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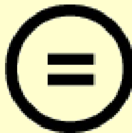
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A THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Growth of nanostructured thin films for enhancing surface and barrier properties using Roll-to-Roll chemical and atomic layer deposition techniques

Srikanth Jagadeesan

Department of Advanced Convergence Technology and Science

GRADUATE SCHOOL

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Growth of nanostructured thin films for enhancing surface and barrier properties using Roll-to-Roll chemical and atomic layer deposition techniques

Srikanth Jagadeesan

(Supervised by Professor Kyung Hyun Choi)

A thesis submitted in partial fulfillment of the requirement for the degree of Doctor of Philosophy

2018.02

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Srikanth Jagadeesan

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// ABSTRACT

In recent days flexible devices have begun to be regularly used in our daily lives for communications, renewable energy resources, and information technology. Conventional glass substrates can provide excellent protection from permeation species, but the glass substrate is rigid due to which it cannot be used for the application of flexible electronics. On the other hand, electronic devices made on flexible plastic substrates such as, organic thin film transistors (OTFTs), solar cells , and organic light emitting diodes (OLEDs) enable low cost, flexible, mass production and weight reduction in these devices. However, flexible polymer substrates can be easily damaged by the atmospheric gas molecules oxygen (O_2) and water (H_2O) and therefore these substrates must be protected with some additional encapsulating nanolayer. Several deposition techniques have been reported for the successful development of encapsulating thin films in order to protect electronic devices. These fabrication techniques include sputtering, thermal evaporation with good surface and barrier properties. However, these methods are only suitable for vacuum coating and rigid device coatings and cannot meet the requirements of atmospheric condition fabrication. Hence the researcher moved to the under atmospheric condition high quality thin film fabrication for flexible electronics applications.Among the variety of thin film process atmospheric roll to roll chemical and atomic layer deposition process have highly contributed thin film industry for mass production.

This thesis report to the inoroganic TiO_2 and Al_2O_3 thin film deposited on a flexible PET substrate by using atmospheric roll-to-roll chemical and atomic layer deposition. The R2R-ACVD deposited (100° C) TiO_2 thin film expressed excellent surface,chemical,optical and electrical properties. The optical transmittance of the film displayed more than 91% in the visible region. The R2R-AALD

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developed single layer Al_2O_3 thin film also exhibited excellent surface,chemical and better barrier properties.

Finally, a multilayer barrier thin film based on polyvinylidene difluoride (PVDF) – silicon dioxide (SiO_2) has been fabricated on the PET substrate through a novel method of joint fabrication techniques. The Inorganic SiO_2 thin film was deposited using a roll to roll atmospheric atomic layerdeposition system (R2R-AALD) while the organic PVDF layer was deposited on the surface of SiO_2 through Electro hydrodynamic atomization (EHDA) techniques. The multilayer barrier thin films exhibited very good surface morphology, chemical composition and optical properties. The total thickness of the multilayer barrier thin film was 520 nm with a high optical transmittance value (85-90%). The obtained value of water vapor transmission rate (WVTR) of the barrier thin film was $\sim 0.9 \times 10^{-2}$ g m^{-2} day^{-1}. This combination of dual fabrication techniques R2R-AALD and EHDA for the development of multilayer barrier thin films are promising for gas barrier application.

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CHAPTER 1

1. Introduction

1.1. Background of barrier coating:

In recent years flexible electronic highly occupied in our daily life in information technology, communications, renewable energy resources. Conventional glass substrate provides supreme, quality of protection from environmental species, but the glass substrates are rigid and brittle nature, therefore which cannot be used in an application of flexible electronics. But many of the research focus to fabricate the electronic device on plastic substrates such as organic solar cell, organic light emitting diode, Flexible liquid crystal display showed in Figure.1.1.The main reason for such organic device arises due to their multifunctional characteristics, tunable properties and high potential use in flexible electronics.[1-5] However, the major disadvantage of this flexible electronics can easily oxidized and damage electrodes by water vapor or oxygen from the ambient environment. Thus the lifespan of organic electronics is the major concern to produce who need to ensure at any rate up to around 20000 hours of continuous use.Upcoming years expected to increase by 50-100 % due to its potential benefits in the market.To counter these issues nanoscale barrier coatings on polymer substrate is the widely accepted solutions.

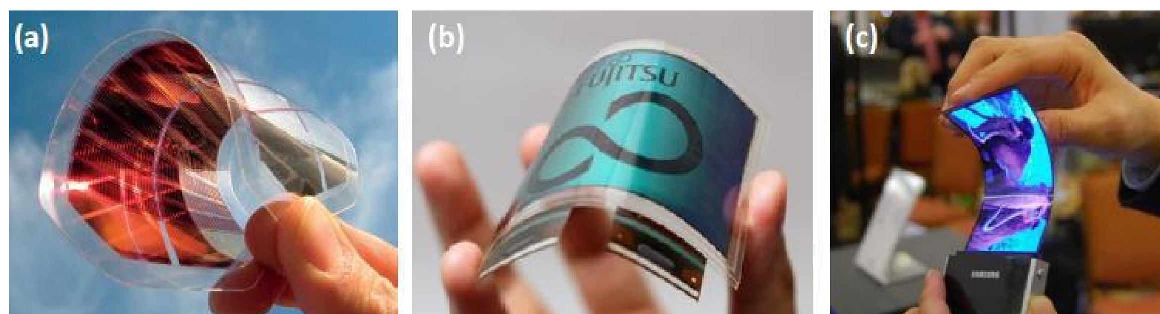

Figure.1.1 Example of flexible electronics devices: (a) Flexible organic solar cell (b) Flexible LCD (c) Samsungs's OLED.[6]

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1.1.1 Permeation mechanism

Various investigations have been devoted to understanding the moisture and gas penetration mechanism.Basically, permeation through the material is an intricate phenomenon with distinction in chemical potential as the main thrust.The Penetration process basically followed few steps.The primary stage is adsorption of the permeant molecule on the surface followed by its diffusion the material layer and ensuing desorption out to the environment.Intramaterial diffusion is clearly a restricting advance and administered by Fick's law which for thin boundaries is:

$$F = -D\ \Delta c/x \qquad (1)$$

where F is the molecular flux; Δc – concentration difference across the barrier; x – barrier thickness; D – diffusion coefficient.

In turn, D is a function of temperature and described by the Arrhenius equation:

$$DD = D_0 \exp\left(-Edd/RT\right) \qquad (2)$$

where D is the diffusion coefficient at temperature T; D_0 is the maximum diffusion coefficient; Ed – the activation energy; R – the gas constant.

Another factor that adds to permeation is the level of porosity. It can be caused either by a non uniform deposition or airborne contaminants.It has been demonstrated that there is a connection amongst's density and size of pinholes with the size of the atmospheric tidy particles. Purposeful contamination was utilized to confirm this theory by Wang et al.[7,8] Particles with known distance across were spread on the protective layer of the electronic device to make artificial dark spots. The dark spots was monitored with respect to time and particle diameter which driven the conclusion that development of dark spots is because of atmospheric molecules. Various studies used to

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investigate the rate of permeation mechanism.[9-11] Tropsha et al. discovered that actuation energies of four distinctive polymer substrates deposited with SiO_2 by PECVD are indistinguishable recommending the chemical interaction between Water molecules and the SiO_2 structure.[9]

1.1.2.Current Barrier Layer Development

Thin film coatings were first industrially applied as permeation barrier layers on polymeric substrates for packaging in the mid-1970s.Thin metallic film (commonly aluminum) were coated onto wide width polymeric substrates, utilizing rapid vacuum metallizers.Today,aluminized polyester and polypropylene polymer films are broadly utilized as a gas barrier in an assortment of packaging applications.The flexible polymers, with 2.5-meter web widths (i.e., the width of the polymeric roll), are routinely covered at speeds up to 1000 m/min for these reasons.Roughly 22,000 million square meters of vacuum deposited barrier layers are being sold into the packaging industry yearly.[12] Metals were the first material to enter the field of barrier coating with the polymer substrate.Some metals used for barrier films were Al, Ag, Mg, and Cu.However, these metals basically have potential drawbacks such as brittle, nor microwaveable and non-transparency.For all barrier layers, the desirable properties include being highly dense, amorphous with no columnar structure, free from defects and, if used for OPV/OLED applications, optically transparent.For the latter requirement, metal oxides and nitrides are typically used. A considerable amount of research has been conducted on a range of different materials and the most common include;Al_2O_3[13,14] SiO_2[15],TiO_2[16],HfO_2.[17] The barrier performance depends not only upon the barrier material, but also the deposition mechanism used.The demand for this requirements barrier coatings research moved towards the essential metals oxides were SiO_2, TiO_2, Al_2O_3. Physical vapor deposition is the first method used to coat polymer substrate. PVD deposited metal oxide coatings only satisfying food and pharmaceutical packaging.[18] However, the PVD technique cannot meet the requirements

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of electronics applications. Magnetron sputtering techniques also able to produce a very denser film by using higher energy to compared PVD techniques.Finally, researchers found chemical interaction based deposition techniques can able to produce high quality of barrier thin film in electronic applications. A high quality of barrier film barrier film through CVD/ALD has the following qualities.

- Low pinhole defects,
- Corrosion resistance,
- Erosion resistance.
- Good adhesion to the substrate,
- Optical transparency for displays,
- Low-temperature process for polymeric substrates,
- Low hydrogen content,
- High material density,
- Featureless structure,

Conventional vaccum based ALD/CVD system has slow processing also it is incompatible in mass production. But current trend R2R procesing chemical and atomic layer deposition which is capable of rapid fabrication of thin films on flexible substrates ensuring mass production.

1.2. Thin film techniques for barrier coatings

There is various innovation techniques available for making of thin films.These technologies can be divided into two main categories i.e.,chemical and physical techniques.The most exceptional techniques for mixture class are sol-gel, plating, compound vapor declaration (CVD), and atomic layer articulation (ALD).These techniques have been requested and presented in Figure.1.2.

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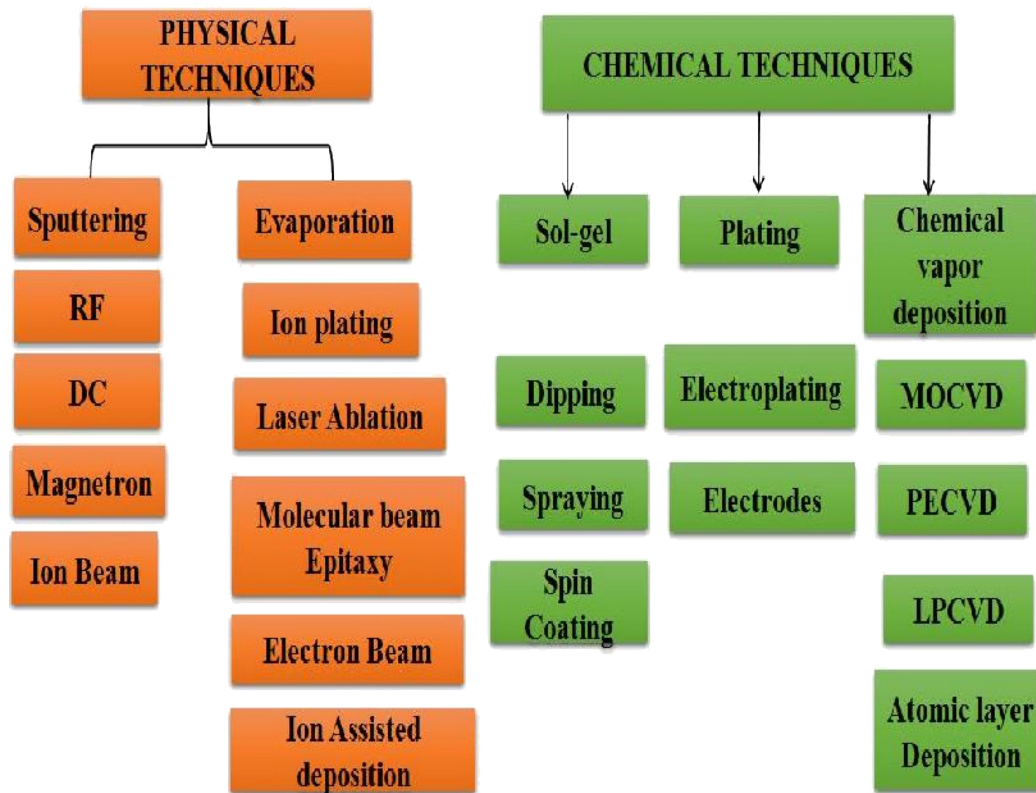

Figure 1.2 Thin film deposition techniques.

1.2.1 Plating

Plating is a method of thin film deposition in which the surface of an object which is metals covered with a thin layer of another metal such as platinum, gold, and silver, etc.It is one of the most prehistoric thin film deposition technique, and in old ages, it has been used to deposit gold and other metals on various structures such as statues.This technique is still widely used for applications like corrosion protection, surface hardening, improve wearability, friction reduction, conductivity adjustment and radiation shielding etc.The technique has been classified into two main methods, i.e.,electroplating and electroless plating.In electroplating, a non-ionic coating is fabricated on a substrate by supplying electrons to an ionic metal.Generally, the equipment consists of a chemical solution with an ionic form of the metal, an anode which is made of metal

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that is being plated and a cathode where a film is being deposited.The electroless plating does not need external electrical power and takes place as a result of several simultaneous reactions in an aqueous solution.The reaction is executed when the reducing agent releases hydrogen and get oxidized, thus resulting in a negative charge on the surface of the part.

1.2.2 Sol-gel

Sol is defined as a stable dispersion of colloidal solid particles or polymers in a liquid where the particles are only suspended by Brownian motions.Whereas gel is stated which is formed when the solid and liquid are dispersed together and results in a porous, three continuous solid network which surrounds a continuous liquid phase.The sol-gel coating process takes place in following steps.

- Dispersion of colloidal particles in a liquid to fabricate a sol.
- Implementation of sol solution on different substrates through techniques such as spraying to fabricate the desired coatings.
- Polymerization of colloidal particles to get a continuous network state of gel by removal of stabilizing components.
- Development of coatings (amorphous/crystalline) by pyrolyzing the organic or inorganic components through heat treatment.

Some advantages of the sol-gel technique are; excellent adhesion, good corrosion protection, high purity products, low-temperature processing, and low cost of fabrication.The main sol-gel methods include dipping, spraying, and spin coating, etc.

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1.2.3 Chemical Vapor Deposition

Chemical Vapor Deposition (CVD) is one of the most efficient and widely used method of materials processing.It is mostly used for thin film fabrication on a wide variety of substrates. The technique can also be implemented to develop bulk materials, composites, and different kinds of powders.The process typically involves a continuous supply of one or more precursors, i.e., chemical reactants to a substrate which is kept at a particular temperature and a thin film are deposited over the surface of the substrate as a result of chemical reactions.During this process, chemical by-products are also produced that are continuously removed out of the reactor along with unreacted precursors. It is an extremely flexible and diverse thin film deposition process.It can be used for deposition of films on a wide variety of substrates including glass, silicon wafers, flexible substrates and bulk objects.Similarly, it can be operated under a wide window of processing temperatures ranging from as low as 50° C to 1500° C.It is because of the supreme capability and efficiency of CVD technology that it has been continuously improved and evolved into a new trend.Some of the most notable trends are metal-organic chemical vapor deposition (MOCVD), plasma enhanced chemical vapor deposition, and low-pressure chemical vapor deposition (LPCVD).It is because of such advanced trends of CVD that its application circle has been greatly extended to new industries. The new trend of R2R-CVD has became a vital technique of electronic industry because its ability to fabricate mass production of the films at atmospheric condition.

1.2.4. Atomic Layer Deposition

Atomic layer deposition (ALD) is a subscale of chemical vapor deposition (CVD) capable of producing supreme quality thin films having low porosity, high density and excellent conformity on various kinds of substrates. The deposition of the films through ALD method take place via

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alternating, self-limiting surface reactions.This self-limiting reactions mechanism results in a saturated growth rate which means that the process reactions proceed to completion, and then stop. In this way, a precise amount of materials is deposited over the surface of the substrate regardless of the exposure to precursors once the saturation threshold is exceeded.

The mechanism of self- limiting growth provide ALD with unique advantages such as:

- Excellent conformity
- Good capability to produce sharp interfaces
- Precise thickness control
- High aspect ratio
- Processing of complex shapes and structures

ALD process involves a reaction sequence in which two independent surface reactions are separated in time.A substrate is placed in a chamber and is exposed to reactants and purge gases with the following sequence:

- Reactant A is pulsed into the reactor and reacts with the substrate
- Products and unreacted reactant A are purged away
- Reactant B is pulsed into the reactor and reacts with the surface
- Products and unreacted reactant B are purged away.

The new trend of ALD technique has been developed and introduced which encompasses the concept of atmospheric spatial ALD, and roll -to- roll processing.The result is an advanced, and efficient roll-to-roll atmospheric atomic layer deposition (R2R-AALD) system which is capable of rapid fabrication of thin films on flexible substrates ensuring mass production.[19]

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1.3. Spatial Atomic Layer Deposition

Despite the fact that the conventional vacuum based ALD approach is very efficient in producing supreme quality films, there are limitations associated with it.The most notable of all is the time required to complete one ALD cycle.Scientific studies have reported that the cycle time may be as long as many minutes and result in deposition of films with a thickness of approximately one angstrom, which greatly reduces the efficiency of ALD technology.[19] Apart from that, the conventional ALD is a vacuum-based technology and has rarely been reported to be used for the fabrication of thin films under atmospheric pressure conditions.The size and design of the ALD reactor also affect the processing parameters of the ALD process. A complex and large ALD reactor would require a long purging time to be evacuated efficiently.Also, a very advanced and sophisticated valving system is needed to operate the ALD system in a steady state.This result in the complexity of the ALD system, and also the composition of the precursors is constantly varied in the reactor.Furthermore, the processable size of the stationary substrate in conventional ALD is very small due to which the ALD technology is unable to be used in applications requiring the cost-effective, large area and mass production of thin films.Such factors have become the source of motivation towards a more appropriate approach, i.e., spatial atomic layer deposition (SALD).[20,21] Unlike conventional vacuum based ALD where the precursors are separated in time, in spatial ALD (SALD) processes, the precursors are being separated in space.Figure.1.3 describes the conceptual design of SALD approach showing the continuous flow of precursors, inert gas, and film deposition over the movable substrate.

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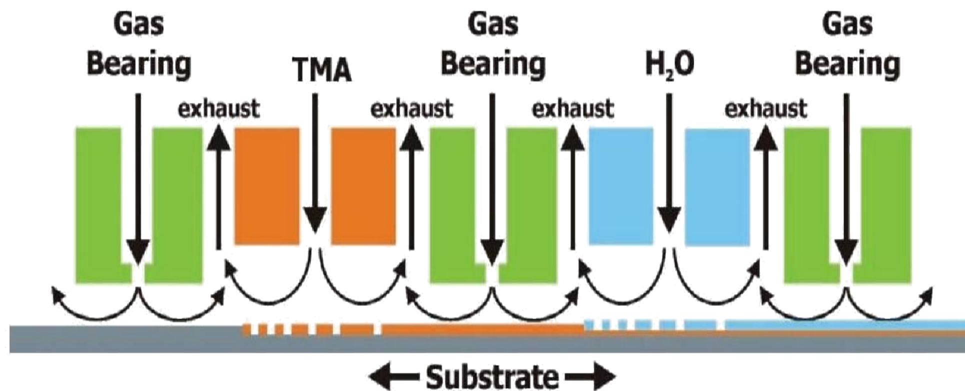

Figure1.3.Schematic of SALD reactor concept showing a continuous flow of precursors, inert gas, and film deposition over the movable substrate.[22]

1.4. Roll-to-Roll chemical &atomic layer Deposition Technique

Mass production of the thin film deposition is one of the key technologies for flexible electronics industries.R2R based ALD & CVD process is expected for continuous and mass production of various thin film fabrication shown in Figure.1.4.Sukang et al. reported roll to roll fabricated 30-inch of graphene films.[23] Recently Takatoshi et al. groups reported roll to roll MWP CVD deposited high-quality graphene thin films.[24] The roll-to-roll atomic layer deposition (R2R-ALD) is a special trend of spatial ALD. In R2R- ALD, the flexible substrate is continuously moving relative to the precursor sources and, therefore, the deposition rate is determined by the speed of the substrate rather than the cycle time of the precursor exposure sequence.[25] Since there is no requirement for pulsing and purging of precursors from a common volume, the growth rates of the deposited films are limited only by the surface kinetics and the reaction rates of each half cycle.Also, there is no need to clean the reactor walls because the precursors never interact with each other and thus avoid any deposition on the reactor walls. Such distinguished characteristics give a great edge and superiority to R2R-

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ALD technology to process various kinds of flexible substrates such as polyethylene naphthalate (PEN), PET, and polyamide,etc.,on a large scale in a very low processing time, and this results in very high production at much lower costs.

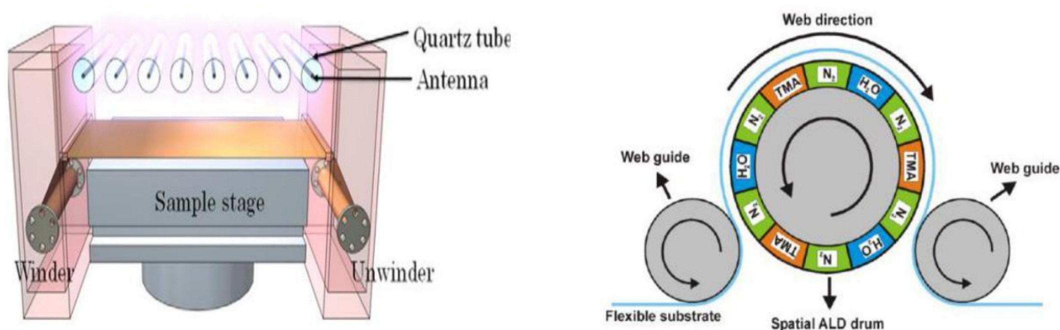

Figure.1.4. The R2R deposition system: (a) R2R-SALD, (b) R2R-CVD.[24,25]

1.5. Inorganic transparent barrier coating on the polymers

The initial commercial transparent coating that appeared on the market was a silicon oxide SiO_X (deposited on polyethylene terephthalate (PET) films.Subsequently, HfO_2, InSnO (ITO) , $ZnSnO_x$, (ZTO) , SiO_xN_y , AlO_XN_Y compounds have been tested for their barrier properties with the polymer substrate.However, most wanted barrier materials in the market until now are aluminum silicon and Titanium oxide compounds due to its multifunctional properties.

1.5.1. Titanium dioxide (TiO_2)

The unique and intriguing properties of nanostructured thin films have prompted tremendous motivation among researchers to explore the possibilities of using them in technological applications.In particular, the optical and electronic properties of nanostructured thin films have

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been of very high interest due to their potential applications in the fabrication of microelectronics and optoelectronic devices.[26]The performance of the thin films for device applications is highly influenced by the crystallite size, morphology, phase and impurity type concentrations.[27] There is always an increasing demand for new technology for the fabrication of nanostructured thin films for functional devices in order to control the phase purity, morphology and the surface properties at the nanoscale which is of great interest to deliver distinctive properties.In this regard, many studies have been recently carried out to produce surfaces and films by tailoring nanostructure.Nanostructured thin films of titanium dioxide (TiO_2) have been regarded as subject of great deal of research due to its exceptional chemical, electrical, optical properties and its potential applications diverse field such as (i) optoelectronic, (ii) photocatalytic (iii) solar cell (iv) photovoltaic, (v) self-cleaning coating (vi) antibacterial activity etc. Generally, TiO_2 nanostructured films exist in two phases viz. a) anatase and b) rutile. Depending on the phase structure of TiO_2, it can be employed for diverging applications.

Some well-known characteristics of TiO_2 are

- it is amphoteric in nature
- it is insoluble in water as well as acids
- it shows high room temperature resistivity, with a specific resistivity of 9500 Ω
- it has a melting point of 1610º C and boiling point of 3000º C
- it shows temperature-dependent paramagnetic susceptibility

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1.5.2.Aluminium oxide (Al_2O_3)

Aluminum oxide is a combination of aluminum and oxygen with chemical formula Al_2O_3.The most generally occurring of several aluminum oxides, and particularly identified as aluminum (III) oxide. It is generally called alumina. The oxides of aluminum materials have pontential applications refractories and abrasives due to their hardness , chemical inertness, high melting point non-volatility and resistance to oxidation and corrosion.[28-31]The significance of alumina as catalyst or catalytic support has likewise been widely applied for some chemical reactions.The trasnparency of alumina film and its variety of properties highly used the field of optics.[32] Al_2O_3 is an electrical insulator having high thermal conductivity.[33] Corundum or α-aluminum oxide is the mostly occurring in crystalline form of aluminum oxide and its hardness make it appropriate for applications as a rough and as a component in cutting devices. conventional depsoition system requires higher enegy to produce Al_2O_3 thinfilm. But development of new cost-effective R2R-CVD &ALD techniques for fabrication of thin film with high purity and large area transparent films has attracted in many researchers.[24,34]

1.5.3. Silicon dioxide (SiO_2)

Silicon dioxide, also called silica (from the Latin silex), is an oxide of silicon with the substance formula SiO_2, most regularly found in nature as quartz and in different living organisms. In many parts of the world, silica is the significant constituent of sand.[35] SiO_2 is the widely utilized dielectric material in the semiconductor industry.The scientists have examined the qualities of SiO_2 materials for different applications, for example, an insulator in capacitors for memory devices metal oxide semiconductor field effect transistors (MOSFETs), and a protection layer , a gas Diffusion barrier , flexible electronics , optoelectronics. SiO_2 has a large band gap (9.0 eV), a

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low spillage present, great security from H_2O, and low polluting influence levels in the film. Consequently, SiO_2 is researched and generally utilized economically to alter numerous applications over an expanded time duration. Transparent barrier coatings, such as silicon oxide (SiO2), on polymers, are receiving much attention in industries for pharmaceutical, food, and beverage packaging applications. Conventional SiO_2 films are made by the thermal oxidation of a silicon substrate under high temperatures. As novel electronic applications, for example, flexible and transparent devices have been rising quickly, deposition techniques have turned into a vital issue to accomplish smooth, conformal, powder free films, and low development temperature. Conventional plasma enhanced chemical-vapor-deposition (PECVD) SiO_2 films still indicate basic problems, for example, a nearly high development temperature, particle generation poor step coverage scope and a moderate growth rate. Accordingly, atomic layer deposition (ALD) has been recently inspired by an appropriate statement strategy for depositing conformal and uniform films under low-temperature deposition conditions.[34,20]

1.6. Scope of the Current Research

The conventional vacuum based CVD/ALD system have been capable to produce good quality thin films, but still they have some serious problems, such as low production, complexity operation and long processing time.Also the conventional CVD/ALD system only sitable for rigid device fabrications due to which it cannot be used for the application of flexible electronics. The current trend of new CVD/ALD technique has been introduced which the concept of atmospheric roll to roll CVD &ALD processing.The outcome is an efficient roll-to-roll atmospheric CVD & ALD system which is capable for rapid fabrication of thin films on flexible substrates ensuring large scale manufacturing.

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Different thin films and various thin film architectures deposited by the R2R-ACVD & ALD process are to be investigate.Thin film materials of interest are Al_2O_3 SiO_2, TiO_2 and organic polymers the purposes for choosing these specific materials which has already been discussed in section 1.5.multilayer structures and other potential nanostructured engineering arrangements will likewise be examined.The benifits of Single and multilayer barrier architectures will be studied .

This work requires the use of the thin film characterisation techniques such as Field Emission Scanning Electron microscopy (SEM), vitality dispersive UV-Visible spectroscopy (UV) 3D surface profiler, Focused Ion Beam (FIB), Thickness measurement system, X-ray Photoelectron Spectroscopy (XPS), Contact angle measurement, Mechanical stability test, barrier permeation test.

CHAPTER 2

2. Experimental procedure

2.1. Materials and method

Tris(tert-pentoxy)silanol (TPS) was purchased from Sigma Aldrich for SiO_2 source, and the Trimethylaluminum (TMA) catalyst precursor was purchased from UP Chemical. Titanium isopropoxide and water were purchased from UP Chemical for TiO_2 source Polyvinylidene difluoride (PVDF) pellets, dimethylformamide (DMF) and ammonia were purchased from Sigma Aldrich.

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2.2. Roll-to-Roll Atmospheric chemical vapor Deposition of TiO_2

The experimental setup of R2R-ACVD for the deposition of TiO_2 thin films is shown in Figure.2.1.The CVD head for delivering the gas is installed over the movable PET substrate.A micro screw gauge used to adjust the head on vertically.The space between the head and the substrate was fixed at 300 μm.The CVD head has all the channels connected to it including precursors, inert gas, and the exhaust. Nitrogen gas (N_2) was used as a carrier gas and protected the wall of the head.Two separate nitrogen cylinders were used to achieve the stable flow rates. The temperature of the precursors, TTIP and water (H_2O), was kept at 50º C, and the temperature was maintained constant.In order to prevent the recondensation of the precursors, the temperature of gas delivery channels was maintained at 100ºC.The TTIP and H2O precursors were injected into the CVD head through N_2 gas at the flow rate of 500 SCCM and800 SCCM, respectively, where the flow rate was controlled using a mass flow controller (MFC).The flow rate of separation nitrogen gas was kept higher (1000 SCCM) to effectively prevent the intermixing of the precursor in the reaction zone.The rotary pump was used for purging the waste gases, and the pressure beneath the CVD head was monitored by a vacuum gauge.The pumping speed of rotary pump was adjusted using the needle valves on the exhaust line.

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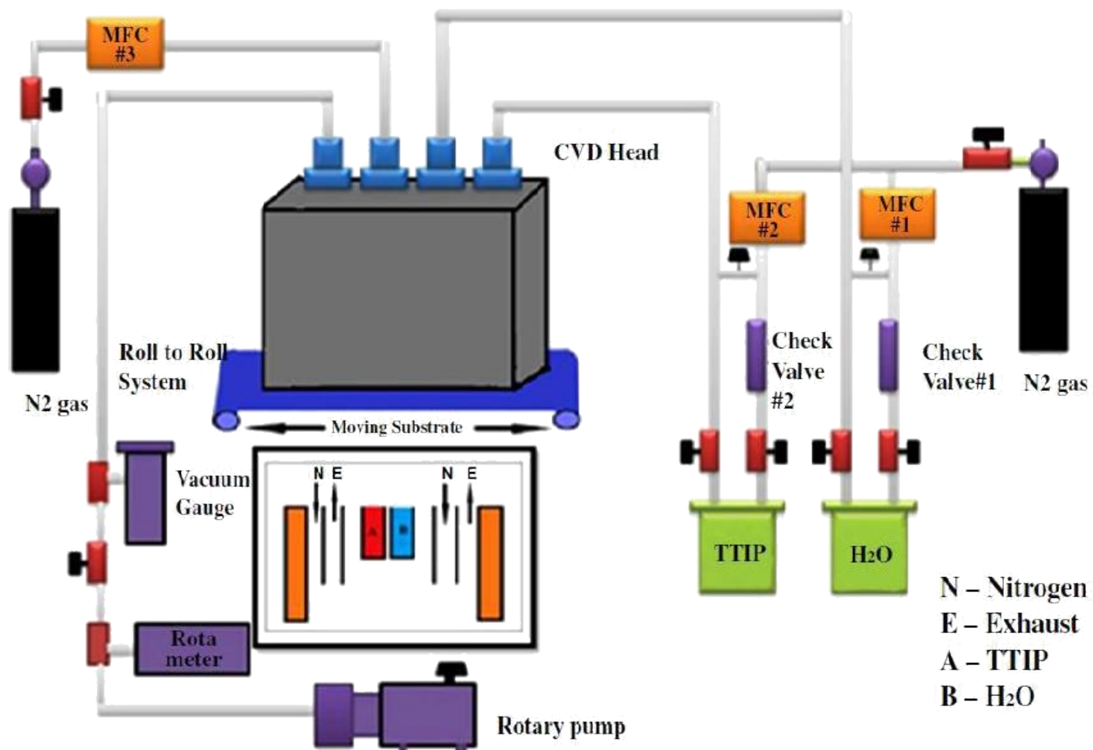

Figure.2.1. Schematic diagram of the roll to roll atmospheric chemical vapor deposition.

A working pressure of 740 Torr, which is close to the atmospheric pressure of 760 Torr, was achieved by maintaining the pumping speed of 7 L /min. The web velocity of the PET substrate was varied in the range of 1–30 mm /S, and its tension was maintained at 10 KgF.A hot plate was used to achieve and maintain the desired substrate temperature.The deposition of a TiO_2 thin film on polyethylene terephthalate substrates with the average arithmetic roughness (Ra) of 1.45 nm was performed at low temperature in the range of room temperature to 75 and 100º C.

The precursor decomposition of (TTIP) is strongly related to the substrate temperature.The substrate temperature can lead to decomposition of the TTIP so that the room temperature and 50 °C temperature synthesized film shows high roughness and non-uniform in nature.This may be because of the slow decomposition occurred in this mechanism at atmospheric pressure

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conditions. Further increasing the temperature to 75 and 100° C showed smooth and uniform morphology which proves that uniform film formation was occurred at high temperature (70° C) and further validates that precursor decomposition is temperature dependent and morphology were confirmed shown in Figure.2.2.The RMS roughness value of thin film at the room temperature, 50, 75 and 100 °C are 3.13, 2.76, 1.99 and 1.87 nm, respectively and it clearly indicates that temperature has a strong influence on the film morphology.

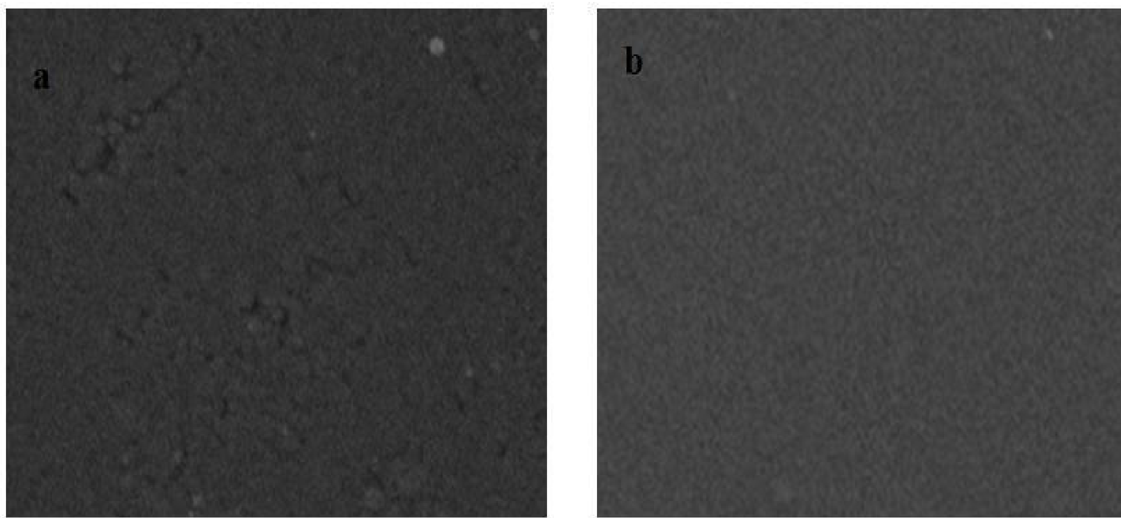

Figure.2.2. FESEM images of TiO_2 thin film on PET substrate. (a)Room temperature slow decomposition nonuniform TiO_2 thin film, (b) Uniform TiO_2 thin film deposited at 100° C.

2.3. Al_2O_3 deposited On PET substrate through R2R-AALD

The gas-delivery head had been installed over the movable substrate.The selected reactor head consist of multiple slits gas delivery channels.It is simple in design, compact, and can be easily installed in any R2R-ALD system.There are three inlets and one outlet at the top of the ALD head. Two of the inlets are connected to the precursor channels, and one inlet is

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connected to the inert gas channel.The outlet is connected to the exhaust channel for the sake of effective purging. A series of 25 slits has been fabricated in the head, three for each precursor, seven for the inert gas, and twelve for the exhaust (purging).The exhaust slits, with the dimensions of 3mm × 90 mm, were chamfered at a specific angle (53.13°) to provide a chimney-shaped design which efficiently removes the by-products and unreacted gases from the surface of the substrate. The dimensions of the precursor slits and the inert gas slits are 1 mm × 90 mm.The precursor slits are separated from each other by the inert gas and exhaust slits, which effectively prevents them from intermixing.The ALD head has been designed in such a way that 5 ALD cycles are achieved when the substrate under go one complete pass i.e. the substrate is first translated forward and then translated backward. It means that one complete pass is comprised of one complete forward and backward translation of the substrate under the ALD head which results in 5 ALD cycles.Al_2O_3 ALD films have been deposited on PET substrate using TMA and water at temperature of 50° C.The TMA and H_2O precursors were kept at a constant 30° C, and the gas delivery channels at 100° C, to prevent the recondensation of the precursors. The flow rates of the gases through the channels were effectively controlled through mass flow controllers (MFCs).The TMA and H_2O precursors were delivered to the ALD head via N_2 gas at 500 sccm and 800 sccm, respectively.The flow rate of the N2 separator gas was maintained at 1000 sccm in order to effectively prevent the intermixing of the two precursors in the reaction zone.A rotary pump was used for purging of the waste gases.A vacuum gauge was used to monitor pressure beneath the ALD head.The experimental setup of R2R-AALD for the deposition of Al_2O_3 thin films is shown in Figure.2. 3.

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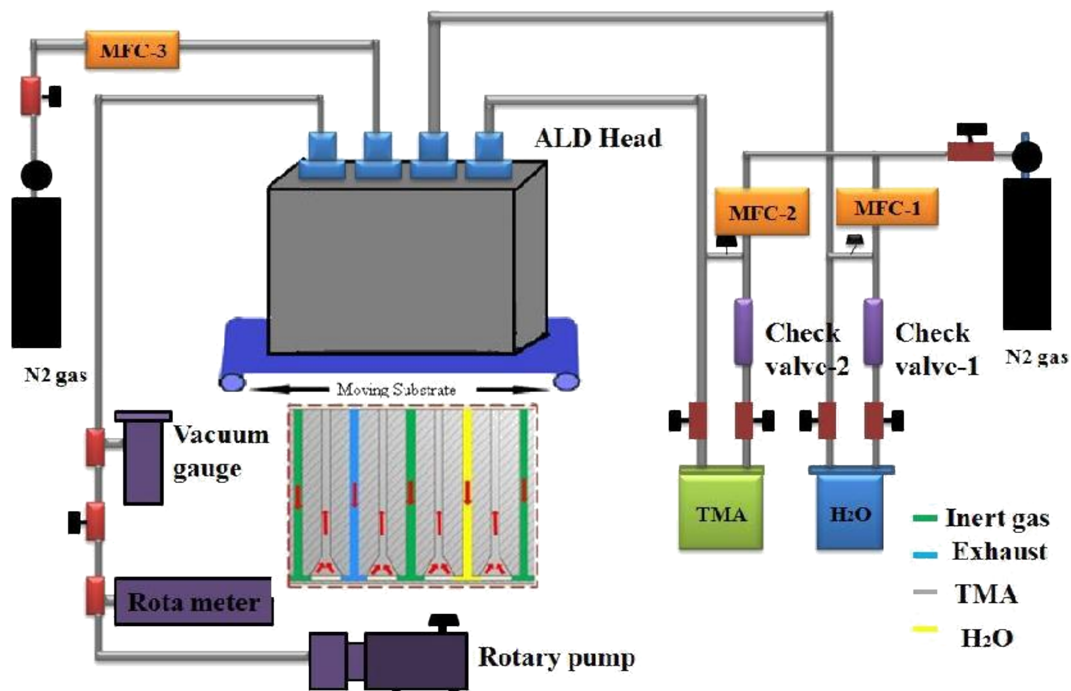

Figure.2.3. Schematic diagram of the roll to roll atmospheric atomic layer deposition.

Table.2.1. The operational parameters of R2R-AALD system

Distance between head and substrate	< 1mm
Web tension	1- 10 kgf
Web velocity	1- 10mm/sec
Substrate temperature	RT - 100° C
Pressure	760 - 650 Torr
Exhaust rate	1-15 L/min
Precursors canisters temperature	RT - 100° C
Precursors channels temperature	RT - 100° C
Precursors and Nitrogen flow rates	1 - 1000 SCCM

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2.4. R2R-AALD SiO_2 thin film On PET substrate

The SiO_2 thin film deposition was done through the R2R-AALD system.The ALD head was placed above the PET substrate, and the distance between the substrate and the head was ~ 400 µm.The precursor channel outlets and exhaust channels were connected to the head.The role of the nitrogen gas was to act as a carrier gas and inert separation gas.The major precursor is Tri(tert-pentoxy) silanol (TPS) as SiO_2 source, and trimethyl-aluminum (TMA) acted as a catalyst.[36] The canister of TPS maintained at 110° C, and the TMA was maintained 10° C.The precursor's channels were maintained at 100° C for preventing the recondensation of the precursor.The delivered flow rate of the precursor TPS and catalyst TMA were fixed at 100 SCCM and 50 SCCM respectively.To prevent the inter mixing of the precursors, nitrogen gas flow rate was fixed at 1000 SCCM. The flow rates were adjusted by the mass flow controllers (MFC).The unreacted gas purged out through the rotary pump, and the reaction pressure was maintained at 740 Torr.This reaction pressure was closely related to the atmospheric pressure. The web velocity of the PET substrate was fixed at 7 mm s^{-1} and the tension was fixed at 10 KgF. This sio_2 thin film was fabricated at 90° C on a flexible PET substrate. The Photographic illustration of the roll to roll atmospheric atomic layer showed in Figure.2.4.

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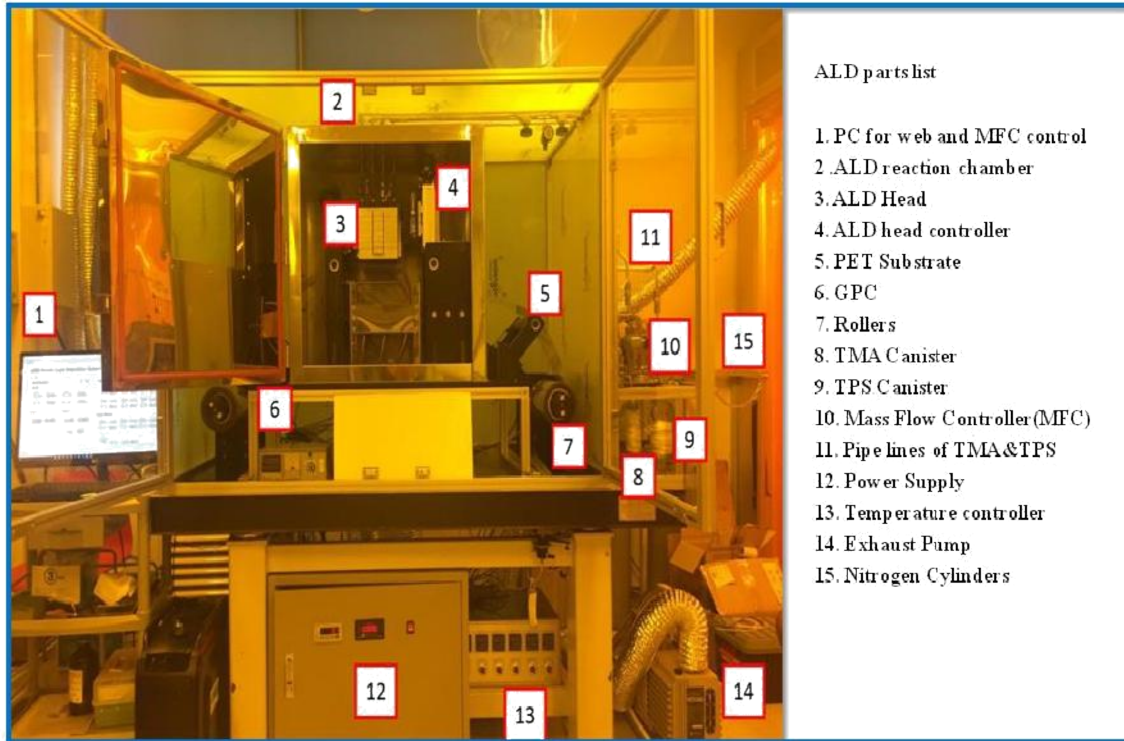

Figure.2.4. The Photographic illustration of the roll to roll atmospheric atomic layer deposition and with their component's information.

2.5. PVDF deposition through EHDA technique

EHDA technique can be used to deposit a variety of materials with supreme and uniform thin films.[37-41]The required flow rate was maintained by the syringe pump (Harvard Apparatus, PHD 2000 Infusion). The PVDF ink filled syringe was connected with the metallic capillary with a diameter of 210 μm.The high electric field between metallic capillary and ground was applied. The EHDA operation had several modes of deposition such as dripping, micro-dripping, stable, unstable, and multi-jet process whose pictures were captured through the high-speed CCD

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camera.The substrate stage was capable of moving in the X-Z direction, and the metallic holder could move in the Y direction.After the careful adjustment between the nozzle and substrate, the uniform spray result was achieved.The PVDF organic thin film achieved at room temperature along the substrate speed of 0.35 mm/sec.The uniform deposition was achieved at the flow rate of 400 μl/h. The prepared sample was sintered at 90° C for 3 hours.The EHDA deposition was performed under various flow rates at a fixed distance of 20 mm. The electrical current was increased for every flow rate by the applied voltage between the stage and nozzle. Optical image representation of the electrohydrodynamic atomization system showed in Figure.2.5.

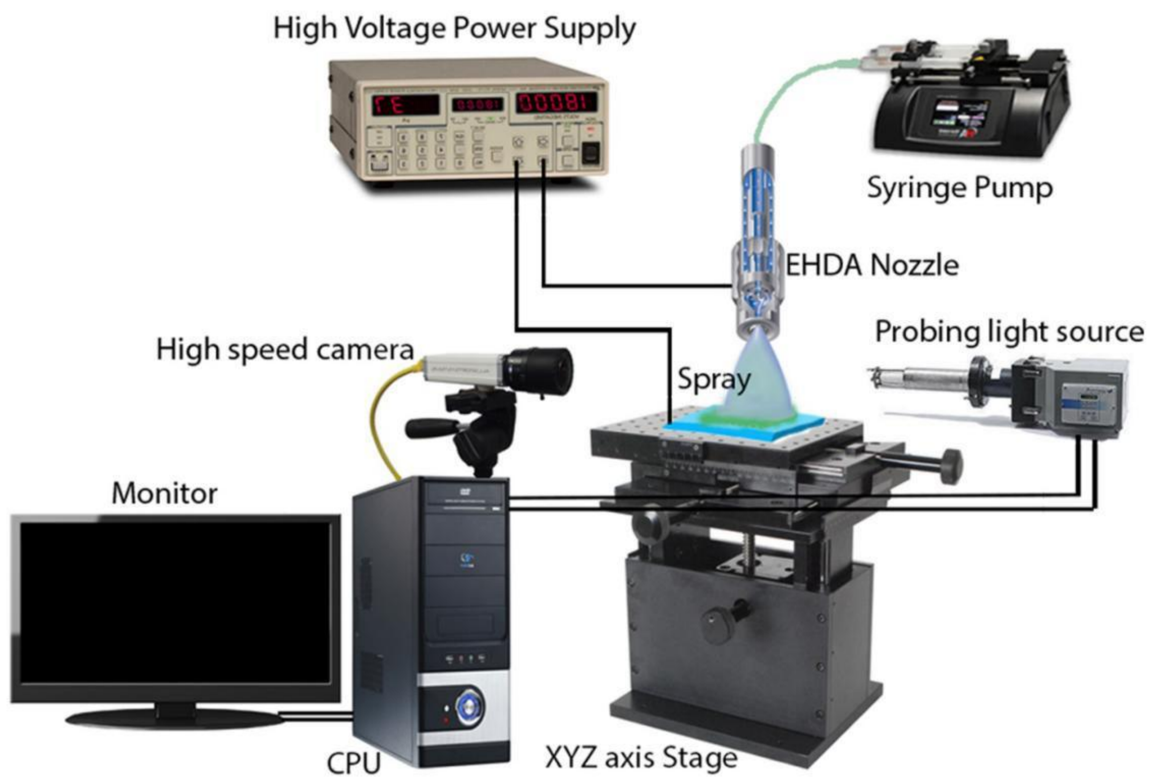

Figure.2.5. Optical image representation of the electrohydrodynamic atomization system for thin film deposition experiment.

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2.6. Multilayer thin film preparation

The hybrid PVDF/SiO_2 multilayer barrier thin film was fabricated by using combined R2R-AALD and EHDA deposition techniques.The schematic diagram of the hybrid barrier thin film preparation is presented in Figure.2.5.The first layer of inorganic SiO_2 thin film was deposited by R2R-AALD. The growth rate of the SiO_2 thin film in a single pass was maintained at ~ 0.90 nm/pass.The second layer of the organic material PVDF was deposited through EHDA deposition process. After depositing the organic thin film, it was sintered at 70° C for 4 hours.

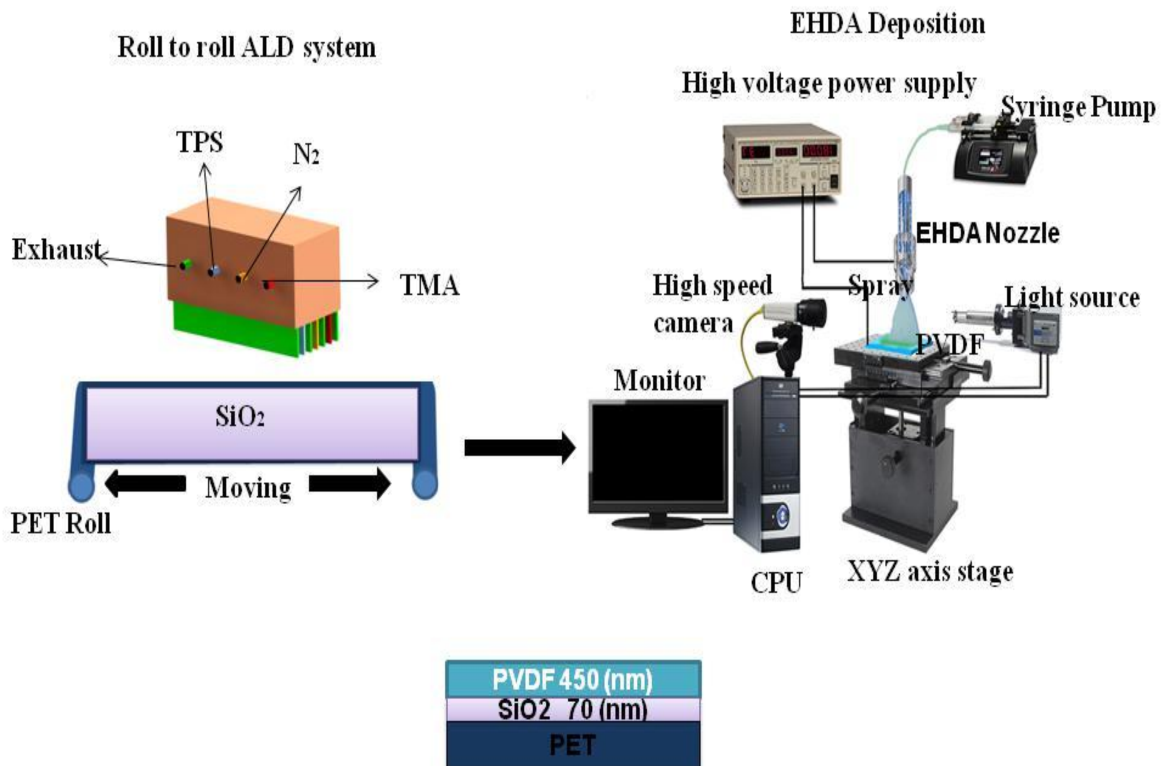

Figure.2.6. Schematic illustration of the multilayer barrier film preparation as well as thickness of each film

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2.7. Thin Film Characterizations

The fabricated thin films were successfully characterized through various techniques.

1. The thickness of the films was measured using a state of the art, nondestructive, thin film thickness measurement system K-MAC ST4000-DLX, and Focused Ion Beam
2. The morphology and conformity of the films were observed using a JSM-6700F FESEM and NanoView high accuracy 3D nano non-contact surface profiler.
3. The chemical composition level was analyzed using VG Microtech XPS analysis equipment using Mg Ka radiation from an X-ray source operating at 12 kV, 15 mA. The XPS analysis was also conducted using another model, i.e., PHI Quantera II VG X-ray photoelectron spectroscopy (XPS) equipment.
4. The contact angle measurements were carried out using SEOPhoenix 3000 Touch using deionized water.
5. The UV characterization was performed using a Shimadzu UV-3150 UV/VIS/NIR spectrophotometer.
6. The electrical characterization was done by using Agilent B1500A Semiconductor Device Analyzer coupled with an MST8000C Probe Station was used.

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CHAPTER 3

3. Result and discussion

3.1. Low temperature deposited TiO_2 Thin Films

Titanium dioxide (TiO_2) is an inexpensive photoactive material, lightweight and eco-friendly in nature. It is a commercial material that has been primarily used as a pigment for coating application due to its highly visible light scattering nature.[42] It has a high refractive index and is chemically stable in the UV and visible region.[43] TiO_2 has been widely used for various applications such as dielectric materials,[44] antireflection coatings, self-cleaning surfaces,[45,46] dye-sensitized solar cells,[47] and a photocatalyst[48,49], TiO_2 has the four phases, anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic), and an amorphous phase.[50] TiO_2 thin films have been fabricated by various methods such as sol-gel, spray pyrolysis, electron beam evaporation, sputtering, plasma-enhanced chemical vapor deposition, metal– organic chemical vapor deposition, and atomic layer deposition.[51] Chemical vapor deposition (CVD) is the most commonly used method in the field of material processing technology, and by using this technique, the solid material is deposited as a film on the substrate material with a uniform distribution over a large area. A variety of materials can be deposited as a thin film by CVD with low defect density and high purity. CVD can be utilized for the production of MEMS technology[52] and graphene fabrication.[53] Different types of CVD techniques for fabricating thin films include plasma-enhanced chemical vapor deposition (PECVD), metal–organic chemical vapor deposition (MOCVD), atmospheric pressure chemical vapor deposition (APCVD), and plasma-assisted chemical vapor deposition (PACVD). Advantages of APCVD are that the film could be synthesized using low-cost equipment and the temperature and gas flow can be controlled to obtain a uniform film over a large surface area.

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Compared to other techniques, this method could be used to fabricate the film without vacuum conditions.[54] The roll-to-roll CVD technique is a well-known method for the mass production of the films that is cost-effective, and it is highly useful for industrial applications.

Many researchers have deposited TiO_2 films at high temperatures, but only a few were able to achieve a low-temperature deposition of TiO_2.Maruyama et al. fabricated amorphous TiO_2 film by applying atmospheric pressure CVD on glass and silicon substrates with temperatures ranging from 200 to 500ºC.[55] Masuda deposited an amorphous TiO_2 thin film on the silicon substrate at room temperature.[56] Sun et al. synthesized amorphous TiO_2 film on glass and PET substrate at room temperature.[57] Yamauchi et al. deposited TiO_2 thin film on the quartz substrate by PECVD with temperatures in the range of 300– 400ºC.[58] Lee et al. deposited a TiO_2 thin film on a silicon substrate by PECVD for the substrate temperature in the range of 100–400ºC.[59] Mathur deposited TiO_2 thin film by DC plasma-assisted CVD below 200ºC.[60] Kolouch deposited TiO_2 thin film on the glass and silicon substrate by using PECVD with temperatures as low as 120º C.[61] Previously Sun et al.[62] synthesized a thin film of TiO_2 at room temperature on a movable substrate. The roll-to-roll atmospheric chemical vapor deposition (R2R-ACVD) system is the best technique to fabricate thin film on a polymer substrate, and it plays a vital role in flexible electronics and has tremendous applications because of its light weight and mechanical stability. In the present study, R2R-ACVD TiO_2 thin film was deposited on a movable PET substrate with different substrate temperatures including room temperature, 50, 75, and 100ºC. The structure and morphology of the TiO_2 films have been characterized by the field emission scanning electron microscopy and 2D surface profiler. Electrical, optical, and chemical properties were determined through current-voltage (I–V) measurement, UV–visible spectrum, and X-ray photoelectron spectroscopy, respectively.

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3.1.1. Film growth

The deposition rate of TiO_2 films over the PET substrate under different temperatures was determined.The observed deposition rate corroborated that temperature has a significant influence on the film formation.The nature of precursor and its stability played a vital role in the deposition rate and topography of the as-deposited film. In the present study, TTIP was used as a precursor due to the very fast hydrolysis rate and the easy formation of TiO_2 which may increase with an increase in the temperature.

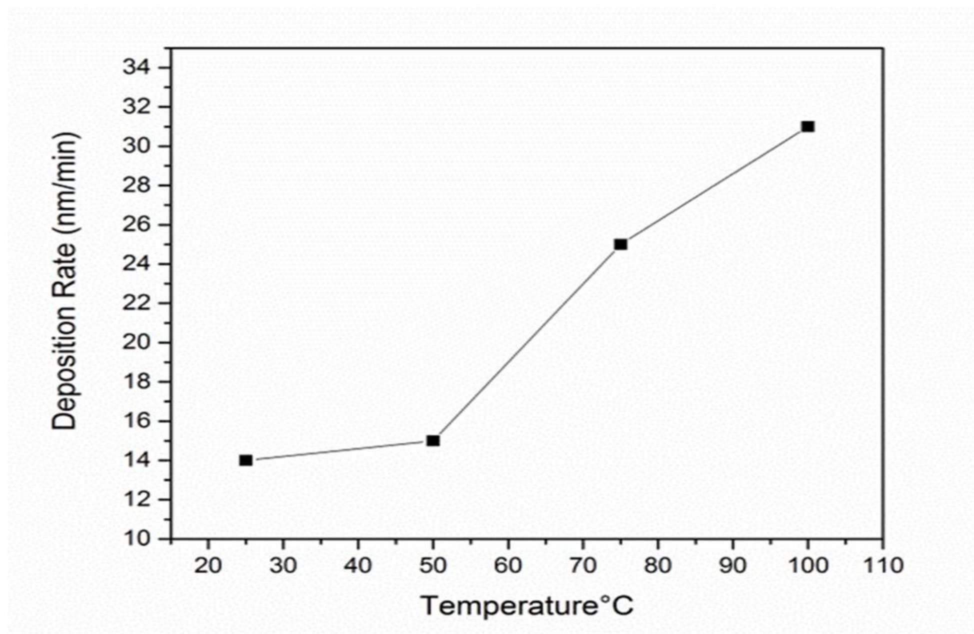

Figure .3.1.The deposition rate (nm/min) of the TiO_2 thin film increased while increasing the temperatures such as RT, 50, 75 and 100 °C.

The 25- cm-long sample was moved back and forth repeatedly for 9.3 min, being continuously exposed to the precursor for the whole duration of the process. The deposition rate of the observed film thickness was 14, 15, 25, and 31 nm per minute with room temperature, 50, 75, and 100º C, respectively. This clearly indicates that the temperature depended on the film

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deposition rate as shown in Figure.3.1.The total thickness of the film at room temperature, 50, 75, and 100ºC was 131, 144, 239, and 310 nm, respectively. The TiO_2 thin film prepared at 100ºC possesses a larger thickness than the lower substrate- temperature film (RT—75ºC). This result indicates that film deposition rate might be dependent on the substrate temperature.[63] Film thickness attained by the R2R-ACVD method is compared with the previously reported literature (Table.3.1). The results revealed that the obtained film thickness is quite comparable to the other reported methods; however, in this method, low temperature and pressure were used for deposition.

Table 3. 1: Summary of the growth rate observed in the Previous Reports

Method	Deposition Temperature (°C)	Growth rate (nm/min)	Reference
	RT	14	This work
	50	15	This work
R2R-CVD	75	25	This work
	100	31	This work
APCVD	RT	75	Zhi-Guang Sun et al.[57]
APCVD	RT	14	Ai-Min Zhu et al.[76]
PECVD	523 K	37	G.A. Battiston et al[77]
PACVD	160	40	Sanjay Mathur et al [60]
LPCVD	350	15	Sanjay Mathur et al.[60]
APPCVD	High voltage	22	Lan-Bo Di et al.[78]
PECVD	270	15	Frenck et al[79]

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3.1.2. Surface morphology

FE-SEM images of the TiO_2 thin film deposited at different temperatures are shown in Figure.3.2.The FE-SEM image of the as-deposited TiO_2 thin film at room temperature and at 50ºC showed that the surface of the film has highly rough morphology (Figure.3.2 (a) and (b)). These FE-SEM results match closely with the results reported in the literature.[64] By further increasing the substrate temperature, the surface roughness of the film diminished (Figure.3.2 (c) and 3(d)). This observation validated the fact that the smooth film surface can be obtained at high substrate temperature, and these results were well matched with what was reported in the literature.[65]The observed nonuniform deposition at room temperature may be due to the slowly occurring diffusion, and it may be due to the slow decomposition of precursor material (alkoxide).The growth of the film formation takes place via diffusion followed by nucleation mechanism.At low temperatures, slow diffusion occurs and may be due to the slow decomposition of the precursor material [66] which results in the uneven nucleation sites for film growth. However, in the case of high temperatures, the decomposition of the precursor is enhanced by the substrate temperature, which results in the more nucleolus formation in the substrate.This enables the uniform diffusion of precursor molecule on the bulk surface. The observed FE-SEM images validated the aforementioned results.

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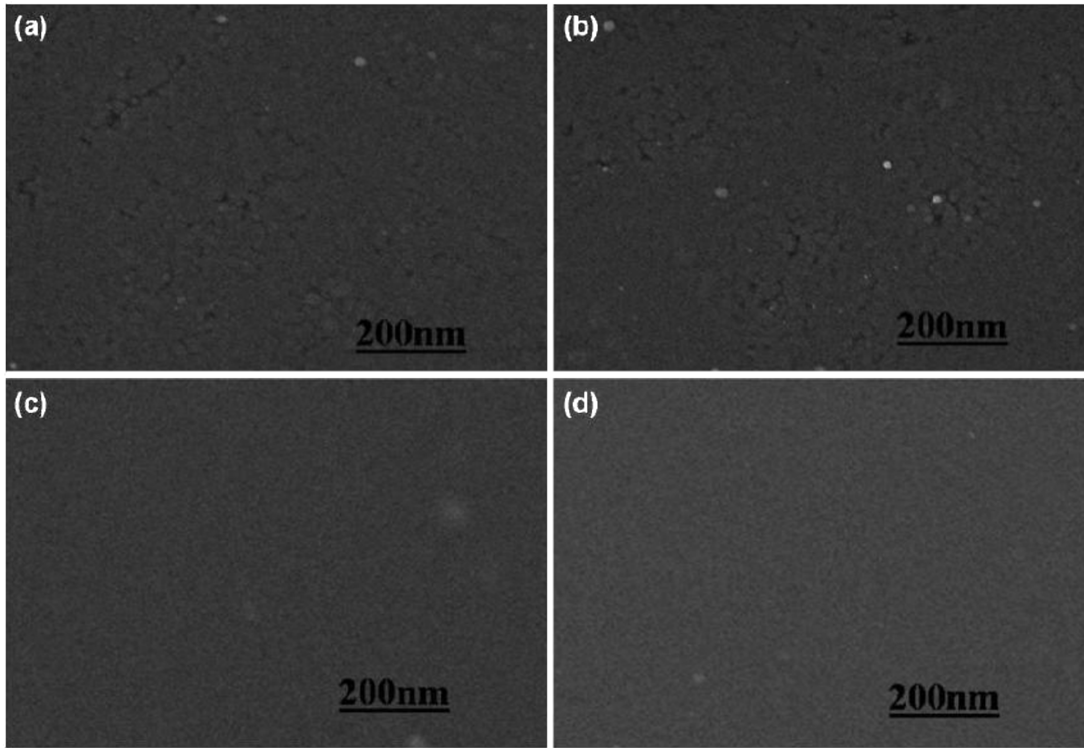

Figure.3.2. FESEM images of TiO_2 thin film on PET substrate. Nonuniform TiO_2 thin film deposited at (a) RT, (b) 50 °C and uniform TiO_2 thin film deposited at (c) 75 °C, (d) 100 °C.

Moreover, to further support the dependence of surface morphology on the substrate temperature, the prepared TiO_2 films were characterized by a 2D nanosurface profiler.Figure.3.3 shows that the room-temperature-deposited TiO_2 film revealed high surface roughness as compared to others. When the temperature increases, the surface roughness of the film decreases.
[67] The temperature-dependent surface roughness results were matched with the reported results.The 2D surface profile of the TiO_2 films grown at room temperature (RT), 50, 75, and 100ºC is shown in Figure.3.3.These 2D surface profile results corroborate with the FE-SEM and film deposition rate measurement results.The root means square (RMS) value extracted from the 2D nanosurface profiler results showed a decreasing value with increasing substrate deposition temperature.

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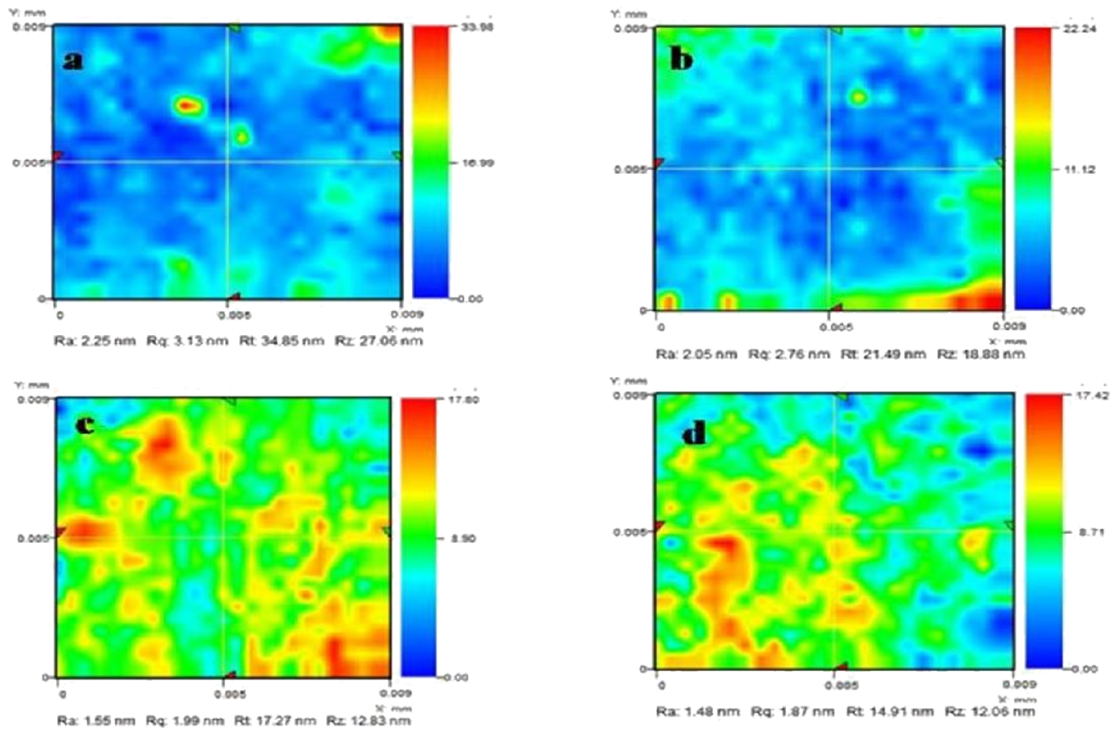

Figure.3.3. 2D surface profile, images of the TiO_2 thin film on PET substrate. High roughness obtained the TiO_2 thin film deposited at (a) RT, (b) 50 °C and low roughness obtained the TiO_2 thin film at (c) 75 °C and (d) 100 °C.

The RMS value for room temperature, 50, 75, and 100ºC is 3.13, 2.76, 1.99, and 1.87 nm, respectively, clearly indicating that temperature has a significant influence on the surface of the film. The least value of Rq 1.87 nm and Ra value 1.55 nm is observed for TiO_2 film deposited at 100ºC. The observed least RMS for TiO_2 prepared at 100ºC is better than the earlier reported methods.[68,69] The topography of the film decides its optical and other properties. Thus, the optical properties of the TiO_2 film were characterized by UV–Vis spectroscopy.

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3.1.3. Optical transmittance

UV–Vis spectrum of TiO_2 thin films prepared by the R2R-ACVD method at the different temperatures is shown in Figure.3.4.The results revealed that 91.2% transmittance was observed for TiO_2 thin film prepared at 100ºC and it is quite higher than the low substrate temperature (RT, 75ºC).All the prepared TiO_2 thin films showed transmittance from 86% to 91.2% in the visible range (400–800 nm). Hocine et al.[70] and other research groups reported that 80–90.2% transmittance was observed for TiO_2 thin films prepared by different CVD methods under different temperatures.In comparison with the earlier reported results, the observed 91.2% transmittance of this study and high surface smoothness at low substrate temperatures are the new reasons for adapting the R2R-ACVD film coating method.Furthermore, the different optical transmittance results further support the morphology-based optical property of the prepared film. FE-SEM and surface profiler clearly show that the room temperature film has a high roughness which leads to low transmittance (86%).From these results, we conclude that it can be a promising candidate for optoelectronics application.[71]

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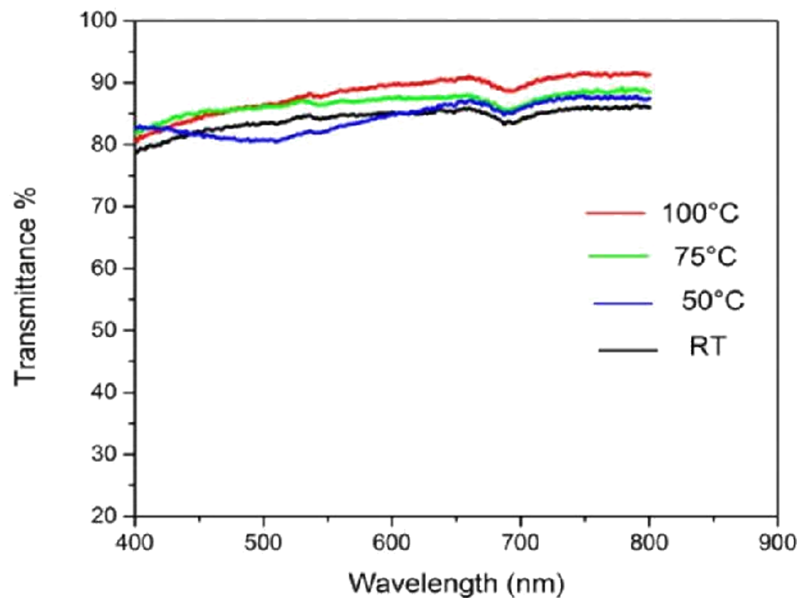

Figure 3.4. Optical property of TiO_2 thin film on the PET substrate by R2R-ACVD at room temperature to 100 °C. The optical transmittance was observed at 91 % in the visible region for 100 °C.

3.1.4. Compositional analysis

The X-ray photoelectron spectroscopy (XPS) analysis was performed to understand the oxidation state and the defects present in the prepared TiO_2 films.The high-resolution XPS spectra of Ti2p and O1s of TiO_2 film prepared at different substrate temperatures are shown in Figure 3.5(a) and (b).From the O1s spectra, it is observed that there are no significant changes in the peak intensity with an increase in the coating temperature; however, the small shift in the peak position indicates the presence of defects in the prepared TiO_2 film.The changes in the binding energy of O1s state clearly show that O concentration on the TiO_2 film was increased.The atomic percentage result also indicates that oxygen concentration was increased with an increase in the temperature (Table.3.2). Moreover, carbon (%) content declined with an increase in the substrate

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temperature, indicating that more decomposition of the precursor occurred. Similarly, the higher percentage of Ti was observed with an increase in the temperature, indicating the denser Ti concentration.The observed atomic concentration of Ti, O, and C evidently supported that film thickness increased by increasing the temperature.Moreover, the high-resolution XPS spectrum of Ti2p displays two peaks at 458.7 and 463.4 eV that are attributed to the Ti 2p3/2 and Ti 2p1/2 levels of TiO_2 and validates the successful synthesis of TiO_2 film, and the valence of Ti is four (Figure.6b).However, when increasing the temperature from RT to 100ºC, the binding energy is shifting from 457.4 eV to 458.7 eV respectively.This may be because when the temperature increases titanium oxides lost oxygen which leads to the existence of Ti4+ and Ti3+ in the synthesized film.[72] However, the synthesized TiO_2 film is highly stable which is in accordance with the FE-SEM and UV–Vis spectroscopy analysis results.[73]

Table 3.2: Atomic Composition of TiO_2 film prepared by R2R-ACVD with different substrate temperature

TiO_2	RT	50 °C	75 °C	100 °C
Atomic %	O1s 61.9 Ti2p 27.8 C1s 10.4	O1s 64.8 Ti2p 29.5 C1s 8.7	O1s 63.1 Ti2p 28.5 C1s 8.7	O1s 65.0 Ti2p 29.1 C1s 6.0

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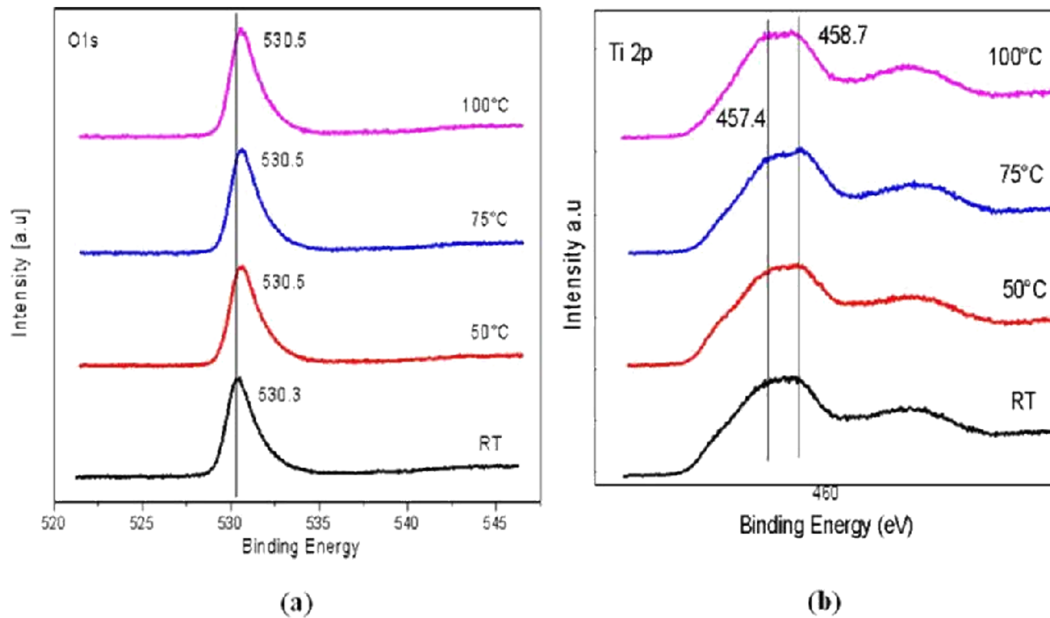

Figure.3.5. The XPS spectra of R2R-ACVD TiO_2 films deposited at different temperatures (a) O 1s and (b) Ti 2p from TiO_2 films

3.1.5. Electrical properties

Electrical properties of the TiO_2 films were analyzed using the Agilent B1500A Semiconductor Device Analyzer coupled with a MST8000C Probe Station. Current (I) voltage (V) characteristics of the TiO_2 thin film fabricated at different temperatures were measured. Initially, the metallic contacts were made on the top of the film using Ag ink by drop casting method. Subsequently, the measurements were carried out under room temperature with the help of two probes on the circular-shaped Ag metallic contacts of the films. Measurement of the metallic contacts distance is 4 mm. Figure.3.6. shows I–V behavior of the R2RACVD method-deposited TiO_2 film indicating a good insulating nature. Moreover, the TiO_2 film prepared at 100º C showed 1.18 nA current, and other TiO_2 films showed an extremely low current (pA). TiO_2 thin films deposited at room temperature are smaller in thickness than the film deposited at 50, 75, and 100ºC. Also, films deposited at room temperature showed extremely lower current (pA)

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because of their discontinuity and nonuniformity. These low-current TiO_2 films could be used in the field of biosensor development and as a good insulator for electronics applications. [74,75].

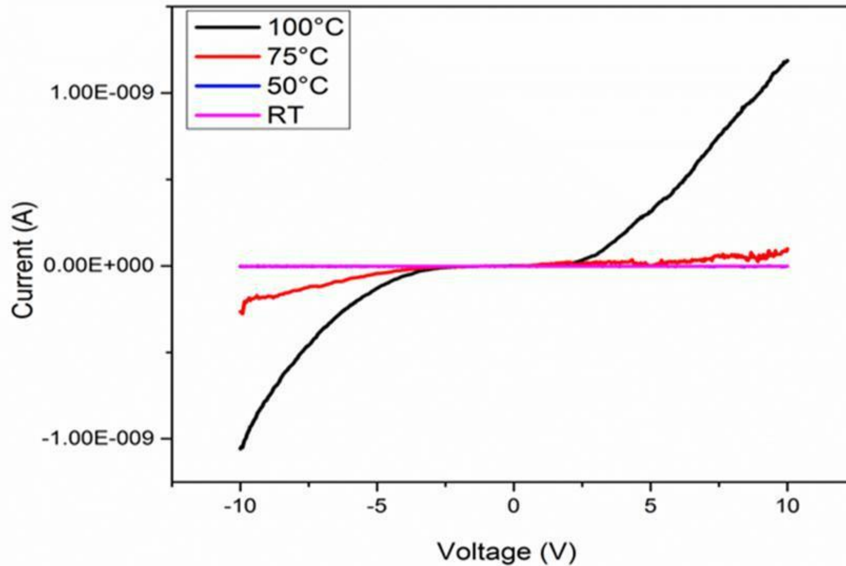

Figure.3.6.The I-V characteristics of TiO_2 film at RT to 100 °C temperature grown on PET substrate

3.2. Single layer Al_2O_3 deposited on PETsubastrate

The trimethylaluminum [Al $(CH_3)_3$, TMA] and water (H_2O) is a important precursor for Al_2O_3 thin film. Al_2O_3 can be coated on polymer substrate due to Al_2O_3 can be deposited at low temperature.[80] The Al_2O_3 coat on polymers provide a pathway to fabricate inorganic-organic composites with novel properties.ALD coated Al_2O_3 thin films can be utilized to gas barrier on polymeric substrates to prevent H_2O and O_2 permeation.Also Al_2O_3 has potential use in microelectronics and microelectronics devices. Many researcher have examined and the Al_2O_3 ALD process at higher temperatures but only few have studied it

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lower many have broke down it under lower temperature.[80-82] The low temperature ALD process is difficult also it need careful assessment for processing.

Previously, different model of roll-to- roll based ALD system have been reporeted to fabricate thin films on various substrate.[83,84] Dickey et al. have shown the deposition of Al_2O_3 and TiO_2 barrier thin films at 75 ºC on polymeric substrates through the vacuum based roll to roll ALD. This system ability to produce barrier thin films at 12 nm on a 10 cm PET web with water vapor transmission rates in the scope of 10^{-4} g/m^2/day under the web velocities of 1 m/s.[85] Kamran et al. achievd a WVTR of ~10^{-3} g/m^2/day under the web speed of 7 mm/s for Al_2O_3 thin film with thickness range from 15-40 nm.[86] Groner et al. fabricated very thin (10-25 nm) Al_2O_3 film and achieving WVTR of 1×10^{-3} g m^{-2} day.[87] They have suggested that the Al_2O_3 deposition can be possible through low substarte temperature.

In this research work R2R-AALD has been described for and its application has been discussed about for the development of low temperature Al_2O_3 films for single layer barrier applications. The precursors TMA and water that were kept at a steady temperature of 30º C. The gas delivery channels were kept at 100 °C to prevent the recondensation of the precursors. The precursors. (TMA and H_2O) were supplied to the ALD head with the help of N_2 gas at the flow rates of 700 SCCM and 1000 SCCM respectively and the flow rates through the channels were controlled by the mass flow controllers (MFCs).The individual seperator nitrogen gas was kept at (1200 SCCM) to avoid the intermixing of precursors in the reaction region. The rotary pump was using to remove unreactant gas from the reaction chamber and ALD was continuosly monitored by vaccum gauge. The nearly atmospheric pressure of 750 Torr was achieved by keeping up the pumping speed of 7 L/minute.The web speed of the PET substrate was changed in the range of 1 mm/sto 10 mm/s and its tension was kept constant at

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10 kgF. The required substrate temperature was achieved through a hot plate. The Al_2O_3 thin film deposition was done at a low temperature range of room temperature (RT) to 50 ºC on PET substrates.

3.2.1. Film Growth

The growth rate per cycle is important characteristic of ALD system.It gives fundamental information about the effectiveness, reliability and the nature of ALD process. In our investigation, the growth rates of Al_2O_3 thin films done by R2R-AALD and measuring the film thicknes by thickness as number of ALD cycles.Figure.3.7(a) indicates thickness of the Al_2O_3 films as a working process cycles deposited at 50 °C under velocity of 7 mm/s.The design of the ALD head achived 5ALD cycles in a one complete pass i.e.forward and backward direction.The exposure times of the precursors based on the speed of the moving web. In this manner, the optimized self-limiting ALD process was affirmed at 50 °C by measuring the film thickness against the web speeds.The Figure.3.7.(b) shows high uncontrolled development rates are recorded for the films deposited under the web speed of more than 7 mm/s.

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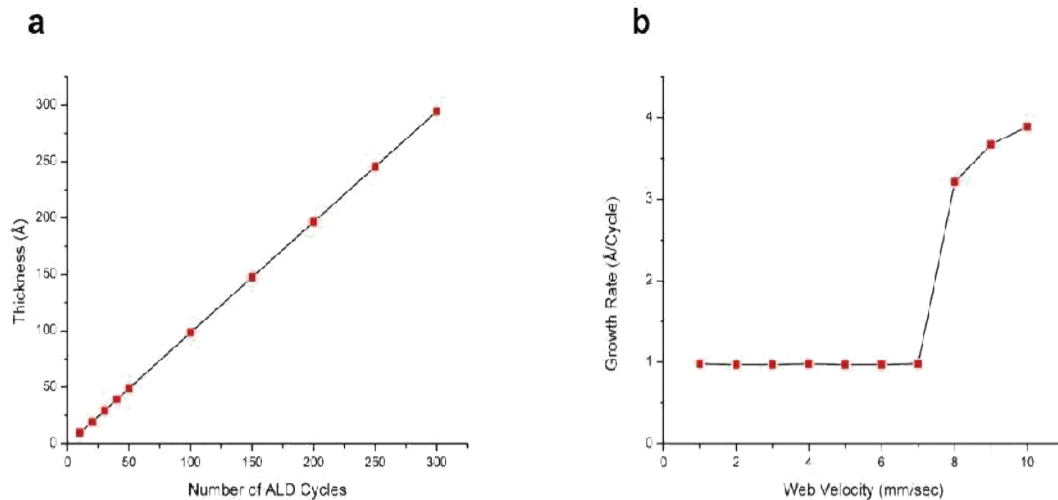

Figure.3.7.Thickness Al_2O_3 films on PET substrates versus the number of process cycles at 50 °C under the web velocity of 7mm/second (a), and growth rates of the Al_2O_3 films versus the web velocity (b).

3.2.2. Surface Morphology

The surface morphology of the Al_2O_3 films deposited at 50 °C by R2R-AALD on PET substrates was examined through FESEM and nano surface profiler.Figure 3.8 (a), (b), shows the FESEM images of the bare PET substrate, and 50 °C deposited Al_2O_3 on PET, respectively. The results clearly showed uniform and smooth Al_2O_3 thin films have been deposited on PET substrates through R2R-AALD.The surface morphology was additionally studied with 3D nano surface profiler. The 2D surface profile results of the 50 °C grown Al_2O_3 films grown shown in Figure. 3.8.(c). 2D surface profile results shows very low roughnes (Ra) values of 1.57 nm have been recorded for the Al_2O_3 thin films under at 50° C.

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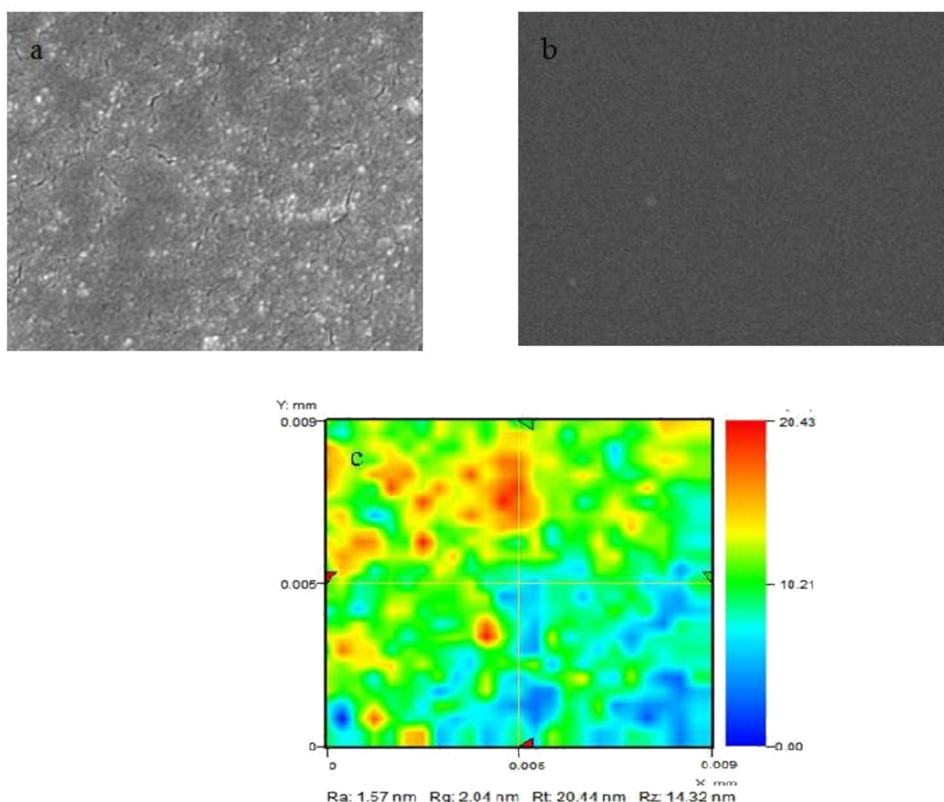

Figure 3.8. FESEM images of the bare PET substrate (a), Al_2O_3-coated PET at 50 °C (b), and 2D surface profile of the Al_2O_3 films grown at 50 °C (c).

3.2.3.Compositional Analysis

The Al_2O_3 thin films deposited at 50° C through R2R-AALD were subjected to X-ray photoelectron spectroscopy analysis to confirm chemical composition level of the thin films.The XPS spectrum of the Al_2O_3 thin film has been displayed in Figure.3.9.

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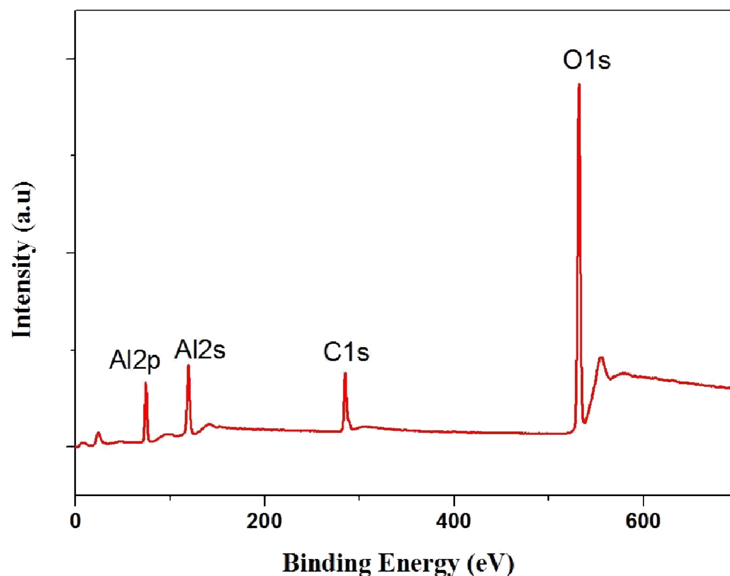

Figure 3.9. The XPS spectrum of Al_2O_3 film deposited at 50 °C.

The required peaks which represent to the deposited Al_2O_3 are Al 2p, Al 2s and O 1s.The Al_2O_3 films, which contains Al 2p, Al 2s and O 1s peaks showed up at the binding energies of 74 eV, 119 eV and 531 eV respectively.The range additionally demonstrated a carbon top, showing up at a coupling vitality of 285 eV.The XPS spectrucm further confirms the carbon peaks at a binding energy at 285 eV. The appearance of this adventitious carbon peak due to the atmospheric air exposed on the sample.

3.2.4. Barrier Properties

The barrier properties of the films including water vapor permeation rate and oxygen permeation rate were analyzed through a commercially available MOCON (AQUATRAN Model 1) test instrument, under 37.8 ºC and 23 ºC respectively at 100% relative humidity using samples of size 3 cm ×3 cm.The barrier thin films of single layer Al_2O_3 water vapor and oxygen permeation rate values of the range 1.2×10^{-1} g m^{-2} day $^{-1}$shown in Figure 3.10.

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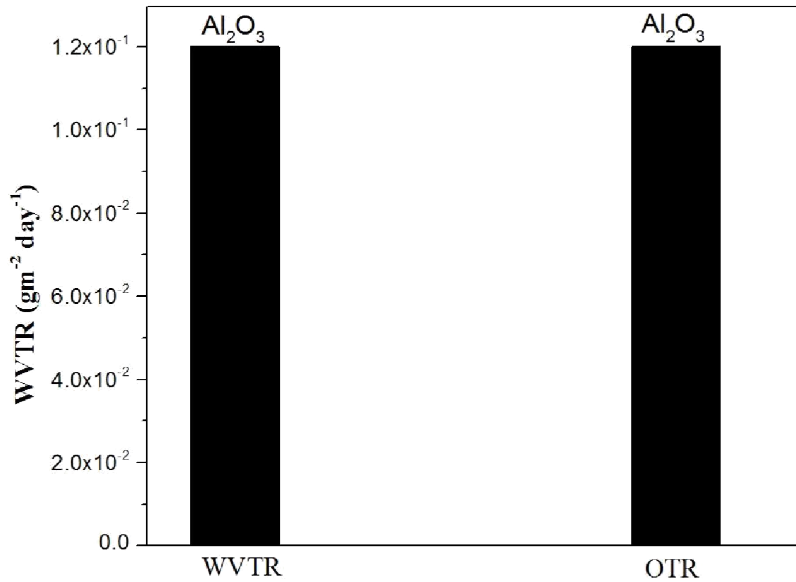

Figure.3.10. The WVTR and OTR values of the 50 °C deposited single layer Al_2O_3 via R2R-AALD.

3.3. Hybrid multilayer barrier coating

In recent years, flexible electronic devices have begun to be regularly used in our daily lives for communications, renewable energy resources, and information technology.[88-90] Conventional glass substrates can provide excellent protection from permeation species, but the glass substrate is rigid due to which it cannot be used for the application of flexible electronics.On the other hand, electronic devices made on flexible plastic substrates such as solar cells, organic thin film transistors (OTFTs), organic light emitting transistors, and organic light emitting diodes (OLEDs) enable low cost, flexible, mass production and weight reduction in these devices.[91,92] However, flexible polymer substrates can be easily damaged by the atmospheric gas molecules oxygen (O_2) and water (H_2O)[93,94] and therefore these substrates must be protected with some additional encapsulating nanolayer.Atmospheric species can be easily oxidized, and damage electrodes hence, decreasing the overall device lifetime.[95,96]

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There are several inorganic materials that play a vital role in polymer substrate encapsulation, such as Al_2O_3, SiO_2, Al_2O_3/ZrO_2, and Al_2O_3/TiO_2, owing to their permeability to environmental species and high optical transparency.[97][98] SiO_2 is a well-known dielectric material, and it can be applied in many research areas, such as the semiconductor industry, flexible electronics, optoelectronics, and passivation layer coating of electronic devices.[99] Several deposition techniques have been reported for the successful development of encapsulating thin films in order to protect electronic devices. These fabrication techniques include sputtering [100] , chemical vapor deposition[101],thermal evaporation[102] with good values of WVTR. However, these methods are only suitable for thick layer coating and rigid device encapsulation and cannot meet the requirements of flexible electronics.[103] ALD is a good choice for defect-free, conformal coatings and high-quality barrier thin films.[104] ALD-grown SiO_2 thin films achieved excellent thin film plays a major role in gas barrier applications.[105] SiO_2 thin film coating on polymer substrate has received great attention in the food packaging, beverage packaging, and pharmaceutical industries.[106] Inorganic thin films displayed effective protection against water and oxygen. However, a low-temperature fabrication process introduced pinholes into the barrier film that can allow atmospheric species through them thereby damaging the device.[107] To solve this permeation issues, organic thin films are recommended for the barrier encapsulation. Organic/inorganic hybrid barrier thin film layers offer supreme protection from atmospheric molecules.[108,109] Furthermore, the organic materials filled the pin holes of the inorganic thin film, leading to the delayed penetration of H_2O and O_2 as well as increasing the diffusion period of atmospheric species. [110,111]

The current trend for using thin film barriers is by using a single inorganic layer[112] or organic-inorganic barrier bilayer.[113] Multilayer [114] barrier can improve the quality of the thin film

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barriers. Jo et al. had prepared SiO_2-PTPT (Poly(trimethylolpropane tri-acrylate) composite barrier for encapsulation purposes with decreasing WVTR results.[115] In multilayer barrier film Kim et al. reported combined thin film techniques for multilayer Al_2O_3/ppTTMSS/Al_2O_3 barrier thin films.[116] Yun et al. reported organic-inorganic barrier thin film from hexamethyldisiloxane (HMDSO) and achieved a WVTR range of 3.6×10^{-6} g m^{-2} day.[117] Chen et al. made ZrO2/zircone hybrid thin film and reported 3.078×10^{-5}g m^2 day-^{1}.[118] Fan et al. reported Teflon/SiO_2 bilayer film and WVTR value for SiO_2 deposited on polycarbonate was shown to be 0.59 ± 0.16 g/m^2 /day.[99] Cheol et al. fabricated S-H nanocomposite with Al_2O_3 using two different combined thin film techniques and displayed 1.14×10^{-5} g/m^2 day.[109] Kim et al. reported Al_2O_3/TiO_2 thin films by plasma enhanced atomic layer deposition method with a WVTR value of 9.16×10^{-5} g m^2 day-$^{-1}$.[95] However, these reported results showed low permeation but required a higher temperature for deposition as well as vacuum condition for the fabrication. There are only a few of them,a which reported atmospheric and roll to roll based technologies that are being utilized for barrier encapsulation applications which can also be part of the mass production and cost reduction technology.

PVDF is a well-known fluoropolymer, and it has piezoelectric property, excellent mechanical stability, and high chemical resistance.[119] Also, the main advantage of PVDF is that it has significant permeability property against small molecules such as nitrogen, carbon dioxide, nitrous oxide, oxygen, and water.[120] There are no reports so far on the coupling of PVDF layer with the inorganic layer as a multilayer barrier for the application of encapsulating flexible substrates through dual fabrication technologies of EHDA and R2R-AALD respectively.

In this paper, the development of PVDF/SiO_2 hybrid barrier thin films through a novel technology of low-temperature R2R-AALD along with EHDA technique have been illustrated

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Figure.2.5.The objective of this study is to couple hydrophobic nature PVDF with SiO_2 thin film for surface passivation of flexible substrates. The novel combination of deposit barrier thin films was investigated for its thickness, surface morphology, chemical composition, and optical properties respectively. The fabricated barrier thin films exhibited good WVTR results. Mechanical robustness of the fabricated multilayer barrier thin film was evaluated, and even after 500 bending cycles, no significant changes in the barrier film were observed. The main advantage of using this joint fabrication technique is the mass production of encapsulating thin films in less time.

3.3.1. Surface Morphology

The surface morphology of the R2R-ALD deposited SiO_2 and EHDA deposited hybrid thin films has been performed through the Field Emission Scanning Electron Microscopy (FESEM) and 2D surface profiler. The hydrophobicity levels of the films were analyzed through the contact angle measurement system. Figure.3.11.(a) illustrates SiO_2 thin film deposited by R2R-AALD which shows uniform and pinhole-free surface morphology. Figure.3.11.(b) shows the EHDA deposited PVDF thin film's surface that is quite nonuniform as seen in the figure. The surface roughness of the SiO_2 thin film deposited by R2R-AALD and PVDF thin film deposited by EHDA are shown in Figure.3.11.(c) and d respectively.Although the surface roughness of as-deposited PVDF thin film deposited through EHDA is poor than the surface roughness of as-deposited SiO_2 through R2R-AALD but it is still superior to other deposited organic thin films through EHDA.The 2D surface profiler arithmetic roughness values of the SiO_2 and PVDF were 1.84 nm and 3.88 nm respectively. Contact angle results revealed the hydrophobicity difference between the SiO_2 and PVDF/SiO2 thin films shown in Figure3.11(e) and (f).The hydrophobic nature of barrier thin films can be induced by increasing the surface roughness and reducing the surface energy.We

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have achieved both these desired parameters for our hybrid barrier thin films by the addition of ammonia in the PVDF mixture that resulted in a higher value of contact angle.The PVDF/SiO_2thin film (CA = 125°) hydrophobicity level is greater than single layer SiO_2 (CA = 90°) thin film. Higher hydrophobicity films are preferable for barrier coating applications. Based on the contact angle results we can verify that multilayer PVDF/SiO_2 thin films can enhance the barrier properties for protecting plastic substrates.

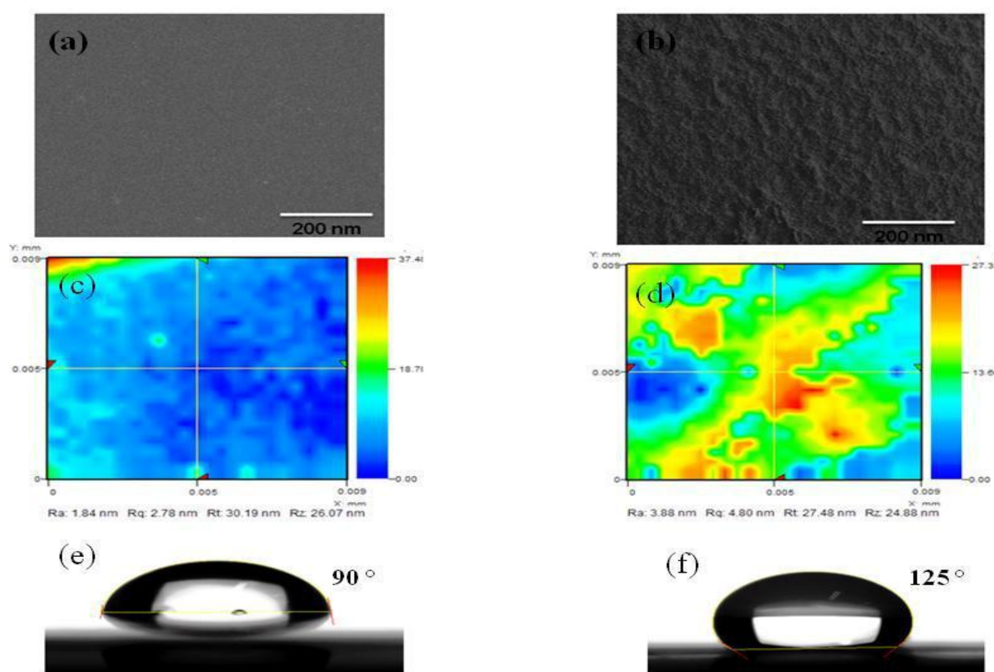

Figure.3.11. The FESEM image of (a) R2R-AALD coated SiO2 thin film, (b) EHDA deposited PVDF, (c) 2D surface profile of the R2R-AALD SiO2 thin film (d) EHDA deposited PVDF (e) Contact angle of the R2R-AALD coated SiO2 (f) PVDF.

The thickness of each layer was analyzed through focused ion beam (FIB) images as shown in Figure.3.12. The thickness of the EHDA deposited organic PVDF layer was 450 nm, and that of R2R-AALD deposited inorganic SiO_2 layer was 70 nm. The higher thickness of the organic layer

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provides the delayed penetration of molecules to the inorganic layer. The results of the FIB image clearly showed the existence of each layer separately.

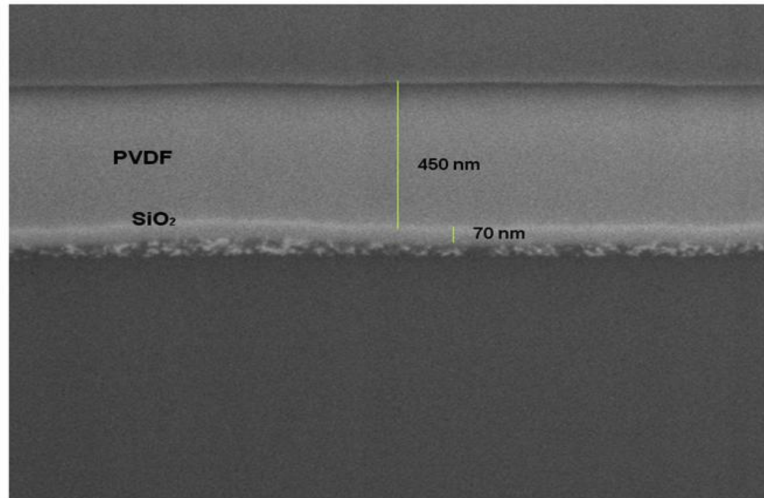

Figure.3.12. The FIB cross-sectional image illustrating the thickness of the each layer.

3.3.2. Compositional Analysis

The chemical composition of each thin film was carried through the X-ray photoelectron spectroscopy (XPS). The XPS analysis for SiO_2, PVDF and hybrid PVDF/SiO_2 thin films are shown in Figure.3.13.The R2R-AALD deposited SiO_2 thin film XPS results exhibited excellent quality chemical composition. XPS results of the EHDA deposited PVDF, and hybrid PVDF/SiO_2 thin films also revealed a good quality chemical composition. Based on these chemical composition results it can easily be deduced that R2R-AALD with EHDA combined technique can fabricate high-quality multilayer barrier thin films. Figure.3.13. (a) presents the XPS results of the R2R-AALD deposited SiO_2 thin film, which contains Si2s, Si2p, Oxygen (O), and Carbon (C) peaks. The binding energy values attributed at 103.2 eV, 284.6 eV and 532.6 eV were a representation of silicon, carbon, and oxygen respectively. The Figure.3.13.(b) shows the pure PVDF, which contains only two major peaks such as carbon (C) and fluoride (F1s) which

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denotes the values of 285.4 eV (C) and 688.1 eV (F1s). The PVDF thin film XPS spectrum does not reveal any irrelevant particle in the film. Finally the hybrid PVDF/SiO_2 thin film XPS spectrum shown in Figure.3.13.(c). Clearly indicates the required peaks of fluoride (F1s), carbon (C), and oxygen (O). This hybrid PVDF/SiO_2 XPS results clearly exhibit that PVDF layer is perfectly coupled with SiO_2 thin films. These hybrid chemical composition results were well matched in the previously reported literature. Based on the XPS results affirmed the fabricated barrier thin films shows pure and excellent quality. Based on the XPS results it is affirmed that the fabricated barrier thin films show pure and excellent quality.

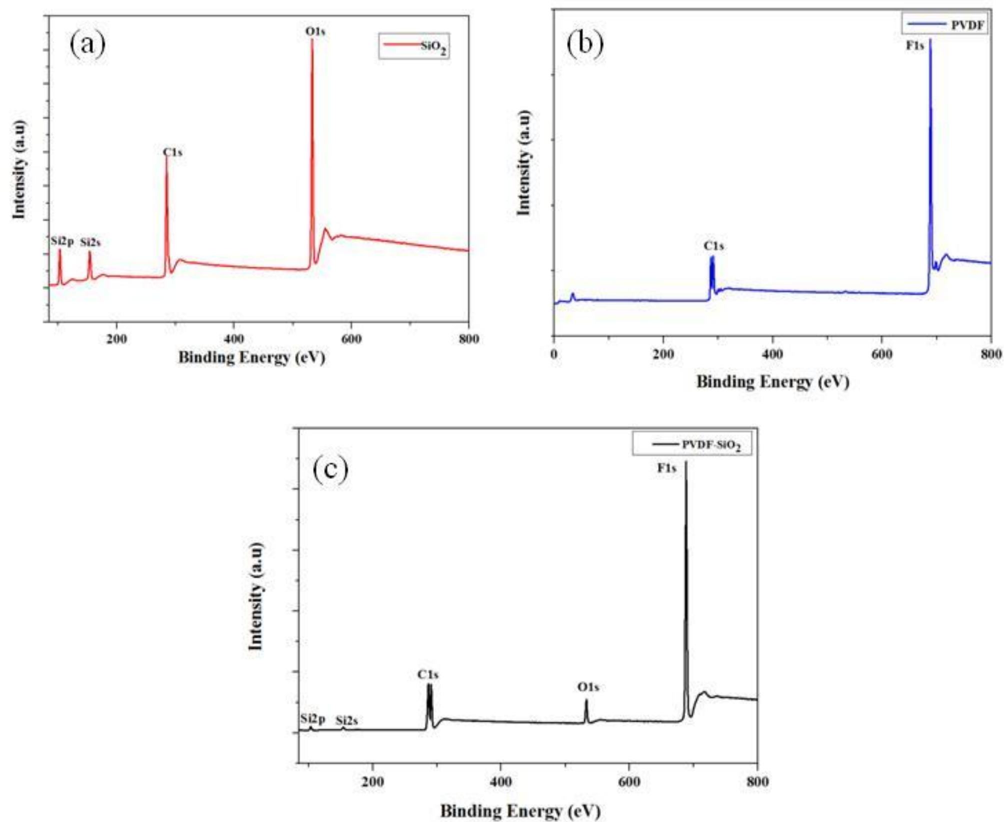

Figure.3.13.XPS spectrum of the multilayer barrier thin film : (a) R2R-AALD SiO_2 thin film (b) EHDA deposited PVDF thin film , (c) Hybrid PVDF/SiO_2 barrier thin film.

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3.3.3. Optical transmittance

The optical properties of the barrier thin films are presented in Figure.3.14. The device to be protected by barrier layer encapsulation requires higher transparency for optical applications. This is because most of the materials have to hinder properties against atmospheric molecules, but it has a poor optical transparency range. Obviously, such materials cannot be applied for the optical applications such as OLEDs, solar cells, and other organic electronics barrier layer production. The transparency range of the barrier PVDF/SiO_2 and SiO_2 thin films were measured by UV-visible spectroscopy. The figure displayed the optical transmittance range of the SiO_2 thin film to be 92% in the visible region. The hybrid PVDF/SiO_2 barrier thin film also exhibited very good optical transmittance, which concludes that the organic PVDF membrane does not damage the optical transmittance property of barrier thin films. These results clearly signify that the fabricated multilayer barrier hybrid thin films are suitable for barrier application in flexible organic electronic devices.

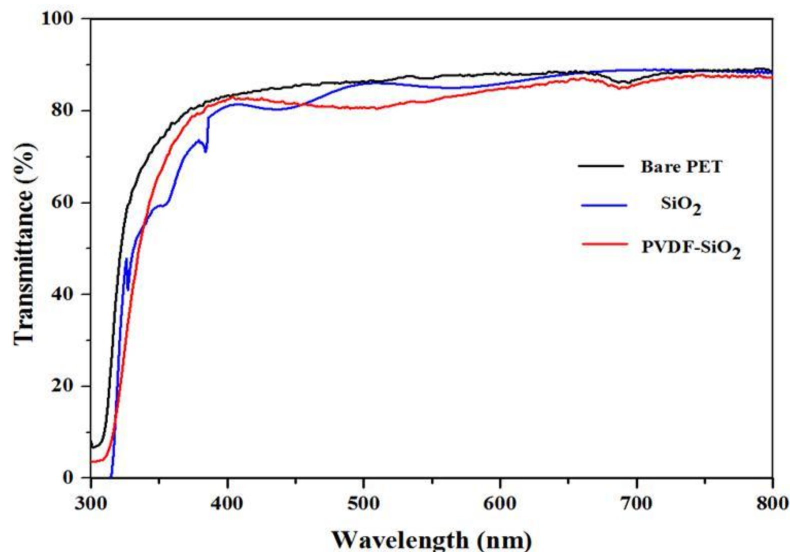

Figure.3.14. UV-vis optical transmittance value of the multilayer barrier thin films with the comparison of bare PET substrate.

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3.3.4. Barrier Properties

The barrier properties such as WVTR permeation range was performed through the MOCON (AQUATRAN Model 1). The process was carried out under the conditions of 37.8 ºC and 23 ºC at 100% relative humidity. The SiO_2 single layer WVTR results show 1.1×10^{-1} g m^{-2} day $^{-1}$. It can be deduced on the basis of the WVTR value that the as-fabricated SiO_2 layer at low temperature has shown better results as compared to the other reported SiO_2 layers deposited at a higher temperature through ALD system. When the PVDF organic layer was introduced on top of SiO_2 layer, the range of WVTR value improved to 0.9×10^{-2} g m^{-2} day $^{-1}$ as shown in Figure.3.15.

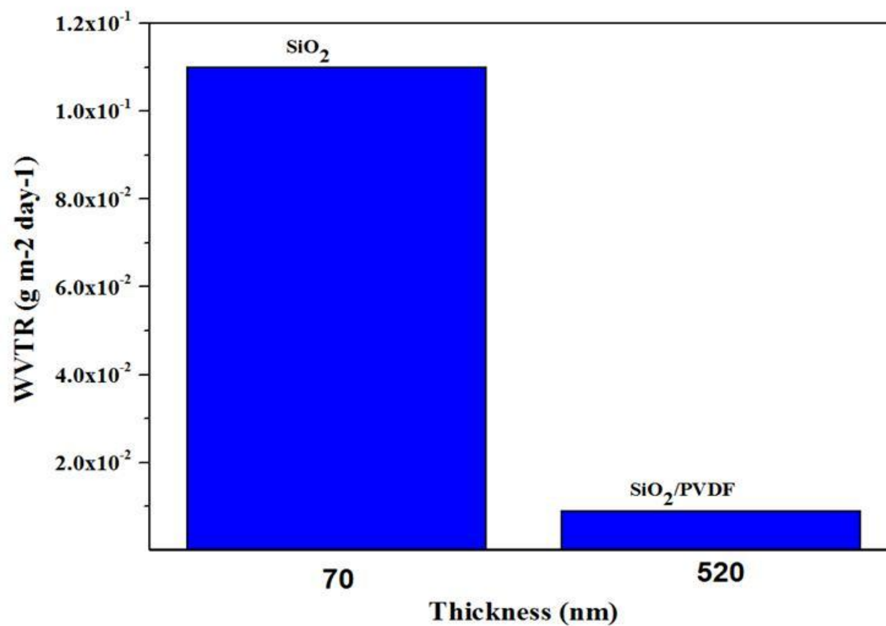

Figure.3.15. The WVTR values of the single and multilayer barrier thin film depending on the film thickness. The image shows that the decrease in WVTR value increases the film thickness.

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The presence of pinholes in the bottom layer of SiO_2 is inevitable that allows the water vapors and oxygen to penetrate through it, however, by depositing the second layer of PVDF, these pinholes are blocked and hence the permeability of water vapors and oxygen is reduced as indicated by the WVTR values. The thickness of SiO_2 is only 70 nm, therefore, higher thickness value of PVDF (450 nm) also plays a vital role in elongating the delay time of water vapors to diffuse through the hybrid barrier thin film. The mechanism of water vapors and oxygen permeability through the hybrid barrier thin film is illustrated in Figure.3.16. The combination of R2R-AALD and EHDA offers a good quality of barrier thin film, and it can be utilized as a gas barrier in the organic electronics industry.

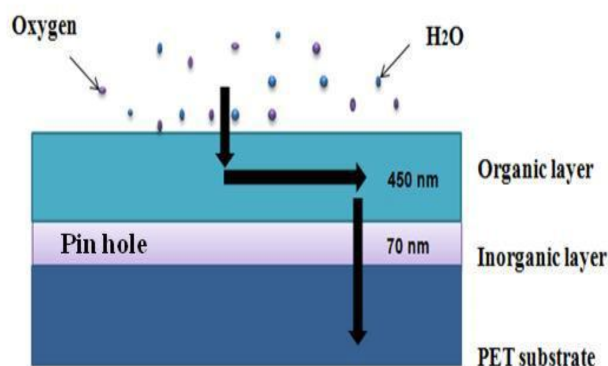

Figure.3.16. The schematic illustration of the multilayer barrier thin film working mechanism in the atmospheric molecules.

3.3.5. Mechanical properties

Determination of the permeation of barrier thin film before and after bending test is shown in Figure.3.17. The importance of the bending test is required for the flexible barrier thin film to

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check its resistance against strain induced by bending machine.The addition of organic PVDF layer on the surface of SiO_2 layer enhances the flexibility of barrier thin film as organic polymers have a high value of elastic modulus that protects them under large applied stress and does not allow cracks to appear on their surface.The barrier thin film was achieved after 500 bending cycles, but there were no significant changes in the obtained WVTR results. Due to Bending test results clearly showed that the organic PVDF layer was mechanically stable and also it perfectly decoupled with the SiO_2 thin film. Based on the mechanical bending test, this PVDF/SiO_2 multilayer barrier thin film can sustain the higher mechanical stress.

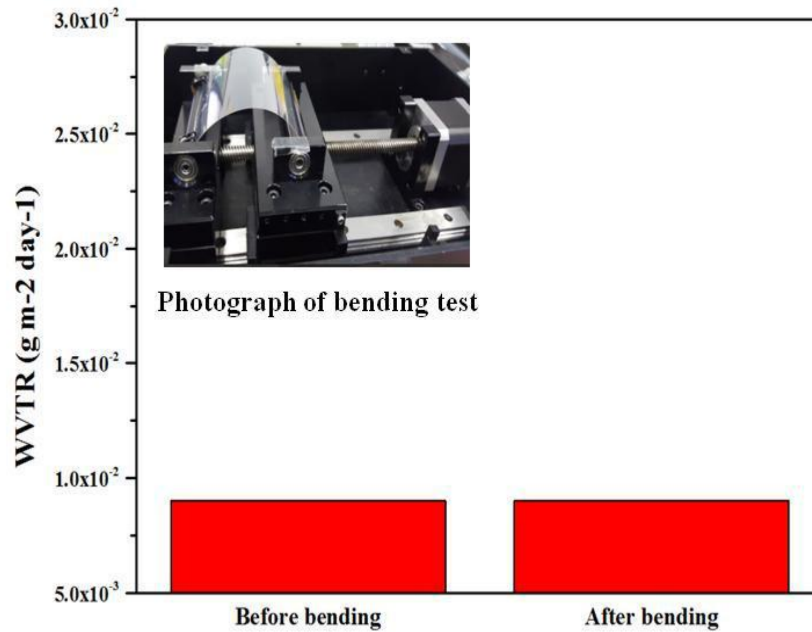

Figure.3.17. The water vapor transmission rate (WVTR) of the multilayer barrier film before and after bending test.

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CHAPTER4

4.Conclusions and future work

The thesis has reported the improving the surface and barrier properties of different thin films through the unique roll-to-roll atmospheric chemical & atomic layer deposition system has realized great achievements and has contributed towards further clearance of R2R deposition system.

The TiO_2 film was successfully fabricated over the flexible polyethylene terephthalate (PET) substrate by roll-to-roll atmospheric chemical vapor deposition method. The fabrication process was performed at different temperatures under atmospheric pressure and successfully characterized using different physiochemical methods. The morphology and topography analysis revealed that TiO_2 film prepared at 100° C showed good surface and film quality. Moreover, TiO_2 film exhibited a 91.2% optical transmittance property which is higher than earlier reported methods. From the aforementioned results, we concluded that the R2R-ACVD method is highly useful in the mass production of TiO_2 film that can be applied in the field of biosensor and electronics applications.

The R2R-AALD system was successfully made single layer Al_2O_3 thin film under 50 °C on PET substrates moving at velocity of 7mm /sec under nearly atmospheric pressure of 740 Torr. Arithmetic roughness (Ra) values of around 1.57 nm was recorded for the Al_2O_3 films, indicating their good surface morphology. The XPS analyses confirmed the growth of single layer Al_2O_3 films at 50° C via the R2R-AALD system. The single layer Al_2O_3 films showed better barrier properties.

In this study, we established a multilayer barrier PVDF/SiO_2 hybrid barrier thin film through combining R2R-AALD and EHDA fabrication techniques. The barrier thin film expressed

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significant physical and chemical properties. The arithmetic roughness of the barrier thin film was 3.88 nm with very good contact angle (125º). The chemical composition results clearly illustrated that the fabricated barrier thin film is of good quality with no impurities. The optical transmittance range of the barrier and SiO_2 thin films were observed more than 85-90 %. The WVTR of the hybrid PVDF/SiO_2 barrier film showed ~ 0.9×10^{-2} g m^{-2} day^{-1}. Even after bending test of more than 500 cycles, no noticeable changes in the barrier films were observed. The combination of R2R-AALD with EHDA developed barrier thin film showed good quality and promising results for gas barrier application in the electronics industry.

The presentation of R2R innovation has made new research openings which can be performed later on.

1. The developed metal oxide and nitride materials for single and multilayer barrier application using R2R deposition system. To fabricates the supreme quality of inorganic barrier thin film using atmospheric low-temperature deposition process (RT-50 ºC).

2. To develop novel superhydrophobic hybrid organic/Inorganic thin films for protecting gas species from the environmental.

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