showing quartz substrate and in this way our first objective has been achieved.



Element	Weight%	Atomic%
C K	29.89	49.92
Si K	70.11	50.08
Totals	100.00	

Figure 12 EDX of Pure parylene & its table

4.5 Characterization of Parylene based composite thin film

4.6 AFM of Parylene based composite thin film

AFM is used to check the topography of the thin film and by comparing the thin films with CVD technique synthesize films we found that its Ra and Rq both are higher than CVD which shows that thin films of parylene based composite which are produced through PLD is much better than CVD technique.

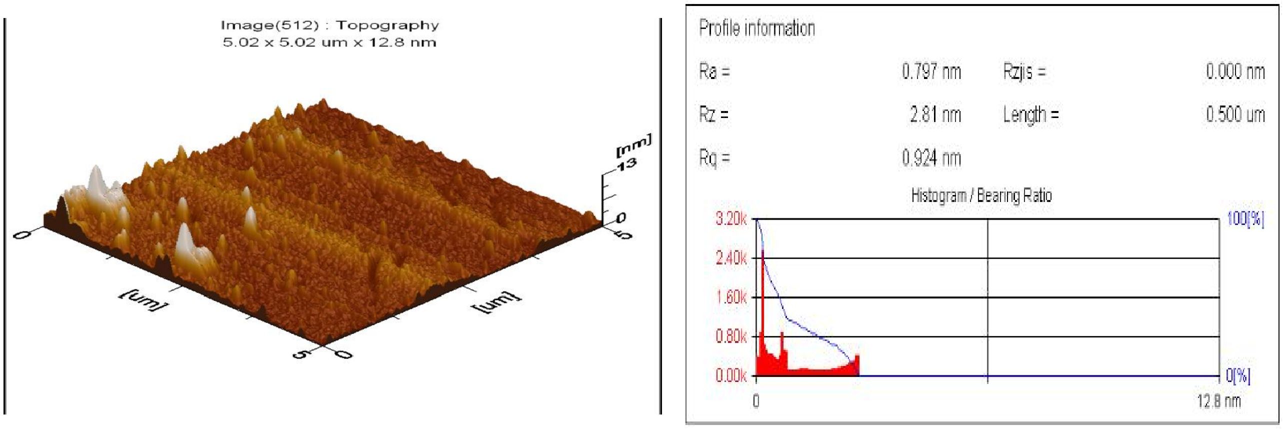
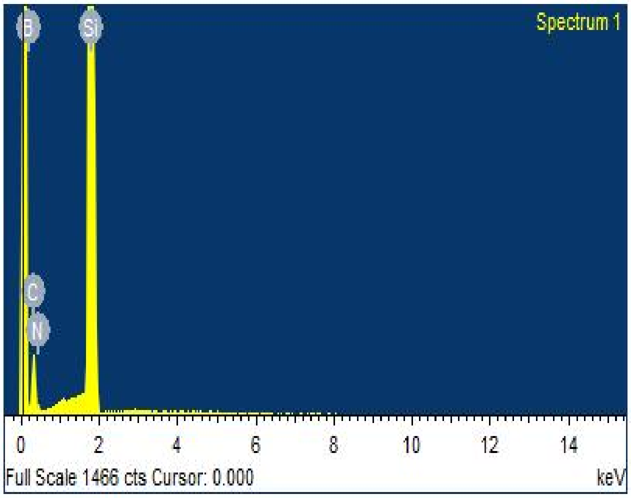


Figure 13 AFM of Parylene composite & its Profile Information

4.7 EDX of Parylene based composite thin film

EDX stands for energy dispersive x-ray spectroscopy which measures the composition and their weight percent of elements present in thin film. The purpose of our doing EDX is to check the composition of Parylene based composite thin film whether the respective elements are deposited on substrate or not so by doing it we found that C element showing the parylene, B & N showing boron nitride while Si element showing quartz substrate and in this way our second objective has also been achieved.



Element	Weight%	Atomic%
B K	21.17	29.54
C K	34.64	43.51
N K	5.98	6.44
Si K	38.21	20.52

Figure 14 EDX of Parylene Composite & its table

Conclusion and Future Recommendations

The Parylene is being widely used for conformal coatings of medical, aerospace, electronics and robotics components. There are wide varieties of attributes which makes it a compelling choice over other materials. The temperature resistance, hydrophobic properties, absence of porosity above to limit of 0.2 µm, chemical resistance and bio-compatibility are notable properties in this regard. In this project we used Pulsed laser depositions for synthesis of Parylene rather than Chemical vapor deposition, which is yet the most prominent industrial technique. The expansion of this would be cost effective, less hazardous and more convenient as compared to conventional use of CVD.

The first phase this project has been completed. The characterizations vindicated that by using PLD we can get identical results to CVD. However, the job is not yet completed. The biological characterization is inescapable to ensure that film formed by PLD is as bio-compatible as the film formed by CVD. The biological characterization is future proceeding of this project.

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[22] “Figure 1. Parylene N,C & D Chemical Structures (right) .”