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	<p>Study of Al<sub>2</sub>O<sub>3</sub> Thin Films Fabricated through Atomic Layer Deposition on Polymer Substrates      Kamran Ali • 2013</p>
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**A THESIS  
FOR THE DEGREE OF MASTER OF SCIENCE**

**Study of Al<sub>2</sub>O<sub>3</sub> Thin Films Fabricated through Atomic  
Layer Deposition on Polymer Substrates**

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**2013.02**

**Study of Al<sub>2</sub>O<sub>3</sub> Thin Films Fabricated through Atomic Layer  
Deposition on Polymer Substrates**

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A thesis submitted in partial fulfillment of the requirement for the of Master of Science

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## Abstract

A broad window of research opportunities has been opened in field of ALD due to the most latest and advanced trends in this technology such as spatial ALD and roll to roll ALD. The roll to roll ALD technology has got a great edge over other trends because it is capability to process various kinds of flexible substrates such as PEN,PET and Polyamide etc. on large scale and this results in very high production at low cost. In this research work high quality  $\text{Al}_2\text{O}_3$  thin films have been deposited on flexible substrates at different deposition temperatures under carefully optimized set of process parameters. The deposition temperature has been varied from room temperature to 200 °C to analyze its effect on the qualities of the films.

In the first phase high quality  $\text{Al}_2\text{O}_3$  thin films has been deposited on polyethylene-naphthalate (PEN), polyethylene terephthalate (PET) and polyamide substrates under different deposition temperatures. The deposited  $\text{Al}_2\text{O}_3$  films were carefully characterizad through various techniques. Ellipsometry, field-emission scanning electron microscope (FESEM), NanoView high accuracy 3D nano non- contact surface profiler, X-ray photoelectron spectroscopy (XPS) and also the UV and IV characterizations are performed for the films. The results showed that  $\text{Al}_2\text{O}_3$  films with excellent morphological features have been deposited at a suitable growth rates under the selected deposition temperatures without any kind of contaminations.

In the last phase  $\text{Al}_2\text{O}_3$  films deposited at different temperatures were exposed to plasma enhanced flourination (PEF) treatment by using  $\text{C}_3\text{F}_8$  gas to ehance their hydrophobicity for the sake of functionality improvement. The results shoed that the treatment was resulted in the production of high quality  $\text{Al}_2\text{O}_3$  films with excellent hydrophobicity.

This research work can act as a roadmap for the roll to roll ALD of  $\text{Al}_2\text{O}_3$  on PEN, PET and polyamide substrates and can provide guide lines regarding various important process

parameters like deposition temperature and ALD process cycles etc. and can also help in room temperature ALD processes.

# 1. Introduction

Atomic layer deposition (ALD) is an advanced thin-film deposition technique that enables the production of high-quality coatings on a range of materials. The technique's layer-by-layer growth assures precise control of film thickness even at relatively low process temperatures. Similar process control, mild deposition conditions and high film quality combined with low thickness is difficult to obtain with other thin-film deposition techniques.

Significant early development for ALD was done under the name Atomic Layer Epitaxy (ALE) with the desire to manufacture thin film electroluminescent (EL) displays. Later, materials deposited by ALD found other applications such as solar cells, microelectronics, gas sensors, optics, and protective coatings. One of the key strengths of ALD is its capability to deposit conformal coatings with uniform thickness on even the most demanding topologies. This property has led to ALD being used in the most demanding applications such as coating of nanometer scale structures like catalytic particles and microelectromechanical systems (MEMS).

Since the inception of this technology the application areas of the ALD process have been greatly extended, and the main drivers for that include the continuous dimensional downscaling of microelectronic devices, requirements for lower film growth temperatures (especially in the case of polymer substrates), and growing list of different materials obtainable by the ALD technique (oxides, nitrides, metals, and even polymers). Due to the increasing demand and advantages of this technology the world is moving towards more productive and economic trends of ALD. The most latest and advanced trends of ALD are spatial ALD and roll to roll ALD. The roll to roll ALD technology has got a great edge over other trends because it is capable to process various kinds of flexible substrates such as PEN, PET and Polyamide etc. on large scale and this results in very high production at low cost. It is the main motivation for my work because at present time this technology is the most suitable candidate to revolutionize the field of atomic layer deposition. It has a high potential for mass production and has also

the capability to process flexible substrates which are of the most priority in printed electronics industry. Modern age printed electronics industries are manufacturing highly sophisticated electronic devices on flexible substrates. Most of these electronic devices are manufactured under room conditions in printed electronics industry and this special feature opens the window of great opportunities to utilize roll to roll ALD in the manufacturing process. The most important opportunity is the use of roll to roll ALD in the fabrication of passivation layers such as  $\text{Al}_2\text{O}_3$  on devices built on flexible substrates to control the water transmission and oxygen transmission in to the device. Apart from the advantages there are some challenges and limitations in roll to roll ALD and one of them is the process temperature. Most of the flexible substrates are sensitive to higher temperatures and get damage if exposed more than a certain period of time. Also if the processing temperature is very high then the first chemical reactant may decompose on the surface before having time to react with the second reactant. In that case the growth rate would be higher than one would expect from ALD an ALD process. Alternately, if the first precursor is stable it may still desorb from the surface before having a chance to react with the second reactant. Under these circumstances the growth rate would be less than expected. This would be more likely with a physisorbed first reactant than a chemisorbed one. Most of the work regarding ALD on flexible substrates has been reported at as low processing temperatures as possible. Very low temperature may also produce undesirable results. When the temperature is very low then the reaction rate may be so slow that the reaction may be too long compared to a practical cycle time (e.g. hours rather than seconds) or may the adsorption of more than one mono layer per cycle can take place or even condense a liquid or solid on the surface of the substrate. To avoid these undesirable conditions the roll to roll ALD process must be carried out under an optimal range of temperature.

$\text{Al}_2\text{O}_3$  ALD using trimethylaluminum ( $\text{Al}(\text{CH}_3)_3$ ) and water ( $\text{H}_2\text{O}$ ) is one of the most studied ALD systems.  $\text{Al}_2\text{O}_3$  ALD can be deposited on thermally sensitive polymers because  $\text{Al}_2\text{O}_3$  ALD can be conducted at temperatures as low as  $33^\circ\text{C}$ . The ability to coat  $\text{Al}_2\text{O}_3$  onto polymers provides a pathway to fabricate inorganic-organic composites with novel properties. The  $\text{Al}_2\text{O}_3$  ALD films can be used to form gas diffusion barriers on polymeric substrates to prevent  $\text{H}_2\text{O}$  and  $\text{O}_2$  permeation. Lifetime



improvements of organic light-emitting diodes (OLEDs) also resulted from plasma-enhanced  $\text{Al}_2\text{O}_3$  ALD films.

This work reports on the atomic layer deposition of  $\text{Al}_2\text{O}_3$  thin films from  $\text{Al}(\text{CH}_3)_3$  and  $\text{H}_2\text{O}$  on various kinds of flexible substrates (PEN, PET and Polyamide) at temperatures down to room temperature. The main focus of this work is to study and analyze the growth characteristics and properties of the  $\text{Al}_2\text{O}_3$  thin films produced under different temperatures on different types of flexible substrates and to extract the most optimal temperature ranges for  $\text{Al}_2\text{O}_3$  ALD on PET, PEN and Polyamide. Apart from that, the importance of this research work is to thoroughly study and analyze all the results and information's which are obtained from conventional thermal ALD and then develop a guide line and roadmap to perform experimentation of roll to roll ALD of  $\text{Al}_2\text{O}_3$  on PEN, PET, Polyamide and other kinds of flexible substrates.

The conditions for ALD are investigated in terms of layer characterizations including thickness measurement, refractive index, U-V, I-V, Contact Angle, surface morphology and chemical compositions.

## 2. Background

### 2.1. Thin Films Fabrication

Thin film technology is simultaneously one of the oldest arts and one of the newest sciences. Involvement with thin films dates to the metal ages of antiquity where they were first used for decorative purposes. Consider the ancient craft of gold beating, which has been practiced continuously for at least four millennia. Thin films are still used today for decorative or protective purposes: to form conductors, resistors, and other types of films in microelectronic circuits; to form photovoltaic devices for conversion of solar energy to electricity; and for many other applications. A thin film might be made of any kind of material, including metals, metal oxides, metal nitrides or mixed materials.

The term thin film does not have a precise definition. In general, it refers to a three dimensional film less than about 100  $\mu\text{m}$  thick and as thin as a few nanometers. A thin film is a liquid or a solid such that one of the dimensions of the film, the film's thickness, is smaller than the other two dimensions, by several orders of magnitude. Typically thin films are made by deposition of individual atoms or molecules, while thick films are made by deposition of particles. Examples of thick film techniques are painting, silk screening, spin-on glass coating, and plasma spraying. The thick film techniques are important and relatively inexpensive, but they do not offer as much control of the material quality as do thin film techniques. Note that films deposited by a thin film technique can be thicker than those deposited by a thick film technique. This thesis presents the thin films fabrication on various kinds of flexible substrates such as PET, PEN and Thick polyamide using the technology of atomic layer deposition.

For a thin film to be useful, it should possess all or most of the following properties:

- a. It should be chemically stable in the environment in which it has to be used.
- b. It should well adhere to the substrate.
- c. It should have a uniform thickness.
- d. It should be chemically pure or of controlled chemical composition.
- e. It should have a low density of imperfections.

All thin film processes contain the four or five major sequential steps.

1. A source of film material is provided.
2. Transportation of the film material or precursors to the substrate
3. Deposition of the film materials
4. Sometimes subsequent annealing of the film is required,
5. Film analysis to evaluate the process.

The results of the analysis are then used to adjust the conditions of the other steps for film property modification. Additional process control and understanding are obtained by monitoring the first three steps during film deposition.

The source of the film-forming material may be a solid, liquid, vapor, or gas. Solid materials need to be vaporized to transport them to the substrate, and this can be done by heat or by an energetic beam of electrons, photons (laser ablation), or positive ions (sputtering). These methods are categorized as physical vapor deposition (PVD). In other cases, the source material is supplied as a gas or as a liquid having sufficient vapor pressure to be transported at moderate temperatures. Thin film processes that use gases, evaporating liquids, or chemically gasified solids as source materials are categorized as chemical vapor deposition (CVD). In both PVD and CVD contamination and supply rate are the major source-material issues. Contamination is also an issue in the transport and deposition steps. Supply rate is important because film properties vary with deposition rate and with the ratio of elements supplied to compound films.

In the transport step, the major issue is uniformity of arrival rate over the substrate area. The factors affecting this uniformity are very different, depending on whether the transport medium is a high vacuum or a fluid. In a high vacuum, molecules travel from the source to the substrate in straight lines, whereas in a fluid there are many collisions among molecules during the transport step. Consequently, in a high vacuum, uniformity of source-material arrival rate at the substrate is determined by geometry, whereas in a fluid it is determined by gas flow patterns and by diffusion of the source molecules through the other gases present. Often, the high-vacuum processes are equated with physical vapor deposition, and the

fluid-flow processes are equated with chemical vapor deposition. However, this is not always a valid association. Although many physical deposition processes do operate in a high vacuum, others like laser ablation and sputtering often operate at higher pressures characteristic of a fluid. Similarly, although most chemical deposition processes operate at fluid pressures, chemical beam epitaxy operates in a high vacuum.

The high-vacuum transport medium has the important advantage of clear access to the deposition surface. This allows energy input from an ion beam and allows the use of analytical techniques involving electron beams, such as electron diffraction and Auger spectroscopy. On the other hand, the fluid medium has the advantage that it functions at atmospheric pressure or at easily achieved moderate vacuum levels. In both media, contamination can be dealt with equally well and using similar techniques.

Many thin film processes operate in plasma. Plasma is a partially ionized gas and is often regarded as the fourth state of matter (solid, liquid, gas, and plasma). Plasmas contain a great deal of energy, which can activate film deposition processes at low temperature. The plasma operating pressure can be such that it behaves either as a fluid or as a high-vacuum medium.

The third step in the thin film process is the actual deposition of the film onto the substrate surface. Deposition behavior is determined by source and transport factors and by conditions at the deposition surface. There are three principal surface factors, which determine the deposition behavior. These factors are:

1. Substrate surface condition
2. Reactivity of the arriving material
3. Energy input.

Substrate surface condition includes roughness, level of contamination, degree of chemical bonding with the arriving material, and crystallographic parameters in the case of epitaxy. The reactivity factor refers to the probability of arriving molecules reacting with the surface and becoming incorporated into the film. This probability is known as the “sticking coefficient,”  $S_c$ , and is a measure of the fraction of incident molecules which adsorb upon the surface i.e. it lies in the range 0-1, where the limits correspond to no

adsorption and adsorption of all incident molecules respectively. In general,  $S_c$  depends upon many variables i.e.  $S_c$  is a function of surface coverage, temperature, crystal face etc.  $S_c$  is generally lower for CVD than for PVD processes.

The third deposition factor is energy input to the surface. It can come in many forms and has a profound effect on both the reactivity of arriving material and on the composition and structure of the film. Substrate temperature is the basic source of energy input, but there are many other sources. Photons are used in photo-assisted and laser-assisted deposition. Positive ion bombardment carries very large amounts of energy. It is present in most plasma processes and in some high-vacuum processes. Chemical energy is carried by inherently reactive source molecules and by molecules that have been dissociated in the course of vaporization or plasma transport. In summary, the three deposition factors of substrate condition, reactivity, and energy input work together with the arriving fluxes to determine the structure and composition of the deposited film.

The final step in the deposition process is analysis of the film. One level of analysis consists of directly measuring those properties that are important for the application at hand, such as the thickness of a film, the breakdown voltage of an insulator, or the index of refraction of an optical film. Many film deposition processes are optimized using the empirical approach of measuring key film properties as a function of the process variables that can be varied in the first three steps of the deposition. A deeper level of analysis involves probing the film's structure and composition, since those are the factors that determine the observed properties. This type of analysis is generally more difficult, but it provides a bridge between the deposition step and the final film properties. This bridge leads to a better understanding of the overall process.

Analysis of the film after deposition can be thought of as the final stage of process monitoring. Monitoring is important at all steps in the thin film process. The more monitoring that can be done during deposition; the better will be both the control and the understanding of the process. For example, the supply rate of each source material can be continuously metered and feedback-controlled. The composition of the transport medium can be analyzed for both reactant concentration and contaminants.

## 2.2 Atomic Layer Deposition (ALD)

Atomic Layer Deposition (ALD) is a chemical gas phase thin film deposition method. It belongs to the group of Chemical Vapor Deposition (CVD) methods. A characteristic of this group is that the films are formed via chemical reactions as opposed to PVD methods where the films are formed mainly via physical material transport.

The film deposition by ALD occurs via alternating, self-limiting surface reactions. As a result of the self-limiting reactions, growth by ALD, or in the ALD mode, is saturated. This means that the film forming reactions proceed to completion, and then stop. Thus, each ALD cycle results in precisely the amount of material deposited regardless of the exposure once the saturation threshold is exceeded.

In ALD, the film growth takes place in a cyclic manner. In the simplest case, one cycle consists of four steps:

1. Exposure of the first precursor
2. Purge by gas flow, or evacuation of the reaction chamber
3. Exposure of the second precursor
4. Purge or evacuation.

First the vapors of the precursor 1 are allowed in to the reactor (1), which reacts with the surface in a saturating manner until a monolayer has been chemisorbed and no further adsorption takes place. Then the reaction stops, so the process is called 'self-limiting'. Any excess precursor is then evacuated or purged out (2). A second vapor, from precursor 2 is entered in to the reactor (3), and then reacts with this surface in a second self-limiting reaction, thus depositing a second layer of atoms onto the first. The second reaction must also return the surface to a state in which it is ready to react with the first reactant. This is followed by another evacuation (4). The cycle of reactions can then be repeated to build up a binary compound atomic layer.

The self-limiting growth mechanism gives ALD a number of advantageous features such as:

- Accurate and simple thickness control
- Large-area and large batch capabilities
- Excellent conformity
- Good reproducibility
- Capability to produce sharp interfaces
- High quality materials can be obtained at low processing temperatures

The most important parameter available in controlling the saturation mechanism of an ALD process is the processing temperature. The overall effect of temperature on the growth characteristics can be illustrated by a temperature window of ALD processing,

The concept of the ALD window can be used to describe the temperature dependent processes which may or may not lead to film growth in the ALD mode (Fig.2.1). Processes leading to non-saturative growth, with either too high or low growth rates, occur outside the ALD window. An increased growth rate may either result from precursor condensation at too low temperatures, or from precursor decomposition at too high temperatures. Alternatively, a decreased growth rate may be a result of incomplete reactions at the low temperature regime, or of precursor desorption at too high temperatures. In the ALD window, the growth rate may or may not be dependent on temperature, depending on the particular process. The growth in the ALD window is, however, always saturated.

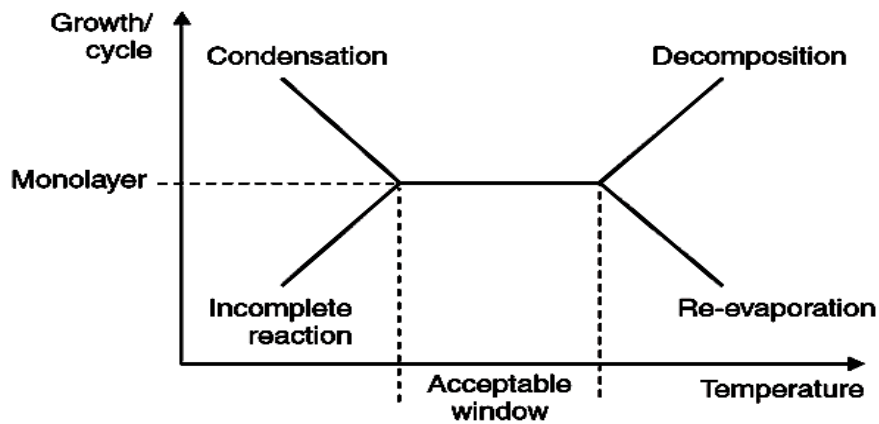


Fig. 2.1: Growth rate vs temperature

## 2.3 ALD Precursors

Chemistry, especially the choice of proper precursors, is the key issue in a successful design of an ALD process. The requirements for ALD precursors are as follows:

- Volatility
- No self-decomposition
- Aggressive and complete reactions
- No etching of the film or substrate materials
- No dissolution into the film or substrate
- Unreactive volatile byproducts
- Sufficient purity
- Inexpensive
- Nontoxic and environmentally friendly

For a successful ALD process the most important precondition is a favorable chemistry of the surface reactions. A unique feature of the ALD process is that each vaporous reactant reacts separately with a solid surface. Accordingly, vapor phase reactions between the reactants are eliminated. At the same time the surface structures formed in each gas-solid reaction must be stable against desorption and stay reactive for the next reaction sequence. For a complete saturation of the monolayer formed in each reaction sequence and for a high material utilization factor, ALD favors highly reactive reactants, which is in contrast to the basic demand on reactants in conventional CVD processes.

The vapor pressure of the reactants in the ALD process must be high enough for effective material transport. In order to prevent condensation of the reactant on the substrate the vapor pressure used must be obtained at a temperature not higher than the substrate temperature used. The reactant must be thermally stable at the substrate temperature i.e. reaction temperature. Reactants that must be heated above room temperature for the necessary vapor pressure need heated transport channels.



Table 1.1, summarizes some of the reactants used in ALD for different materials.

Film	Precursors	Temperature °C	Application
Al <sub>2</sub> O <sub>3</sub>	Al(CH <sub>3</sub> ) <sub>3</sub> , H <sub>2</sub> O or O <sub>3</sub>		High-k dielectric
AlN			
Cu	CuCl, Cu(thd) <sub>2</sub> or Cu(acac) <sub>2</sub> with H <sub>2</sub> , Cu(hfac) <sub>2</sub> xH <sub>2</sub> O with CH <sub>3</sub> OH	360-410, 175-300, 250, 203-300	Interconnect
HfO <sub>2</sub>	HfCl <sub>4</sub> or TEMA, H <sub>2</sub> O		High-k dielectric
Mo	MoF <sub>6</sub> , MoCl <sub>5</sub> or Mo(CO) <sub>6</sub> with H <sub>2</sub>	200-500, 500-1100, 200-600	
Ni	Ni(acac) <sub>2</sub> , 2 step process NiO by O <sub>3</sub> reduced afterwards by H <sub>2</sub>		
SiO <sub>2</sub>	SiCl <sub>4</sub> , H <sub>2</sub> O		Dielectric
Ta	TaCl <sub>5</sub> ,		Barrier
TaN	TBTDET, NH <sub>3</sub>	260	Barrier, deposited with plasma enhancement
TaO <sub>2</sub>			
Ti	TiCl <sub>4</sub> , H <sub>2</sub>		Glue layer, deposited with plasma enhancement
TiN	TiCl <sub>4</sub> or TiI <sub>4</sub> , NH <sub>3</sub>	350 - 400	Barrier
TiO <sub>2</sub>			High-k dielectric
TiSiN			
W	WF <sub>6</sub> , B <sub>2</sub> H <sub>6</sub> or Si <sub>2</sub> H <sub>6</sub>	300 - 350	Interconnect plug fill
WN			Barrier
WN <sub>x</sub> C <sub>y</sub>	WF <sub>6</sub> , NH <sub>3</sub> , TEB (triethylboron)	300 - 350	

Table 1.1: Precursors and deposited film materials

A wide variety of materials can be deposited using ALD and the most commonly deposited materials are represented in the periodic table given below.

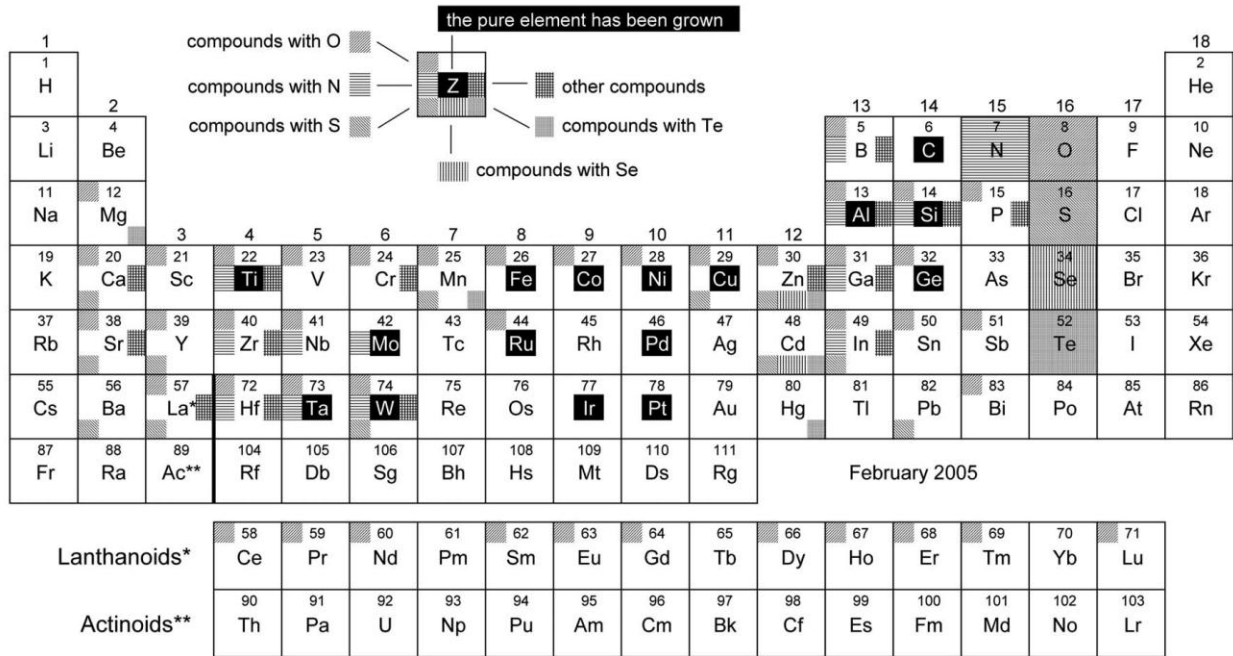


Fig. 2.2: Overview of the materials grown by ALD

## 2.4 Applications of Atomic Layer Deposition.

### TFEL Displays

The first applications in this respect were electroluminescent films for large area, thin film electroluminescent displays (TFEL). This results from the need for a film growth method to deposit dense, void-free thin films of equal thickness onto large-area substrates. With its inherent self-limiting film growth, the ALD method is best suited for this application. In fact, Suntola's invention, among others, described the formation of epitaxial ZnS layers for such purposes. In addition, ion diffusion barriers as well as dielectric layers or transparent electrodes needed in TFELs were made by ALE.

## **Compound Semiconductors**

ALD was further also applied to the epitaxy of III-V and II-VI compound semiconductors. Especially the growth of GaAs and GaAs-based ternary alloys like AlGaAs or InGaAs for transistors and semiconductor optical devices attracted widespread attention in this respect but also other III-V materials such as phosphides and nitrides have been grown by ALD techniques. Among the II-VI compounds, considerable work has been conducted with respect to chalcogenides such as sulfides, selenides, and tellurides . In most cases this research was driven

by the need for optically active materials in TFEL devices, but has recently experienced more attention by the emerging field of phase-change memory devices. However, with molecular beam epitaxy (MBE), metal-organic vapor phase epitaxy (MOVPE) and metal-organic CVD (MOCVD) continuing to be the dominant techniques for the growth of III-V semiconductors, until about ten years ago ALD has mainly been applied to the niche market of the TFEL displays for which it had originally been developed.

## **High-k Oxides and Conductive Nitrides**

Only with the increasing demand for ultra-thin, high-quality films for manufacturing semiconductor electronic devices, ALD has been gaining increasing attention. Especially the formation of high-permittivity insulators, or high-k dielectrics, based on alumina, zirconia, hafnium oxide or different rare earth oxides is under consideration . Current applications of these ALD-grown films include capacitor dielectrics for dynamic random access memory (DRAM) devices. Furthermore, approaches for the gate dielectric/metal stack in the next CMOS generations using ALD-grown high-k oxides and metal electrodes are under intense study to date. Particularly, high-k gate oxides deposited by ALD have been introduced into semiconductor manufacturing at the 45 nm technology node, for example by the Intel Corporation. For future technology nodes, ALD is also seen as an enabling technology for CMOS devices that integrate semiconductor materials other than silicon. Especially for III-V

semiconductors or germanium, adequate solutions for the gate insulator and passivation have to be found. In this respect, there are several approaches and promising examples of ALD high-k films both for III-V and Ge integration.

Emphasis is further put onto the conductive nitrides, carbides, and carbonitrides of Ta, Ti or W. ALD processes to deposit such films are mainly being developed with respect to electrodes for DRAM memory capacitors, gate electrodes in combination with high-k dielectrics as well as diffusion barriers in ULSI copper metallization technology.

### **Photovoltaics**

With photovoltaics gaining considerable attention to date, ALD work is also being conducted in this subject area, for both bulk semiconductor and thin-film solar cells. Among the materials fabricated by ALD for these purposes are semiconducting films as well as passivation layers and electrodes. In this respect, ALD is also gaining momentum for applications with alternative photovoltaic devices such as dye-sensitized and organic solar cells.

### **Fuel Cells**

Apart from the photovoltaic technology, fuel cells are becoming increasingly important as alternatives to conventional forms of energy supply, be it for powering electrically driven cars or as substitute for solid-state batteries to power electronic gadgets like laptops. As compact yet energy-efficient solid oxide fuel cells (SOFC) require their components such as ceramic or metallic films to be fabricated ultra-thin and potentially also with high surface area per unit volume, ALD is being explored as a method to form the functional films required, such as solid electrolytes, ion conductors, as well as noble metal films for catalyst layers or electrodes.

### **Organic Electronics and TFT Displays**

Another noteworthy and continuously emerging application area of ALD is the field of organic electronics. For most such devices like organic light emitting diodes (OLEDs) and polymer-based electronic circuits capping layers as moisture and gas diffusion barriers are indispensable. With its ability

to deposit dense, ultra-thin films, ALD has been shown to be a viable method for providing such films even at the low processing temperatures the organic substrates demand. Organic and inorganic displays such as OLED arrays or thin film transistor (TFT) devices require transparent conductive oxide layers (TCO) for electrodes or as the active element. While so far indium tin oxide (ITO) has mostly been the material of choice for such purposes, alternatives are sought as indium resources are finite and thus becoming increasingly expensive. ALD-grown, doped zinc oxide such as aluminum zinc oxide (AZO), as well as B or Ga doped ZnO are likely as replacements since their properties can be controlled by direct doping during deposition. Such approaches have been demonstrated both on organic substrates as well as for transparent TFT display devices.

### **Novel Nanostructures and Organic/Inorganic Composites**

With the advent of novel, synthetic nanostructured materials ALD is more and more also becoming an enabling technology for an increasing number of applications in micro and nanotechnology. For example, ALD is finding applications in micromechanics and micro optics, such as for conformal depositing wear-resistant coatings and encapsulating layers in micromechanical devices, for replicating template structures to form photonic crystals or other functional nanostructures.

Furthermore, there are approaches of creating composite materials, such as carbon nanotubes that are coated with magnetic, oxidic, or catalytically active materials, as well as organic and biological materials such as polymer fibers or cotton whose structure is being replicated in inorganic, ALD-grown films. Even viruses and DNA molecules have been used as templates for ultra-thin films deposited by ALD techniques. With respect to organic materials, a related method dubbed molecular layer deposition (MLD), first described in the early 1990s, is again gaining attention, both for the formation of ultra-thin polymer films with layer-by-layer control as well as for growing composites of polymers and inorganic compounds.

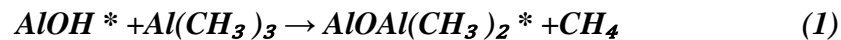
Most of these examples, however, make use of metal oxides or other metal compounds such as nitrides, carbides or sulfides. The ALD of metallic films, in contrast, still requires great research efforts since in most cases the processes are more sophisticated. To a large extent this is due to the character of the ALD

technique itself, for ALD is based on reacting a metal or semiconductor compound with a second reaction partner to form the desired material, as will be described hereafter. Consequently, the method is best suited to form compounds. In contrast, the precursors must be reduced for growing elemental metals by ALD directly. This puts great challenges on the precursor selection as well as the ALD processes themselves.

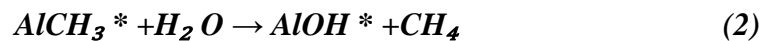
## 2.5 Atomic Layer Deposition of Al<sub>2</sub>O<sub>3</sub>

The Al<sub>2</sub>O<sub>3</sub> films can be grown from trimethylaluminium (TMA; Al(CH<sub>3</sub>)<sub>3</sub>) and water (H<sub>2</sub>O) or ozone (O<sub>3</sub>). The TMA-H<sub>2</sub>O process is considered to be a near-ideal ALD process and the reaction mechanisms are well understood. Al<sub>2</sub>O<sub>3</sub> is non-toxic and non-flammable and has a melting point of 2050 °C. In controlled conditions Al<sub>2</sub>O<sub>3</sub> forms highly even and uniform surface films, and is for this reason considered to be an excellent diffusion barrier. The growth of Al<sub>2</sub>O<sub>3</sub> films is relatively straightforward by means of ALD.

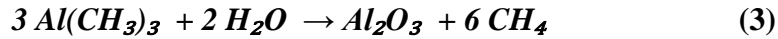
Water vapor in the air is adsorbed onto most surfaces, forming hydroxyl (OH-) groups. When the substrate is placed in an ALD reactor chamber and TMA is pulsed into the chamber, the TMA (g) reacts with the (OH-) groups on the surface of the substrate as shown in reaction (1). Methane (CH<sub>4</sub> (g)) is simultaneously produced as a by-product, whereas the asterisk represents surface species.



The reaction continues until the surface is passivated with Al-O-Al(CH<sub>3</sub>)<sub>3</sub> (s). TMA does not react with itself, which terminates the reaction to one layer. The deposition continues by pulsing H<sub>2</sub>O into the reaction chamber. H<sub>2</sub>O reacts with the methyl groups (CH<sub>3</sub>) forming O-Al bridges and OH- groups as shown in reaction (2). Again, CH<sub>4</sub> is produced as the by-product, and pumped away.

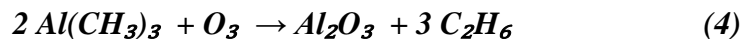


The excess H<sub>2</sub>O again does not react with the OH- groups, thus terminating the reaction to one atomic layer. After these two half reactions, one ALD cycle is completed. The whole ALD cycle can be described as reaction (3).



The number of surface OH--groups influences the number of chemisorbed species. Although considered near-ideal, there are some drawbacks to the TMA-H<sub>2</sub>O process. Steric hindrance of precursors can influence on the film growth. In addition, the applied layer does not always form a fully smooth surface and the layer can have islets.

The use of O<sub>3</sub> instead of H<sub>2</sub>O as the oxygen source is in some cases desired due to the higher activity of O<sub>3</sub> in ligand elimination. Another reason for favoring O<sub>3</sub> is that it does not absorb as easily as H<sub>2</sub>O into the reactor walls, thus facilitating purging. Due to these properties, better quality films could be obtained. On the other hand, a morphological characterization study has shown that O<sub>3</sub> can also yield lower-quality films than H<sub>2</sub>O. The films can be less dense and rougher, especially at low growth temperatures. When O<sub>3</sub> is used as the oxygen source for the preparation of Al<sub>2</sub>O<sub>3</sub> films, the following reaction (4) is suggested to take place.



The complex reaction mechanism and the use of O<sub>3</sub> in the fabrication of Al<sub>2</sub>O<sub>3</sub> layers have been previously studied mainly for the needs of microelectronic applications. It is assumed that during the O<sub>3</sub> pulse, O<sub>3</sub> decomposes into O<sub>2</sub> and monoatomic O which is the active species. The efficiency of this decomposition reaction is believed to be temperature-dependent. The study of O<sub>3</sub> decomposition showed that the use of O<sub>3</sub> could yield lower growth per cycle (GPC) rates compared to the corresponding H<sub>2</sub>O process. The different growth mechanism and high reactivity of O<sub>3</sub> may result in a different film structure.

## 2.6 Applications of Al<sub>2</sub>O<sub>3</sub> thin films

Aluminum oxide has suitable properties for many applications.

- As thin films, Al<sub>2</sub>O<sub>3</sub> can be used as a dielectric, passivation and protecting material. The most important use is the surface passivation of electronic devices and solar cell to prevent the water vapors transmission and oxygen transmission in to the devices.
- It has a moderately high dielectric constant ( $\kappa = 9$ ), and a high electric field strength. Aluminum oxide also has a high band-gap, 8.7 eV. These properties make it an attractive material for gate dielectric in metal-oxide-semiconductor (MOS) transistors.
- Al<sub>2</sub>O<sub>3</sub> ALD films on electrostatically actuated polysilicon cantilever beams prevent electrical shorting and increase the number of actuation cycles before device failure.
- Al<sub>2</sub>O<sub>3</sub> ALD films on bilayer (Au/Si) cantilever beams prevent creep during high temperature holding.
- Al<sub>2</sub>O<sub>3</sub> ALD films on surface-micromachined gears can serve as friction and wear-resistive coatings.
- Thin Al<sub>2</sub>O<sub>3</sub> ALD films (25Å) can serve as adhesion layers for the attachment of hydrophobic precursor molecules, which results in robust and reliable hydrophobic coatings to prevent moisture-induced stiction.
- Alloys of Al<sub>2</sub>O<sub>3</sub> ALD and ZnO ALD can be used to prevent stiction due to dielectric charging in gold RFMEMS devices.
- In a biocompatibility test, adherence of vascular smooth muscle cells was superior on Al<sub>2</sub>O<sub>3</sub> ALD surfaces when compared to glass surfaces.
- Al<sub>2</sub>O<sub>3</sub> ALD films have been used to construct nano-scale devices such as deformable membranes and cantilever beams.
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### 3. Experimental

#### 3.1. Reactor Design for ALD.

The schematic and experimental setup of the ALD reactor is shown in Fig. 3.1 and Fig. 3.2.

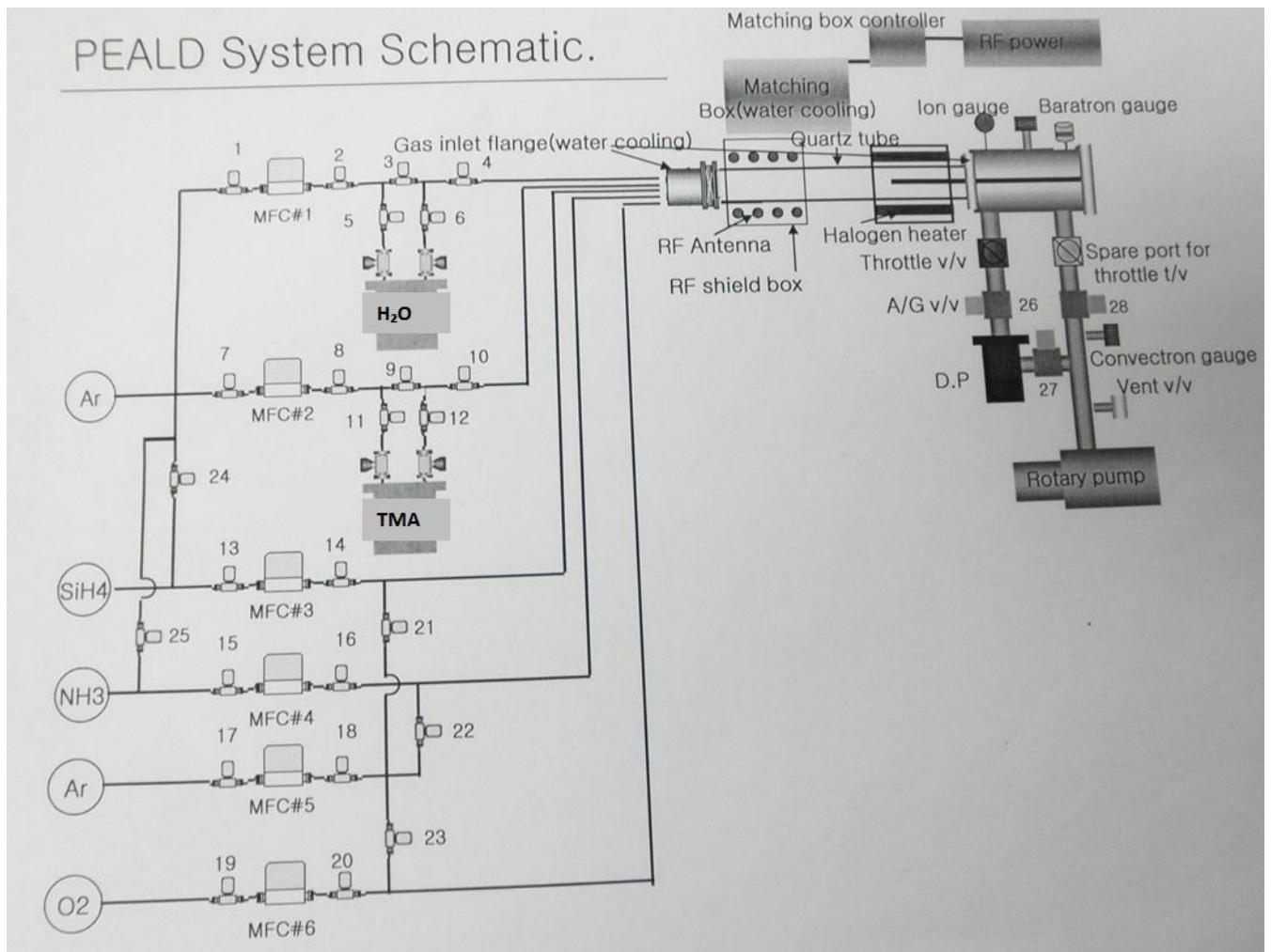


Fig. 3.1: The schematic of the ALD reactor.

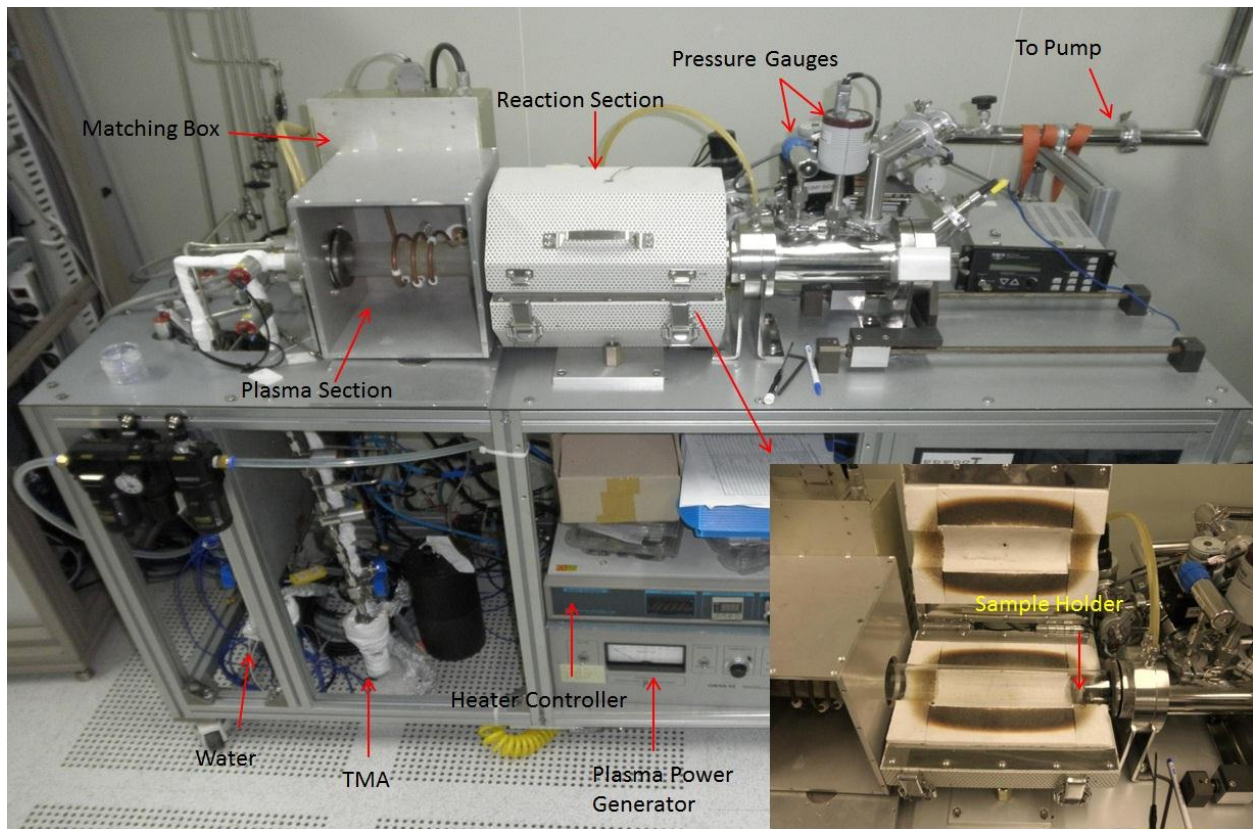


Fig.3.2: Experimental setup of the ALD reactor.



Fig.3.3: Control system of the ALD reactor.

The apparatus has been designed in such way that it can be used in both PEALD modes as well as in thermal ALD mode. Depending upon the requirement, different gases can be used by selecting the respective gas channel as shown in the Fig.3.1. In this case argon was used as a carrier gas and the maximum allowable size of the sample is 3X3 cm<sup>2</sup> and the system was used in thermal ALD mode. The main parts of ALD experimental setup are:

1. Reaction section
2. TMA and Water canisters.
3. Heater Controller
4. Pressure Gauges
5. Vacuum Pump
6. Mass Flow Controllers
7. ALD control system

The precursors are heated to the required temperature using heating tapes and the vapors are transported to the reaction section through argon gas. The flow of argon gas is precisely controlled by mass flow controllers (MFC). The precursors are transported to the reaction section in separate pulses for a controlled period of time and react with the substrate. After each pulse the byproducts and unreacted gases are purged out using vacuum pump. The temperature inside the reaction section is controlled by heater controller. The vacuum inside the reactor is monitored by vacuum gauges. The heating tapes, Vacuum gauges, MFC's, Valves and ALD Cycle time are controlled by their control system shown in Fig.3.3. The control panel is a touch screen device and allows the user to easily set, monitor and control all the operating parameters of ALD process.

### 3.2. Precursors and Substrates.

The precursors used in this research work are trimethylaluminum (TMA,  $\text{Al}(\text{CH}_3)_3$ ) and water. The reason for using these precursors is their ability to produce  $\text{Al}_2\text{O}_3$  passivation coatings on flexible substrates such as PEN, PET and polyamide for electronic devices. Also  $\text{Al}_2\text{O}_3$  passivation coatings on the flexible substrates is the main candidate for roll to roll atomic layer deposition technology which is the most latest trend in the field of ALD. The TMA / $\text{H}_2\text{O}$  process still seems a good choice as one of the most representative processes, for at least four reasons.

First, the TMA/ $\text{H}_2\text{O}$  process represents “thermal ALD.” The advantage of thermal ALD over various “energy enhanced” ALD processes is that thermal ALD processes fulfill best the requirement of self-terminating reactions on complex three-dimensional 3D substrates. In energy enhanced processes, typically utilizing energetic but unstable reactants such as ozone or plasma, problems with conformality may arise through reactant decomposition, at least on 3D substrates.

Second, the TMA/ $\text{H}_2\text{O}$  process deposits an oxide material and uses water to deposit it. Oxides are the inorganic materials most frequently grown by ALD, and water is the most frequently used oxygen source.

Third, the TMA/ $\text{H}_2\text{O}$  process uses trimethylaluminum as the aluminum source. If a choice is made to review the growth characteristics of aluminum oxide (the growth of another metal oxide could as well have been chosen), TMA is a justified choice as the aluminum source, as it is perhaps the most commonly used aluminum source in ALD.

Further advantages of using TMA, as a general example, is that the reactions are rather ideal: the reactions are truly self-terminating, the TMA reactant is highly reactive and many types of compounds have been grown from it (oxides, nitrides, arsenides, and pure Al), and the gaseous reaction products (methane) are rather inert. Many other reactant classes, such as elements, halides, alkoxides, would have difficulties fulfilling at least some of these criteria, whereas alkyls, cyclopentadienyls, and perhaps amidinates fulfill them better. A disadvantage in using an alkyl reactant, as a general example, is the fact that alkyls are available for a limited selection of elements. Some reaction mechanisms are likely to be

specific for the particular reactant or for the reactant group. A similar disadvantage of having reactant-specific or reactant-group-specific reactions would be encountered, however, for reactants from other groups as well.

Fourth, the TMA/H<sub>2</sub>O process is one of the most studied ALD processes. There is therefore a lot of material and literature work available to be considered before any experimentation.

Although it will not be possible to transfer the specific conclusions regarding the TMA/H<sub>2</sub>O process directly to other ALD processes, it is likely that if a specific physicochemical phenomenon is an issue for the TMA/H<sub>2</sub>O process, it will be so also for other ALD processes. Additional physicochemical phenomena may play a role in the surface chemistry of other ALD processes, caused, for example, by the occurrence of reactant decomposition (either purely thermally or through the use of energy-enhanced processes) or the formation of non-inert gaseous reaction products. Understanding these unideal phenomena should be possible through building additional models on top of the models describing ideal ALD systems.

The flexible substrates used in the present studies are Polyethylene terephthalate (PET), Polyethylene naphthalate (PEN) and Polyamide. The substrates were not pretreated before the deposition process. The reason is that roll to roll ALD is carried out under room conditions and therefore the aim is to check the quality of the coatings deposited on flexible substrates without any pretreatment. These substrates are easily available and are most commonly used in electronic industry and also in the research sector.

### 3.3 Thin Films Deposition

The thin films deposition was carried out in ALD reactor shown in fig. 5. The The ALD cycle was carefully optimized before conducting the experiments. This work contains the results of:

1.  $\text{Al}_2\text{O}_3$  thin films fabricated through atomic layer deposition on different kinds of polymeric substrates such PEN, PET and thick polyamide.
2. Plasma enhanced flourination (PEF) treatment of  $\text{Al}_2\text{O}_3$  thin films using  $\text{C}_3\text{F}_8$  gas to improve the hydrophobic properties of thin films.

The carefully optimized ALD cycle is maintained the same for all the experiments performed and is given below:

Sequence	Time (Sec)
TMA feeding	2
Ar purging	10
$\text{H}_2\text{O}$ feeding	2
Ar Purging	10

Table 2.1: ALD process cycle

Substrate	Temperature( °C)	No. Of Cycles
PET	RT	500
	50	
	100	
	150	
	200	
PEN	RT	500
	50	
	100	
	150	
	200	
Polyamide	RT	500
	50	
	100	
	150	
	200	

Table 2.2: ALD deposition temperatures and number of cycles.

Using the same ALD cycle and temperature range  $\text{Al}_2\text{O}_3$  coatings were deposited on PEN substrates for the PEF treatment. The operating parameters for plasma enhanced fluorination treatment using  $\text{C}_3\text{F}_8$  are given below:

Treatment	Power(watt)	Vacuum(Torr)	Time (min)
Argon Cleaning	100	0.5	5
O <sub>2</sub> Cleaning	100	0.5	5
C <sub>3</sub> F <sub>8</sub> (Fluorination)	200	0.5	2

Table 2.3: Operating parameters for PEF treatment

The Al<sub>2</sub>O<sub>3</sub> thin films were prepared under the parameters shown in table 2.4 for the plasma enhanced treatment.

Substrate	Temperature	No. Of Cycles
PEN	RT	500
	100 °C	
	200 °C	

Table 2.4: Operating parameters of Al<sub>2</sub>O<sub>3</sub> ALD for C<sub>3</sub>F<sub>8</sub> plasma treated samples.



### 3.4 Thin Films Characterizations.

The deposited  $\text{Al}_2\text{O}_3$  films were carefully characterized through various techniques. The refractive index, film thickness and consequently the film growth rate were measured using a Gaertner L116D ellipsometer, the film's morphology and conformality were observed by using a JSM-6700F field-emission scanning electron microscope (FESEM) and NanoView high accuracy 3D nano non-contact surface profiler. The chemical composition and the impurity level were analyzed using VG Microtech XPS analysis equipment using Mg-K $\alpha$  radiation from an X-ray source operating at 12 kV, 15 mA. The UV characterization was done using Shimadzu UV-3150 UV/VIS/NIR spectrophotometer and For electrical characterization, the Agilent B1500A Semiconductor Device Analyzer coupled with MST8000C Probe Station having a current resolution of 1fA was used. The contact angle measurements were carried out with SEO Phoenix 3000 Touch using deionized water.

## 4. Results and discussions

### 4.1. Thickness measurement and Al<sub>2</sub>O<sub>3</sub> ALD growth rates.

The growth rates of Al<sub>2</sub>O<sub>3</sub> thin films deposited with TMA and H<sub>2</sub>O precursor on flexible substrates were studied as a function of deposition temperature and the results are presented in Fig. 4.1.

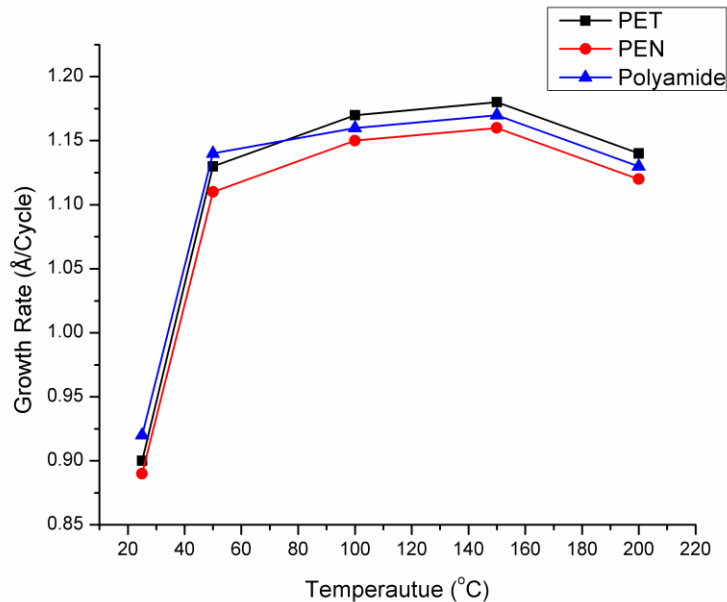


Fig.4.1: Growth rates of Al<sub>2</sub>O<sub>3</sub> thin films deposited on PET, PEN and Polyamide as a function of deposition temperature.

The results indicate that the Al<sub>2</sub>O<sub>3</sub> growth rate behavior as a function of deposition temperature was almost identical for PEN, PET and polyamide. The growth rates reached to the maximum values of 1.18Å/cycle, 1.16Å/cycle and 1.17Å/cycle for PEN, PET and polyamide substrates at a temperature of 150 °C. The growth rates are low at lower temperatures because of thermal activation barriers due to low temperature although there are higher Al-OH and Al-CH<sub>3</sub> surface coverages. The growth rates were decreased when the temperature was raised more than 150 °C. The decrease in growth rates at higher temperature can be explained by decrease in Al-OH and Al-CH<sub>3</sub> surface coverage although the reaction kinetics are more rapid. The OH groups are not stable at elevated temperatures: they may condense with

each other causing dehydroxylation of the surface. This dehydroxylation increases with increasing temperature causing decrease of the surface hydroxyl group density and results in low growth rates at higher temperatures.

The optimized self-limiting ALD process was confirmed by the measurements of film thickness against the number of TMA-H<sub>2</sub>O ALD cycles. Fig. 4.2 shows the Al<sub>2</sub>O<sub>3</sub> film thickness as a function of process cycles at 100 °C for PEN, PET and polyamide.

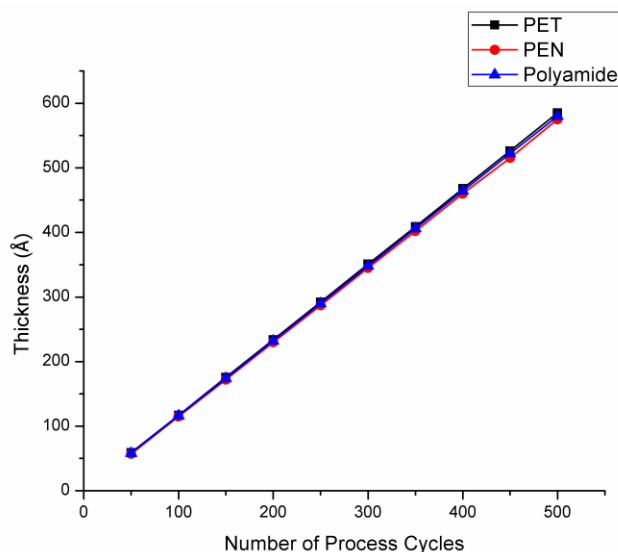


Fig. 4.2: Thickness of deposited Al<sub>2</sub>O<sub>3</sub> films on PET, PEN and polyamide substrates versus number of process cycles at 100 °C with 2.0 s exposure times.

These process cycles were performed using the following sequence: TMA feeding (2.0 s)/ purging (10 s)/ H<sub>2</sub>O feeding (2.0 s)/ purging (10 s). The growth rates are clearly constant versus number of process cycles and they are almost identical at the same deposition temperature of 100°C. Growth rates of 1.17 Å/cycle, 1.15 Å/cycle and 1.16 Å/cycle were observed for PET, PEN and polyamide substrates respectively. A linear dependence between the film thickness and number of process cycles repeated has been verified and confirmed the self-limiting mechanism of ALD. The linearity of the growth rates exhibits highly conformal Al<sub>2</sub>O<sub>3</sub> deposition on the PET, PEN and polyamide substrates.

The refractive index of the  $\text{Al}_2\text{O}_3$  films tends to decrease with decreasing deposition temperature. The results of these measurements are shown in Fig.4.3.

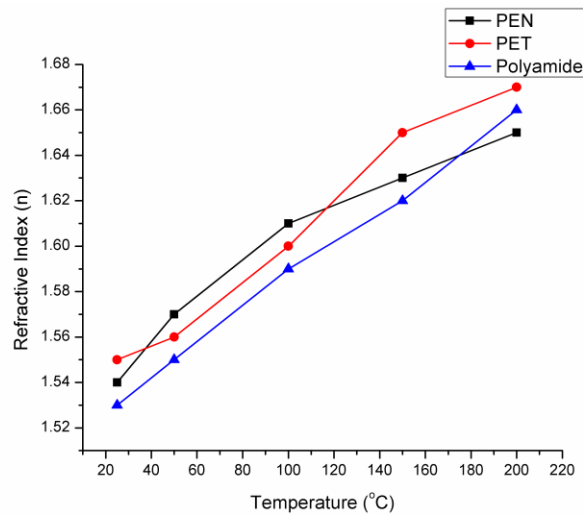


Fig.4.3: Refractive index of  $\text{Al}_2\text{O}_3$  vs deposition temperatures.

The refractive index was increased from 1.54, 1.55, and 1.53 at room temperature to 1.65, 1.67 and 1.66 at a deposition temperature of 200 °C for PEN, PET and polyamide substrates respectively. The increase in refractive index with the increase in deposition temperatures supports the good quality films.

## 4.2. Optical Properties of $\text{Al}_2\text{O}_3$ ALD thin films.

Aluminum oxide has enormous potential to be of use in optoelectronics and microelectronics devices. The properties of deposited  $\text{Al}_2\text{O}_3$  thin films depend on the deposition process and optimized parameters. To use the optical coating thin films in optoelectronic device formation having minimum optical signal transmission loss due to scattering of light, the reduction in defects and voids formation and improved surface morphology are the basic requirement.

The transmittance and absorption spectra of the  $\text{Al}_2\text{O}_3$  films deposited on PEN and polyamide substrates at deposition temperatures of room temperature (RT), 100 °C and 200 °C were measured to investigate

their optical properties. The optical transmission properties of  $\text{Al}_2\text{O}_3$  thin films deposited on PEN substrates at deposition temperatures of RT, 100 °C and 200 °C are shown in Fig. 4.4.

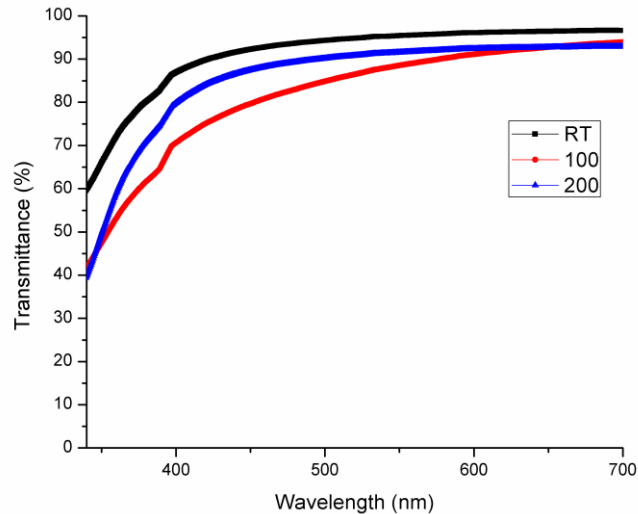


Fig. 4.4: The optical transmission properties of  $\text{Al}_2\text{O}_3$  thin films deposited on PEN substrates at deposition temperatures of RT, 100 °C and 200 °C.

As seen in Fig. 10, the transmittance spectra of the  $\text{Al}_2\text{O}_3$  films deposited at room temperature was more than 90 % in the visible region and decreases to the range of 80 % to 90 % for the films deposited at 200 °C. The films deposited at 100 °C showed optical transmittance in 70 % to 80 % range in the visible region. This decrease in optical transmittance can be attributed to the difference in the thickness of the thin films fabricated at different deposition temperatures. At room temperature the deposition rate is lower than that of at 100 °C and 200 °C which results in films of lower thickness with higher optical transmittance in visible range. The optical transmittance of the films deposited at 200 °C was higher than the films deposited at 100 °C because the deposition rate was lower at 200 °C than at 100 °C. This resulted in films with lower thickness and higher optical transmission at 200 °C as compared to films deposited at 100 °C.

The optical transmission properties of  $\text{Al}_2\text{O}_3$  thin films deposited on polyamide substrates at deposition temperatures of RT, 100 °C and 200 °C were also analyzed in visible range and the results are shown in Fig.4.5.

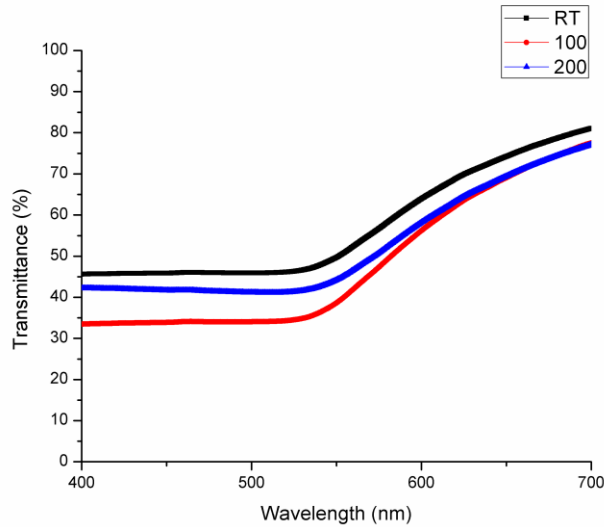


Fig.4.5: The optical transmission properties of  $\text{Al}_2\text{O}_3$  thin films deposited on polyamide substrates at deposition temperatures of RT, 100 °C and 200 °C.

Although the optical transmission of  $\text{Al}_2\text{O}_3$  thin films deposited on polyamide substrates is very low as compared to films deposited on PEN substrates yet the results showed a similar behavior of optical transmission dependency on deposition temperature as was noticed for PEN substrates. Maximum optical transmittance was observed for films deposited at room temperature because of minimum film thickness and minimum optical transmission was observed for films deposited 100 °C because of maximum film thickness due to maximum growth rate of  $\text{Al}_2\text{O}_3$  films. The lower optical transmission of  $\text{Al}_2\text{O}_3$  thin films deposited on polyamide substrates can be attributed to the nature of the polyamide substrates itself and not to the nature of  $\text{Al}_2\text{O}_3$  films because polyamide substrates are much darker in nature.

Fig.4.6 shows the absorbance of  $\text{Al}_2\text{O}_3$  thin films deposited on PEN substrates at deposition temperatures of RT, 100 °C and 200 °C.

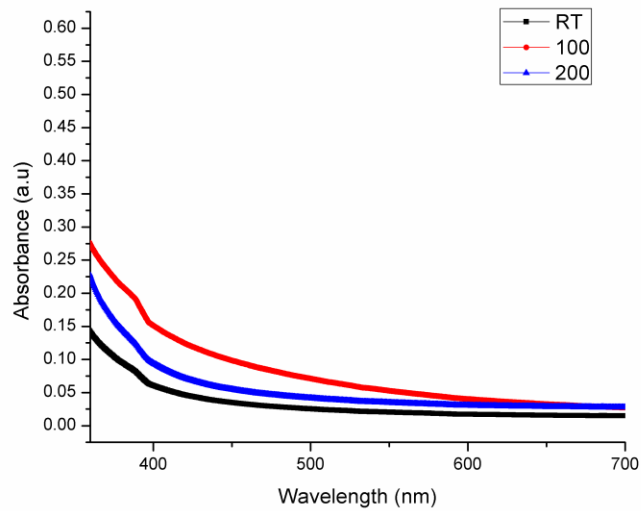


Fig. 4.6: absorbance of  $\text{Al}_2\text{O}_3$  thin films deposited on PEN substrates at deposition temperatures of RT, 100 °C and 200 °C.

It was observed that, absorbance increases with increase in thickness of the thin film in visible range. The films grown at room temperature were of minimum thickness and maximum thickness was observed for films grown at 100 °C. This behavior lead to the maximum absorbance of  $\text{Al}_2\text{O}_3$  thin films in visible range deposited at 100 °C and minimum absorbance for films deposited at room temperatures.

The absorbance of  $\text{Al}_2\text{O}_3$  thin films deposited on polyamide substrates at deposition temperatures of RT, 100 °C and 200 °C were also analyzed in visible range and the results are shown in Fig. 4.7.

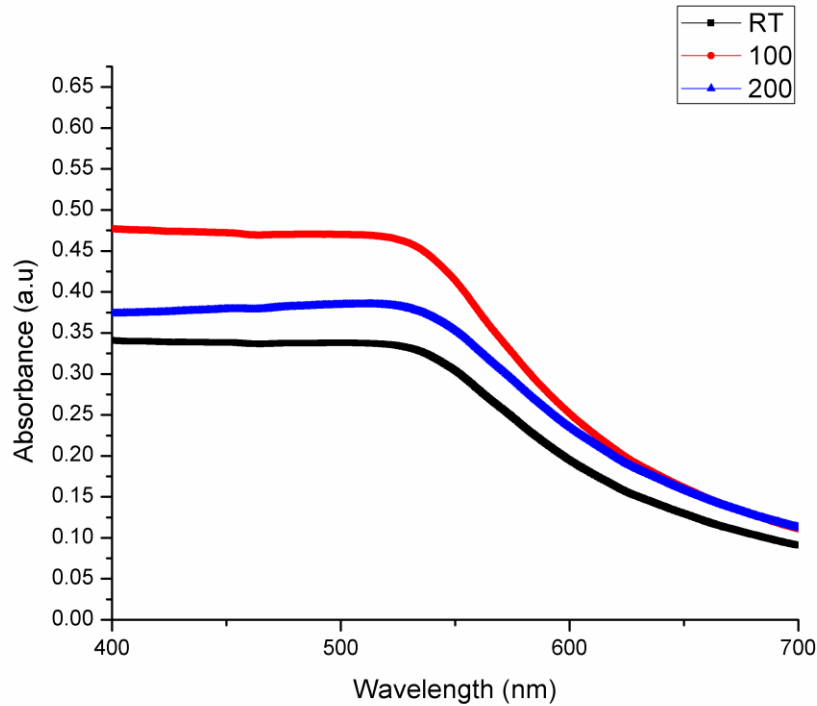


Fig. 4.7: absorbance of  $\text{Al}_2\text{O}_3$  thin films deposited on polyamide substrates at deposition temperatures of RT, 100 °C and 200 °C

The results showed a similar trend of absorbance dependency on deposition temperature as was observed for PEN substrates. The absorbance was minimum for the films deposited at room temperature and maximum for the films deposited at 100 °C. The films grown at room temperature were of minimum thickness and films grown at 100 °C were of maximum thickness. This lead to the conclusion that the absorbance is greatly related to the film thickness and it increases as the film thickness is increased. Very high absorbance was observed for  $\text{Al}_2\text{O}_3$  thin films deposited on polyamide substrates as compared to those deposited on PEN substrates because of the much darker nature of polyamide substrates.

The optical characterizations concluded that there is a strong dependency of optical properties i.e. transmittance and absorbance of  $\text{Al}_2\text{O}_3$  thin films on the deposition temperatures. The dependency trend was almost similar for both kinds of substrates i.e. PEN and polyamide. The thickness of  $\text{Al}_2\text{O}_3$  thin films deposited through ALD mainly depends upon the deposition temperature. Depending upon the growth behavior of  $\text{Al}_2\text{O}_3$  thin films under different deposition temperature the thickness will vary which



ultimately results in the variation in transmittance and absorbance properties of Al<sub>2</sub>O<sub>3</sub> thin films. The optical transmittance increases in visible range with the decrease in film thickness and the absorbance decreases with the decrease in film thickness and vice versa. Increase in absorbance with decrease in transmittance is co-related with each other with respect to thickness variation.

### 4.3. Electrical Properties of Al<sub>2</sub>O<sub>3</sub> ALD thin films.

The electrical properties i.e. I-V of Al<sub>2</sub>O<sub>3</sub> thin films deposited on PEN substrates were investigated vs. film thickness and deposition temperatures and the results are shown in Fig. 4.8 and Fig. 4.9.

Fig. shows the I-V plots of Al<sub>2</sub>O<sub>3</sub> thin films with different thickness ranging from 52 Å to 176 Å grown at 100 °C on PEN substrates. The results showed that Al<sub>2</sub>O<sub>3</sub> films were highly insulating and a decrease in current was observed with the increase in Al<sub>2</sub>O<sub>3</sub> films thickness. The results showed very low currents on the order of nano amperes (nA) at low applied potentials. However at higher electric potentials increase in current was observed up to applied potentials at which a catastrophic break down took place. This break down voltage was also increased with the increase in film thickness.

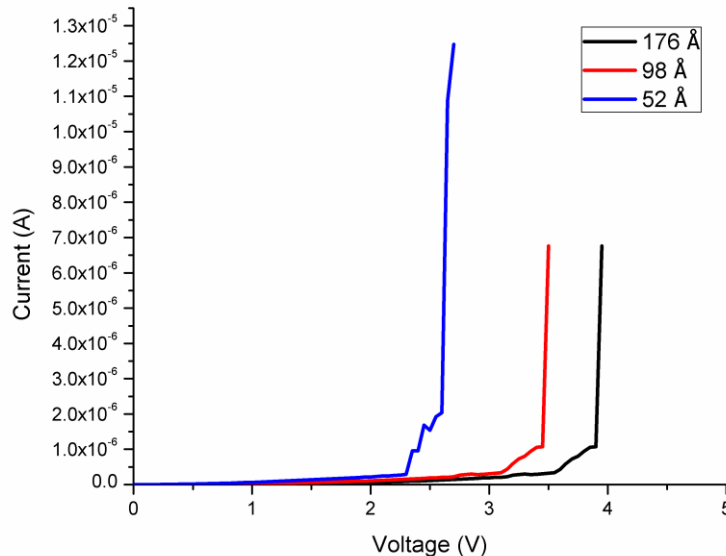


Fig. 4.8: the I-V plots of Al<sub>2</sub>O<sub>3</sub> thin films with different thickness ranging from 52 Å to 176 Å grown at 100 °C on PEN substrates

The I-V plots of Al<sub>2</sub>O<sub>3</sub> thin films deposited at different temperatures of RT, 100 °C and 200 °C on PEN substrates are shown in Fig. 4.9. The results showed very low currents on the order of nano amperes at low voltages for all the films deposited at different temperatures and then an increase in current was observed with the increase in voltage until a catastrophic break down was observed at higher voltages. The catastrophic voltage was increased with the increase in applied voltage. This behavior is attributed to the film thickness which is achieved at different deposition temperatures. The films grown at room temperature are of minimum thickness because of minimum growth rates of Al<sub>2</sub>O<sub>3</sub> thin films during ALD due to which the current values are maximum and the films grown at 100 °C are of maximum thickness because of maximum growth rates of Al<sub>2</sub>O<sub>3</sub> thin films during ALD due to which the current values are minimum.

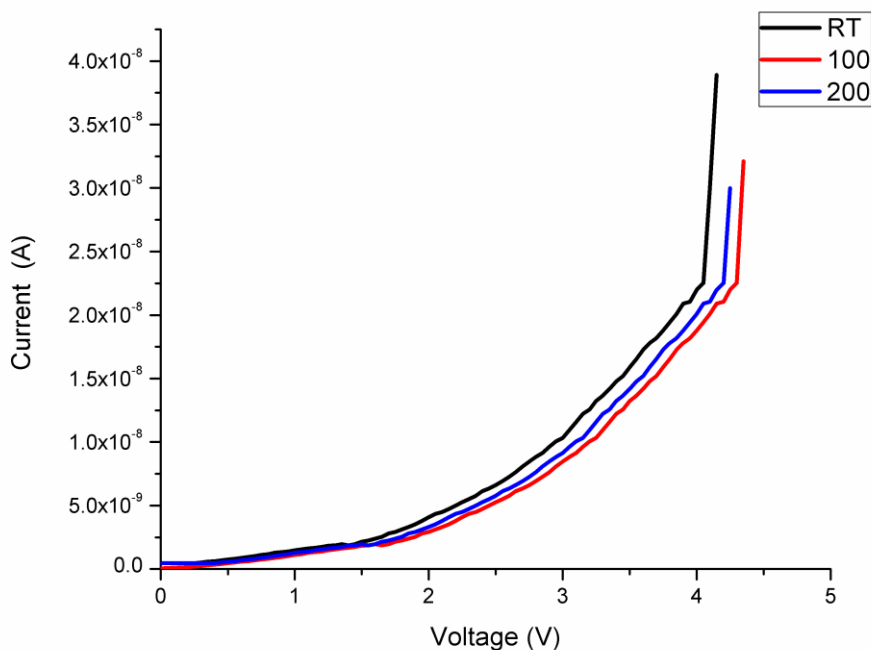


Fig. 4.9: The I-V plots of Al<sub>2</sub>O<sub>3</sub> thin films deposited at different temperatures of RT, 100 °C and 200 °C on PEN substrates.

The electrical characterizations conclude that the film thickness and the deposition temperatures have a mark effect on the I-V characteristics of the  $\text{Al}_2\text{O}_3$  films. The current is decreased with the increase in film thickness. The deposition temperature indirectly affects the electrical properties by controlling the film thickness. The films grown at low deposition temperatures are of low thickness and results in higher current values as compared to the films grown at higher temperatures with higher thickness of the films.

#### **4.4. Surface Morphology and Conformality of $\text{Al}_2\text{O}_3$ ALD thin films.**

The surface characteristics of the  $\text{Al}_2\text{O}_3$  films deposited on PEN, PET and polyamide substrates were investigated through field-emission scanning electron microscope (FESEM) and NanoView high accuracy 3D nano non- contact surface profiler. Fig. 10 shows the FESEM images of  $\text{Al}_2\text{O}_3$  films deposited on PEN substrates at different deposition temperatures of RT, 100 °C and 200 °C. The results showed that the surface uniformity increase with the increase in deposition temperature and more uniform particles were formed as the temperature was increased. The uniformity and particles size were less uniform and less fine for the films deposited at room temperatures Fig. 4.10(a), and Fig. 4.10(b). The uniformity of the films increased gradually and the more fine particles were formed as the temperature was raised from RT to 100 °C Fig. 4.10(c), and Fig.4.10(d) and 200 °C Fig. 4.10(e) and Fig. 4.10(f).

The FESEM analysis were also conducted for  $\text{Al}_2\text{O}_3$  films deposited on PET and polyamide substrates at different deposition temperatures of RT, 100 °C and 200 °C. The results were almost similar to those obtained from FESEM analysis of  $\text{Al}_2\text{O}_3$  films deposited on PEN substrates. Fig. 4.11 and Fig. 4.12 shows the FESEM images  $\text{Al}_2\text{O}_3$  films deposited on PET and polyamide substrates respectively at different deposition temperatures of RT, 100 °C and 200 °C. It is clear from the figures that the uniformity of the films was increased with the increase in deposition temperature from RT to 200 °C and also more uniform and fine size particles were obtained with the increase in temperature.

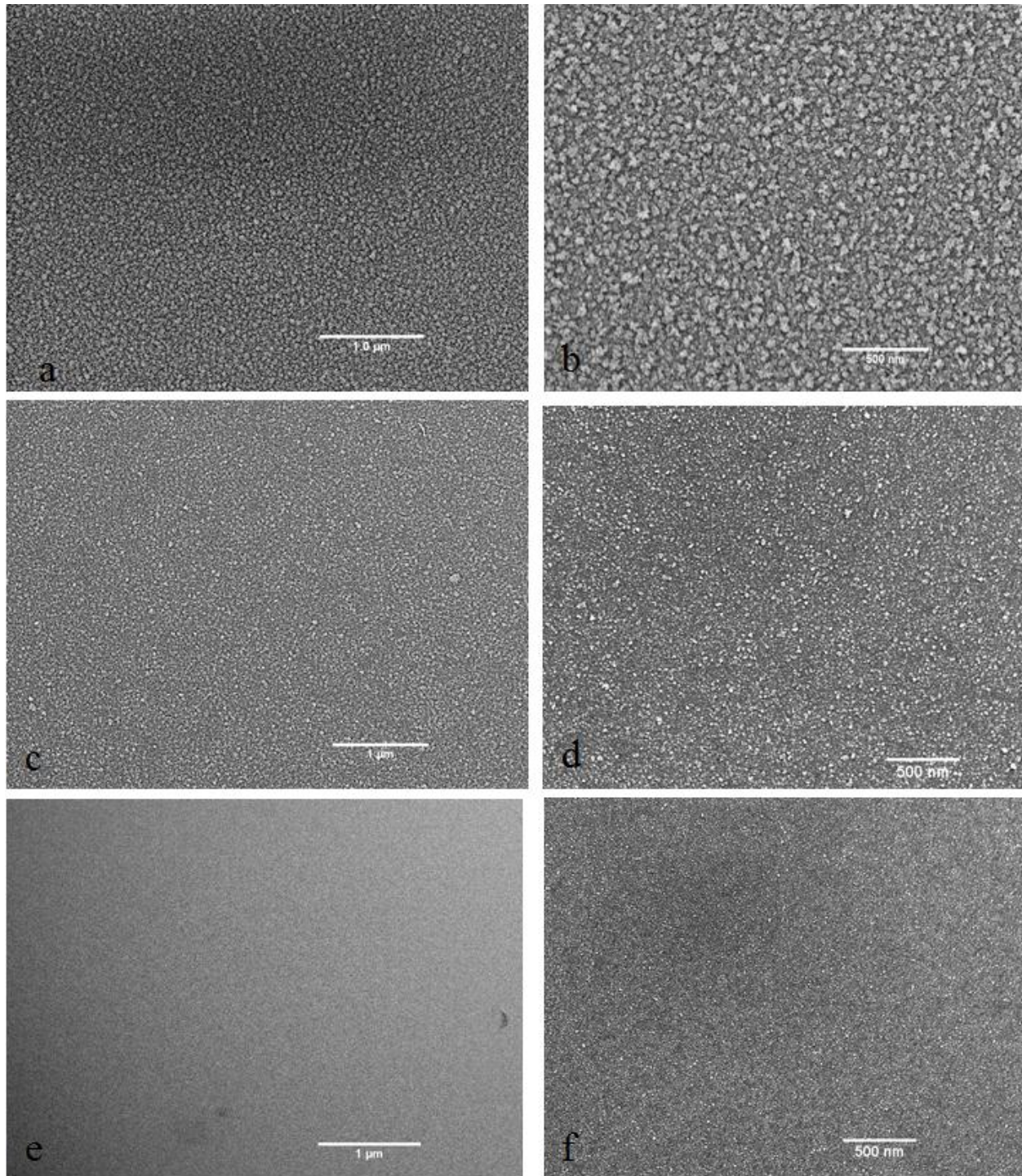


Fig. 4.10: The FESEM images of  $\text{Al}_2\text{O}_3$  films deposited on PEN substrates at different deposition temperatures of RT(a ,b), 100 °C (c ,d)and 200 °C (e ,f).

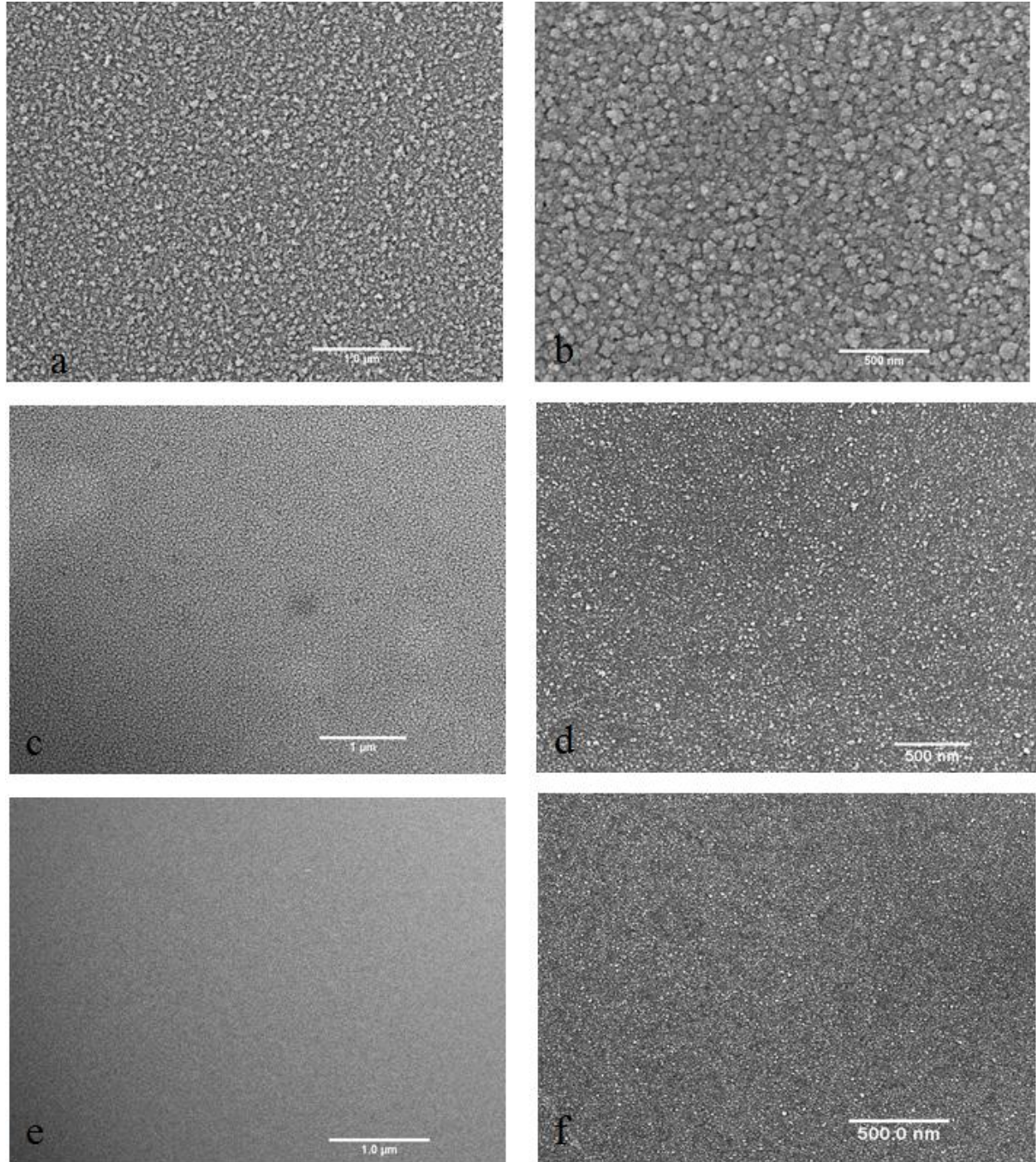


Fig. 4.11: The FESEM images of  $\text{Al}_2\text{O}_3$  films deposited on PET substrates at different deposition temperatures of RT(a ,b), 100 °C (c ,d) and 200 °C (e ,f).

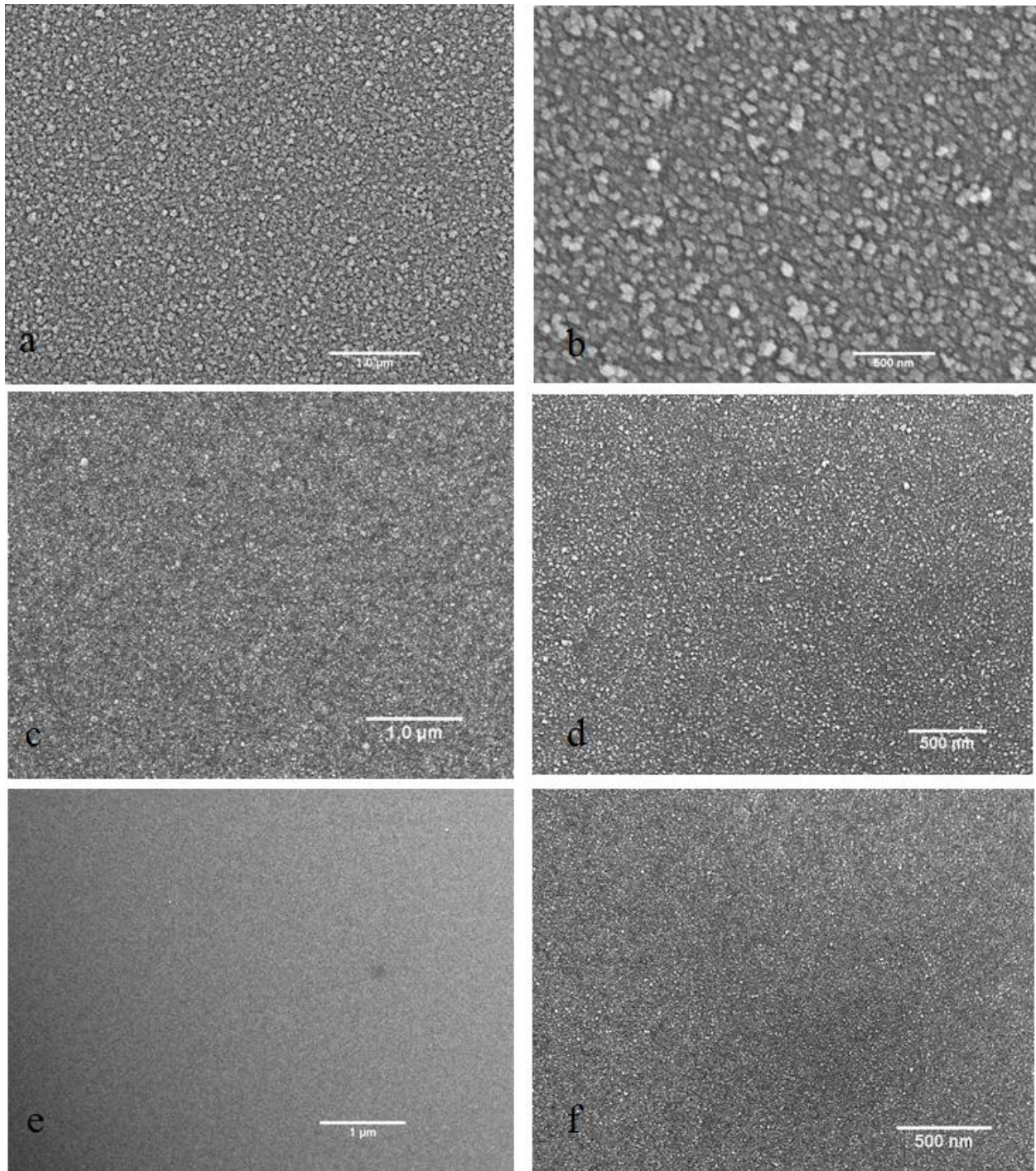


Fig. 4.12: The FESEM images of  $\text{Al}_2\text{O}_3$  films deposited on Polyamide substrates at different deposition temperatures of RT(a ,b), 100 °C (c ,d)and 200 °C (e ,f).

The surface morphology was also investigated with NanoView high accuracy 3D nano non- contact surface profiler. As obvious from FESEM analysis the surface morphology features were almost similar for the  $\text{Al}_2\text{O}_3$  films deposited on PEN, PET and Polyamide substrates at different deposition temperatures of RT, 100 °C and 200 °C. Therefore,  $\text{Al}_2\text{O}_3$  films deposited on PEN and polyamide substrates were selected for the investigation. The 3D surface profile, 2D surface profile and the X- profile of the  $\text{Al}_2\text{O}_3$  films deposited on PEN substrates at different deposition temperatures of RT, 100 °C and 200 °C are shown in Fig. 4.13, Fig. 4.14 and Fig. 4.15. The results showed that the surface roughness of the films was reduced with the increase in deposition temperature. The Ra value of 1.96 nm for the films deposited at room temperatures was reduced to 1.76 nm for the films deposited at 200 °C. A similar trend was observed for the films deposited on polyamide substrates at different deposition temperatures of RT, 100 °C and 200 °C. The surface morphology was improved with the increase in deposition temperature by decrease in surface roughness. The Ra value of 1.88 nm for the films deposited at room temperatures (Fig. 4.16) was reduced to 1.23 nm for the films deposited at 200 °C (Fig. 4.18) This decrease in surface roughness with the increase in temperature supports the results obtained from FESEM analysis.

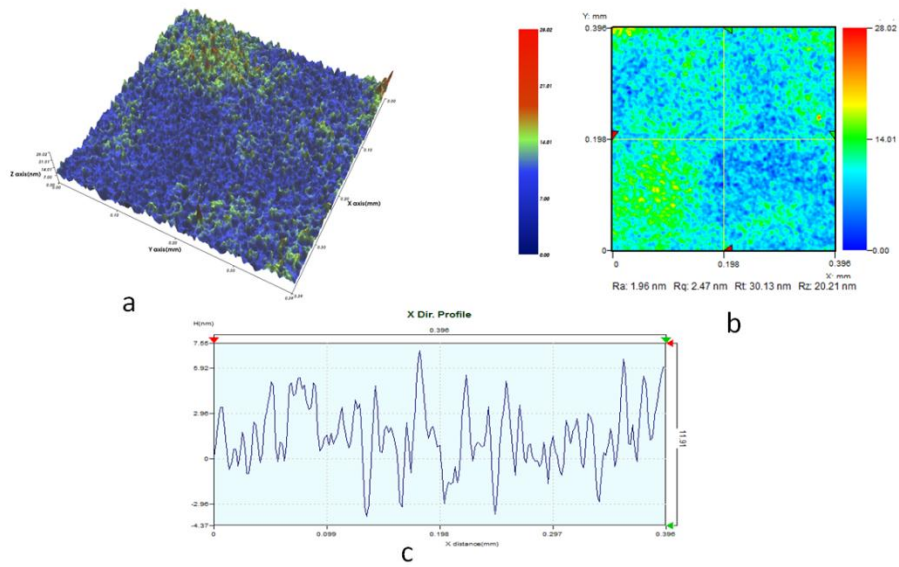


Fig. 4.13: The 3D surface profile, 2D surface profile and the X- profile of the  $\text{Al}_2\text{O}_3$  films deposited on PEN substrates at room temperature.

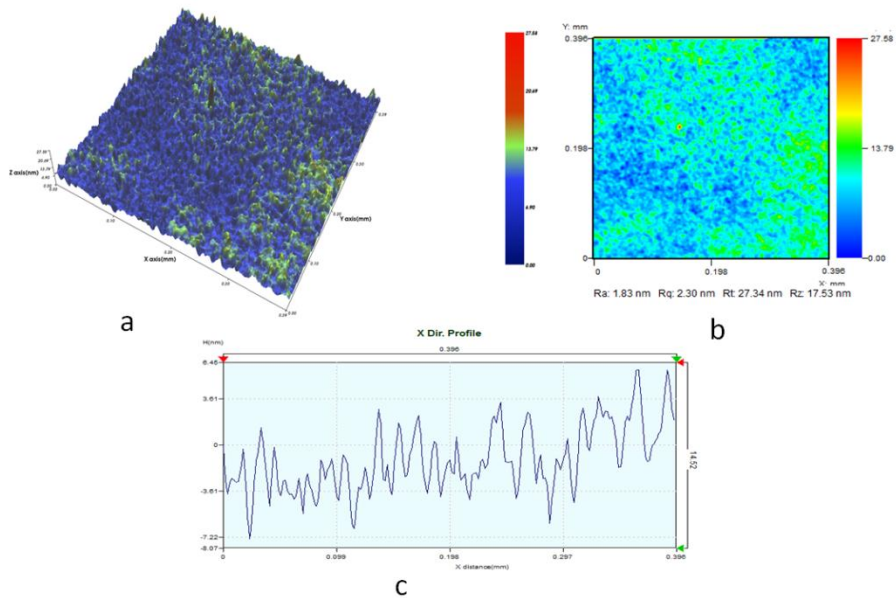


Fig. 4.14: The 3D surface profile, 2D surface profile and the X- profile of the  $\text{Al}_2\text{O}_3$  films deposited on PEN substrates at 100 °C.



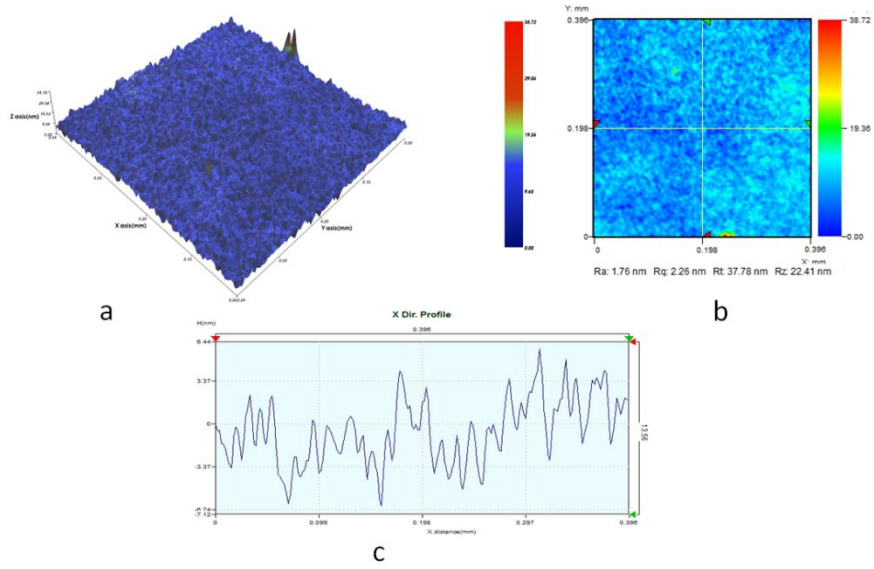


Fig. 4.15: The 3D surface profile, 2D surface profile and the X- profile of the  $\text{Al}_2\text{O}_3$  films deposited on PEN substrates at 200 °C.

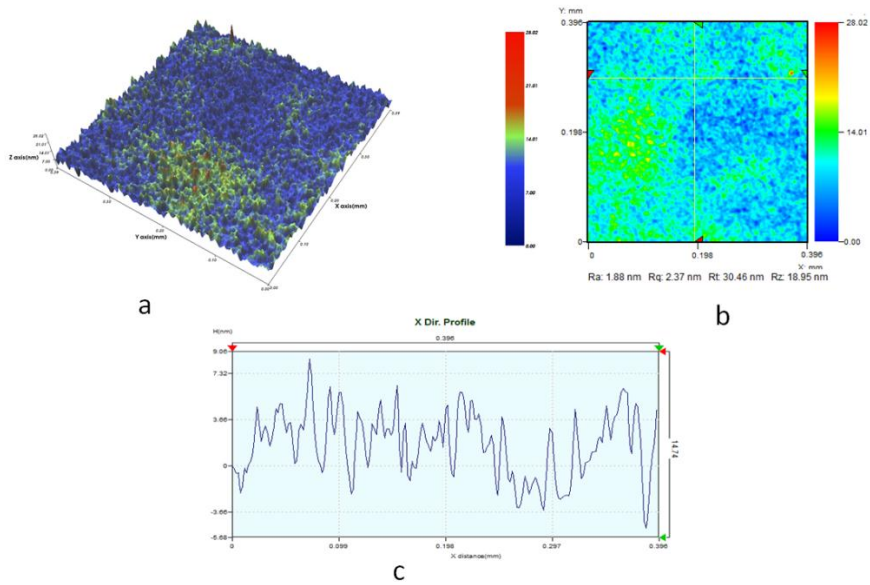


Fig. 4.16: The 3D surface profile, 2D surface profile and the X- profile of the  $\text{Al}_2\text{O}_3$  films deposited on polyamide substrates at room temperature.

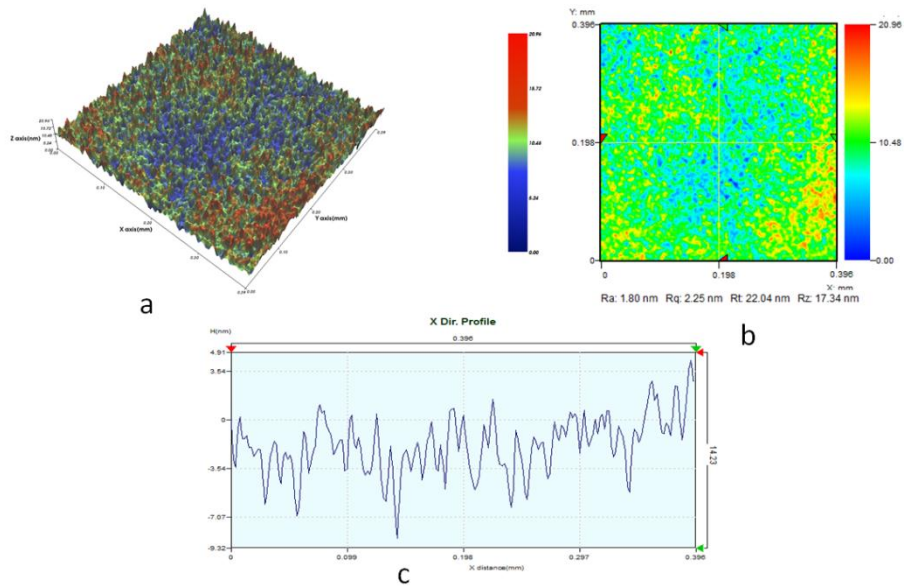


Fig. 4.17: The 3D surface profile, 2D surface profile and the X- profile of the  $\text{Al}_2\text{O}_3$  films deposited on polyamide substrates at 100 °C.

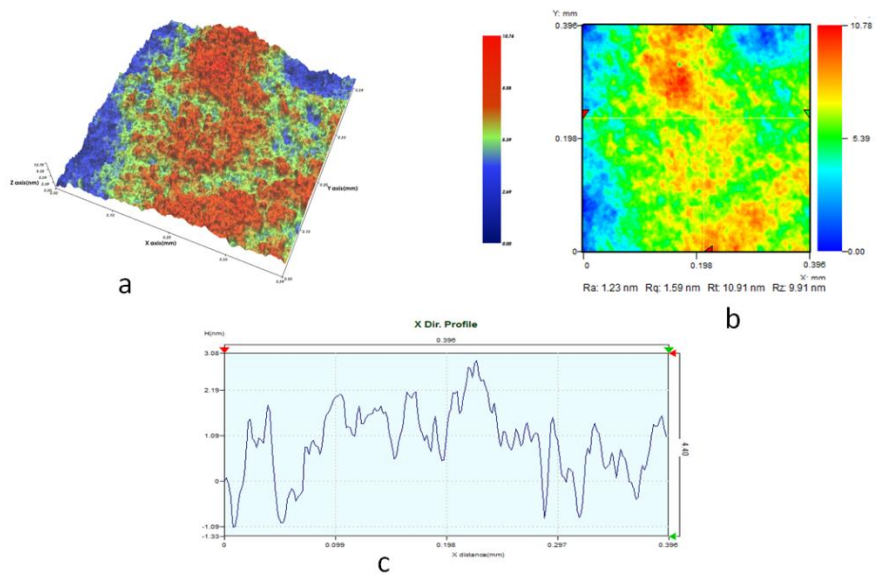


Fig. 4.18: The 3D surface profile, 2D surface profile and the X- profile of the  $\text{Al}_2\text{O}_3$  films deposited on polyamide substrates at 200 °C.

#### 4.5. Composition analysis of Al<sub>2</sub>O<sub>3</sub> ALD thin films.

The chemical composition and the impurity level of the Al<sub>2</sub>O<sub>3</sub> films deposited on PEN, PET and polyamide substrates at different temperatures of RT, 100 °C and 200 °C were investigated through X-ray photoelectron spectroscopy XPS analysis. The XPS survey spectra of cleaned Al<sub>2</sub>O<sub>3</sub> films deposited on PEN substrates at deposition temperatures of RT, 100 °C and 200 °C are shown in Fig. 4.19, Fig. 4.20 and Fig. 4.21 respectively. The spectra of the films showed only the peaks of O 1s, Al 2p and Al 2s indicating the presence of oxygen and aluminum, respectively. In all spectra of Al<sub>2</sub>O<sub>3</sub> films deposited on PEN substrates at deposition temperatures of RT, 100 °C and 200 °C, the Al 2p, Al 2s and O 1s peaks appeared at binding energies of 74-75, 119-120 eV and 531-532 eV, respectively. The energy separation between the Al 2p and O 1s peaks is 456- 457 eV and is in agreement with a previous analysis of Al<sub>2</sub>O<sub>3</sub> films. The analysis showed no carbon detection in the films deposited at these temperatures indicating that the carbon concentration is at least below the detection limit of XPS. Therefore, the results conclude that the high purity Al<sub>2</sub>O<sub>3</sub> films have been produced without any impurity contamination.

The XPS analysis were also carried out for the Al<sub>2</sub>O<sub>3</sub> films deposited on PET and polyamide substrates at different temperatures of RT, 100 °C and 200 °C. The results were almost similar to those obtained for Al<sub>2</sub>O<sub>3</sub> films deposited on PEN substrates and are shown in Fig. 4.22 to Fig. 4.27. The XPS survey spectra of Al<sub>2</sub>O<sub>3</sub> films deposited on PET and polyamide substrates also showed no contamination and the Al 2p and O 1s peaks appeared at binding energies of 74-75 and 531-532 eV respectively indicating the presence of only oxygen and aluminium in the films.

The X-ray photoelectron spectroscopy XPS analysis concluded that high purity good quality Al<sub>2</sub>O<sub>3</sub> films has been produced through the current process of ALD on PEN, PET and polyamide substrates at different temperatures of RT, 100 °C and 200 °C. The results showed no effect of the substrate material on the purity of films under the present process of ALD.

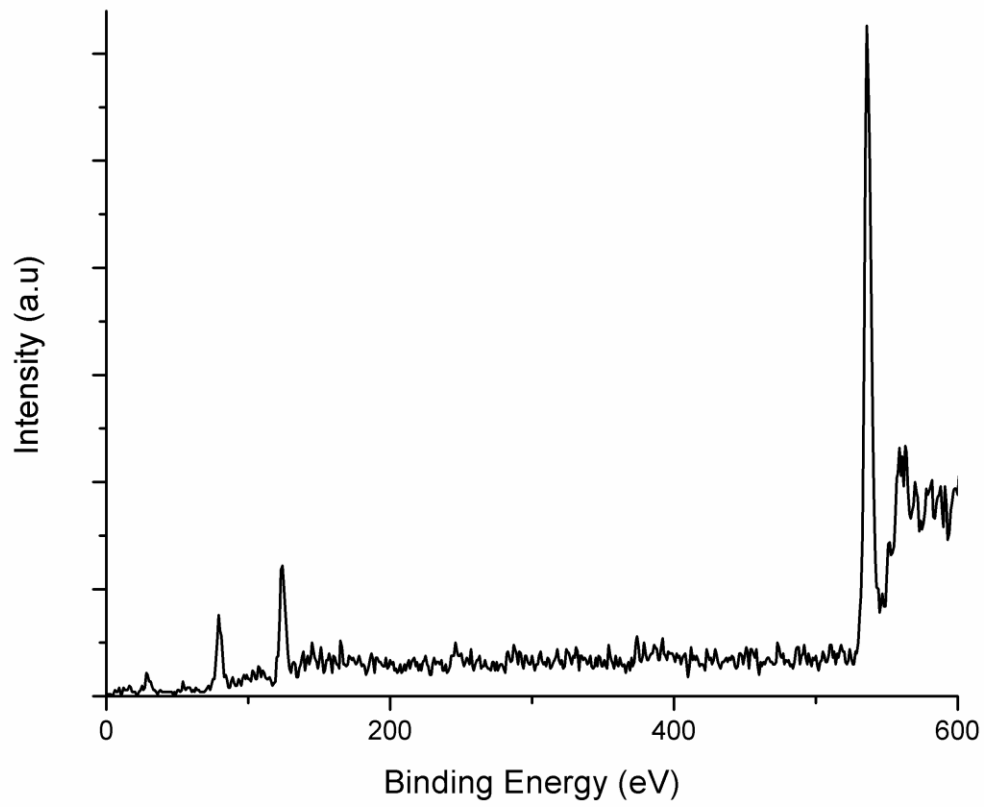


Fig. 4.19: The XPS survey spectra of  $\text{Al}_2\text{O}_3$  films deposited on PEN substrates at room temperatures.

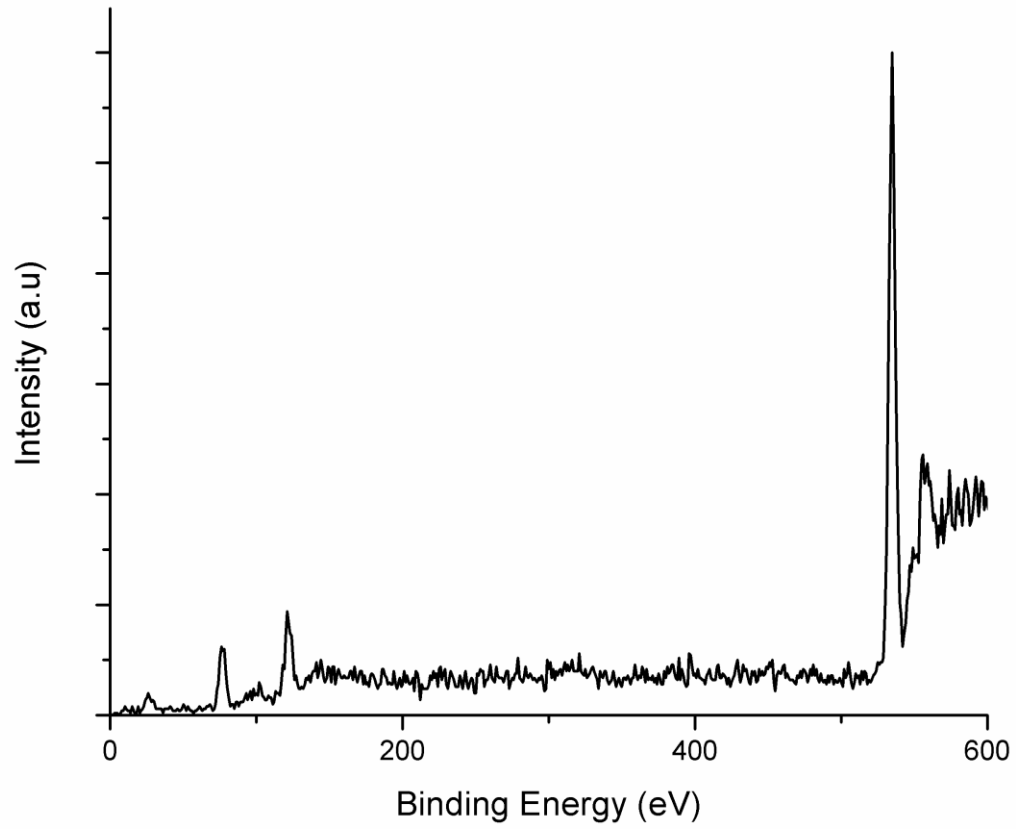


Fig. 4.20: The XPS survey spectra of  $\text{Al}_2\text{O}_3$  films deposited on PEN substrates at  $100\text{ }^\circ\text{C}$ .

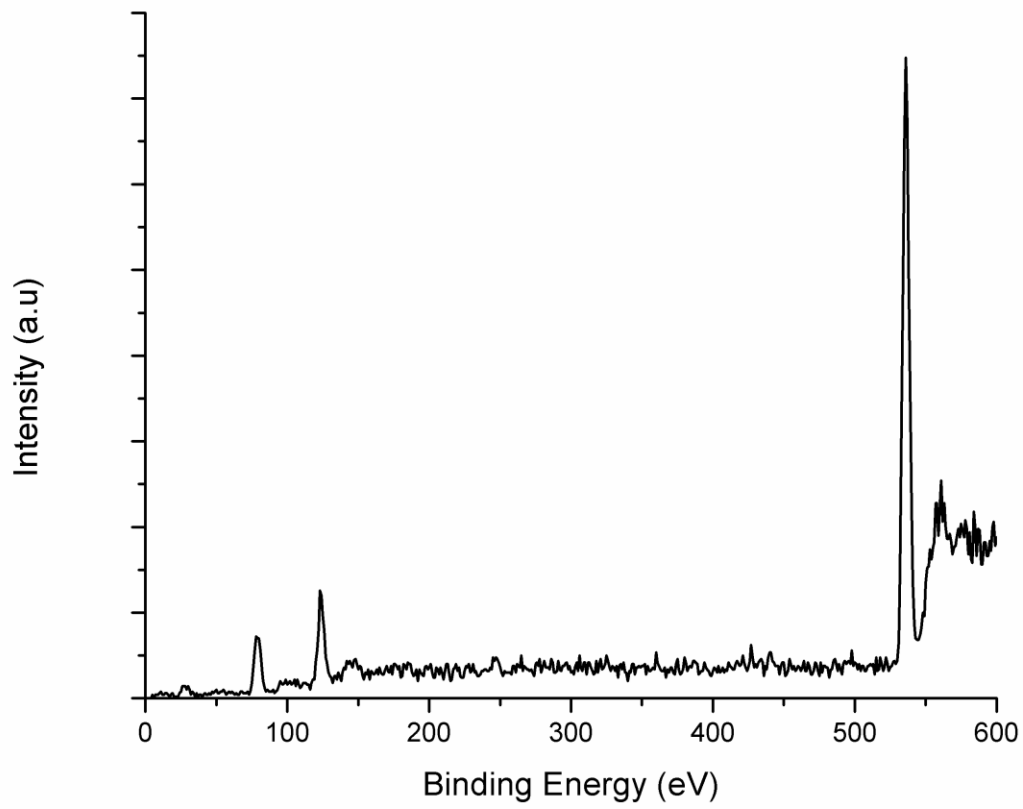


Fig. 4.21: The XPS survey spectra of  $\text{Al}_2\text{O}_3$  films deposited on PEN substrates at 200 °C.

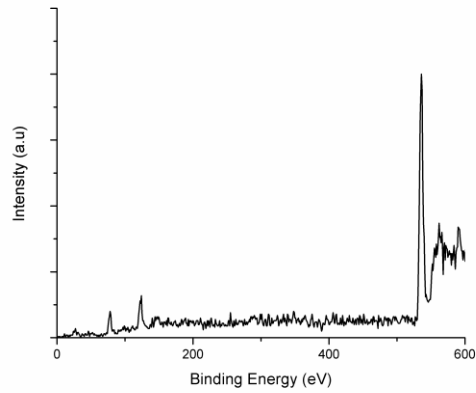


Fig. 4.22: The XPS survey spectra of  $\text{Al}_2\text{O}_3$  films deposited on PET substrates at room temperature.

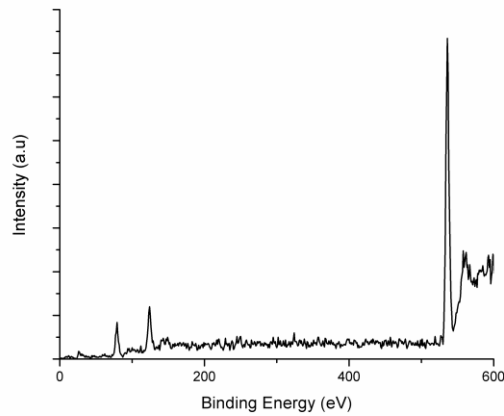


Fig. 4.23: The XPS survey spectra of  $\text{Al}_2\text{O}_3$  films deposited on PET substrates at 100 °C.

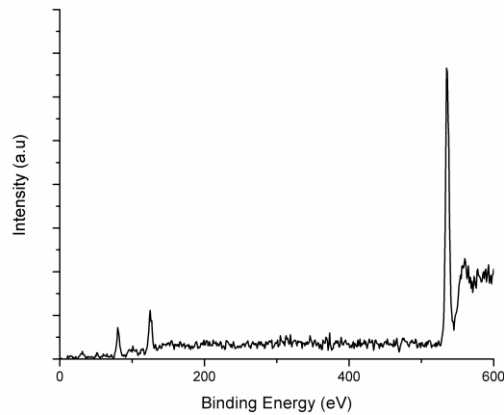


Fig. 4.24: The XPS survey spectra of  $\text{Al}_2\text{O}_3$  films deposited on PET substrates at 200 °C.

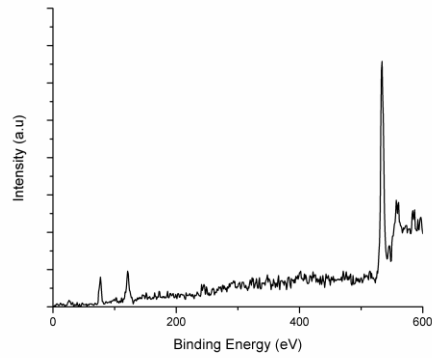


Fig. 4.25: The XPS survey spectra of Al<sub>2</sub>O<sub>3</sub> films deposited on Polyamide substrates at room temperature.

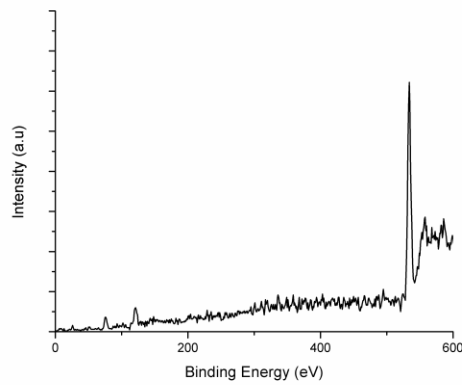


Fig. 4.26: The XPS survey spectra of Al<sub>2</sub>O<sub>3</sub> films deposited on Polyamide substrates at 100 °C.

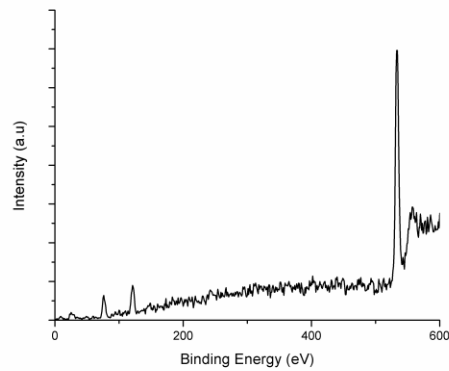


Fig. 4.27: The XPS survey spectra of Al<sub>2</sub>O<sub>3</sub> films deposited on Polyamide substrates at 200 °C.



## 5. Enhancement of Hydrophobicity of Al<sub>2</sub>O<sub>3</sub> film with C<sub>3</sub>F<sub>8</sub> plasma treatment.

The Al<sub>2</sub>O<sub>3</sub> film is mostly used as a passivation layer in most of the electronics devices such as MEMS and solar cells. These passivation coatings improve the efficiency of the devices by reducing the water vapors transmission and protecting the devices against humidity and thus results in longer life time of the devices.

In this work highly conformal Al<sub>2</sub>O<sub>3</sub> film has been deposited on PEN substrates under optimized temperature of RT, 100 °C and 200 °C. The surface morphology of these films was analyzed with FESEM and the results are shown in Fig. 5.1(a, c and e). The analysis confirmed very uniform and smooth surfaces of the coatings and the surface quality was enhanced with the increase in deposition temperature. The successfully fabricated high surface quality Al<sub>2</sub>O<sub>3</sub> film deposited under different temperatures were than subjected to plasma enhanced fluorination (PEF) treatment involving C<sub>3</sub>F<sub>8</sub> gas under the optimized process parameters shown in Table 2.3. The treatment resulted in the enhancement of the hydrophobicity of Al<sub>2</sub>O<sub>3</sub> film and also changed their surface morphology. As shown in Fig. 5.1 (b, d and f). The C<sub>3</sub>F<sub>8</sub> plasma treated Al<sub>2</sub>O<sub>3</sub> films are less smooth as compared to C<sub>3</sub>F<sub>8</sub> plasma untreated films. The 3D surface profile, 2D surface profile and the X- profile of the C<sub>3</sub>F<sub>8</sub> plasma treated Al<sub>2</sub>O<sub>3</sub> films deposited on PEN substrates at different deposition temperatures of RT, 100 °C and 200 °C are shown in Fig. 5.2, Fig. 5.3 and Fig. 5.4. The NanoView high accuracy 3D nano non- contact surface profiler analysis showed that the surface roughness of these C<sub>3</sub>F<sub>8</sub> plasma treated Al<sub>2</sub>O<sub>3</sub> films is very low and the Ra value is 1.54 nm for the films deposited at room temperature and it decreases with the increase in deposition temperature and reached to a minimum value of 0.47 nm for the films deposited at 200 °C. The contact angle analysis were carried out for both C<sub>3</sub>F<sub>8</sub> plasma untreated Al<sub>2</sub>O<sub>3</sub> films and also for C<sub>3</sub>F<sub>8</sub> plasma treated Al<sub>2</sub>O<sub>3</sub> films to check the effect of C<sub>3</sub>F<sub>8</sub> plasma enhanced fluorination treatment. The results showed that the treatment has resulted in a major enhancement of hydrophobicity and are given in

Fig. 5.5. The contact angle was increased from 49.5° to 93.2° with the treatment for the films deposited at room temperature and increased from 38.08° to 83.77° for the films deposited at 200 °C. The reason for major enhancement in case of films deposited at room temperature is the little bit more surface roughness as compared to other samples. The surface roughness for all the films was less than 100 nm therefore the roughness effect on the hydrophobicity can be neglected. This showed that the major factor in the enhancement of hydrophobicity was only the C<sub>3</sub>F<sub>8</sub> plasma enhanced fluorination treatment.

The chemical composition was also investigated for both the of the C<sub>3</sub>F<sub>8</sub> plasma untreated Al<sub>2</sub>O<sub>3</sub> films and C<sub>3</sub>F<sub>8</sub> plasma treated Al<sub>2</sub>O<sub>3</sub> films to check the effect of C<sub>3</sub>F<sub>8</sub> plasma enhanced fluorination treatment. For this purpose the samples produced at 100 °C were analyzed and the XPS survey spectra results are shown in Fig. 5.6 and Fig. 5.7. In Fig. 5.6, the spectrum of the films after cleaning showed only the peaks of Al 2p, Al 2s and O 1s at binding energies of 74-75, 119- 120 and 531-532 eV, respectively indicating the presence of oxygen and aluminum in the films. The energy separation between the Al 2p and O 1s peaks is 456- 457 eV and is in agreement with a previous analysis of Al<sub>2</sub>O<sub>3</sub> films. The analysis showed no carbon detection after cleaning in the films deposited at 200 °C indicating that the carbon concentration is at least below the detection limit of XPS. Therefore, the results conclude that the high purity Al<sub>2</sub>O<sub>3</sub> films have been produced without any impurity contamination.

Fig. 5.7 shows the XPS spectrum of the C<sub>3</sub>F<sub>8</sub> plasma treated Al<sub>2</sub>O<sub>3</sub> films produced at 100 °C. The spectrum showed the peaks of Al 2p, Al 2s, and O 1s at binding energies of 74-75, 119-120 and 531-532 eV, C 1s peak at 285 eV, F auger at 599 eV to 600 ev and F 1s at 685 eV which is in agreement with a previous analysis. These XPS analysis confirmed that the C 1s, F auger and F 1s peaks were originated in the spectrum because of PEF treatment with C<sub>3</sub>F<sub>8</sub> and concluded that the enhancement in hydrophobicity was the result of C<sub>3</sub>F<sub>8</sub> PEF treatment.

The effect of the C<sub>3</sub>F<sub>8</sub> plasma treatment on optical properties of the films was also analyzed through U-V characterizations and the transmittance and absorbance graphs are shown in Fig. 5.8 and Fig. 5.9. The results showed good transmittance of light in visible range and the films that were deposited at room

temperature showed maximum transmittance and the minimum transmittance was recorded for the films deposited at 100 °C. This is because of higher thickness of Al<sub>2</sub>O<sub>3</sub> films that are produced at maximum growth rates at 100 °C. The absorbance results are showed very low absorbance in visible range and maximum absorbance was recorded for the films deposited at 100 °C and minim absorbance was recorded for the films deposited at room temperature. This was also the effect of thickness of the films which is the result of deposition temperatures.

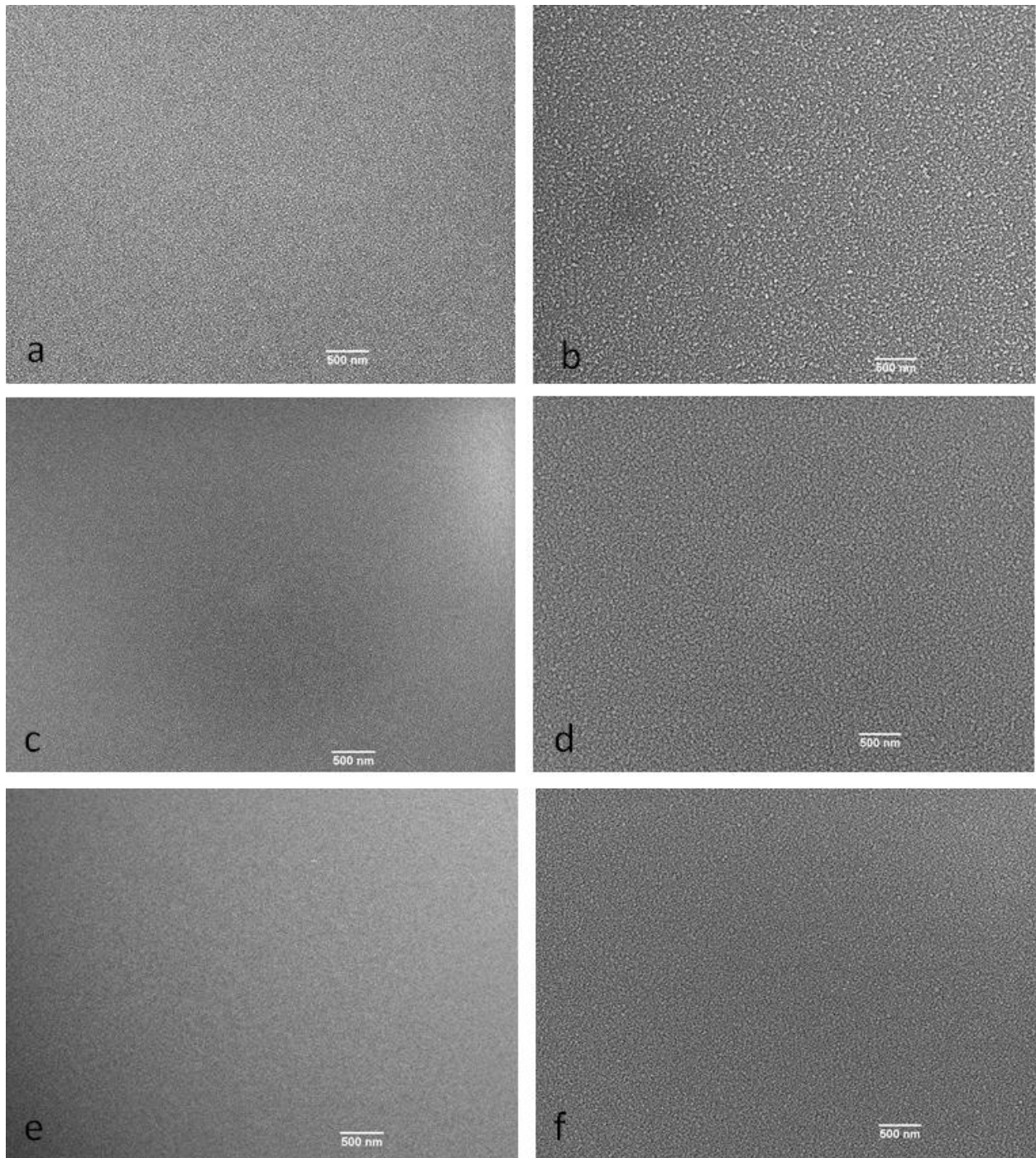


Fig.5.1: FESEM images of  $C_3F_8$  untreated and treated  $Al_2O_3$  films deposited at RT (a,b), 100 °C (c,d) and 200 °C (e,f).

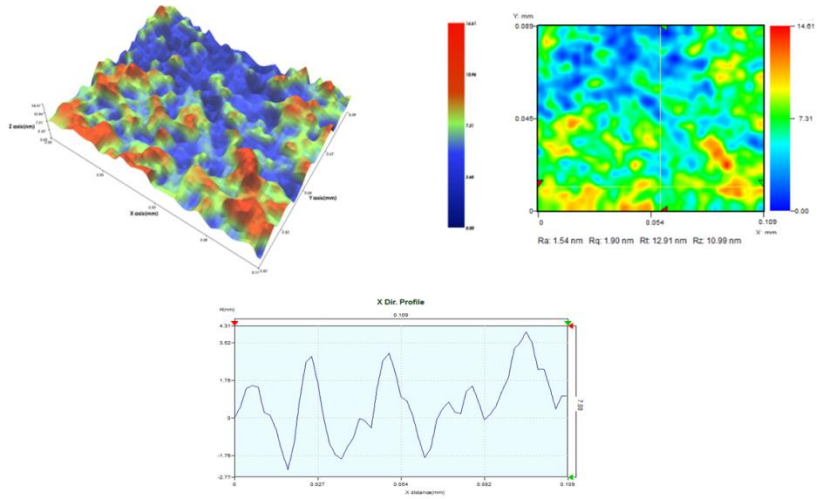


Fig. 5.2: The 3D surface profile, 2D surface profile and the X- profile of the  $C_3F_8$  treated  $Al_2O_3$  films deposited at RT on PEN substrates.

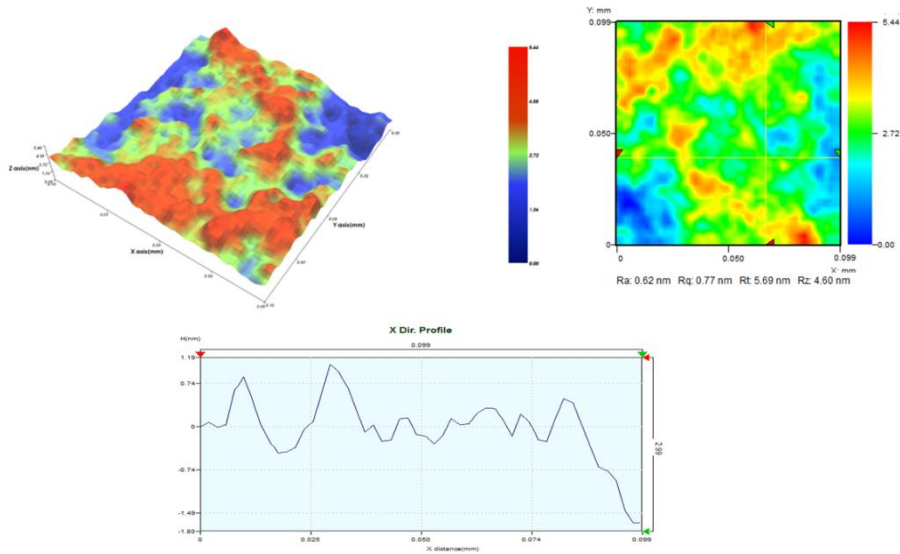


Fig. 5.3: The 3D surface profile, 2D surface profile and the X- profile of the  $C_3F_8$  treated  $Al_2O_3$  films deposited at 100 °C on PEN substrates.

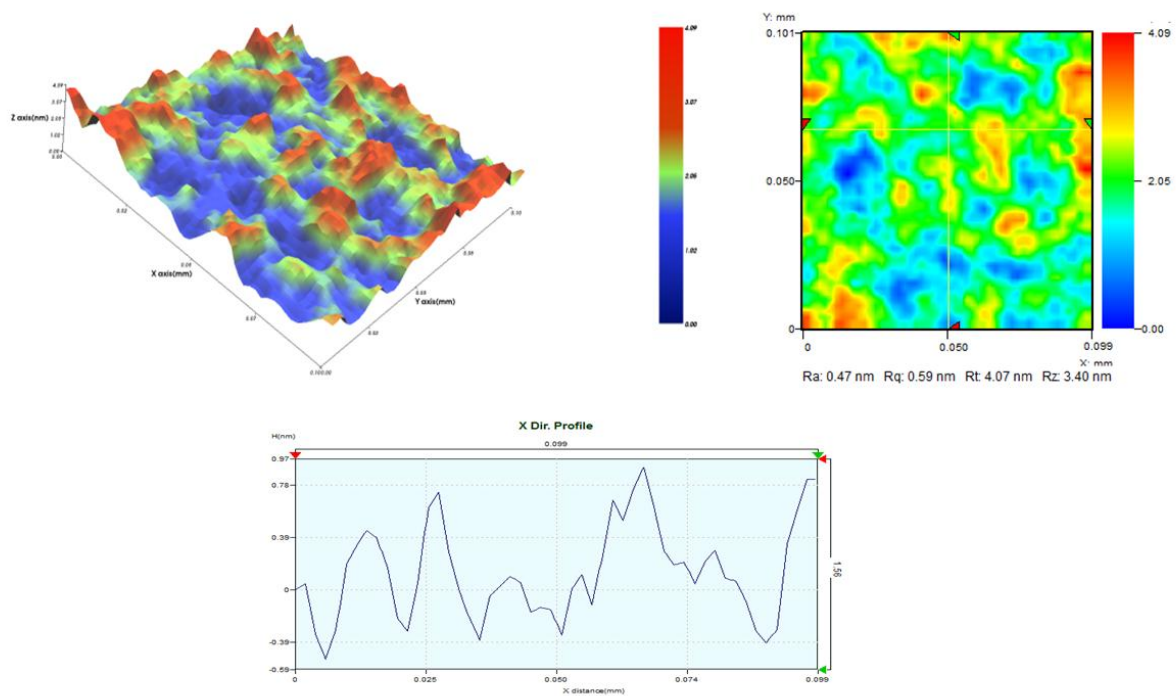


Fig. 5.4: The 3D surface profile, 2D surface profile and the X- profile of the  $C_3F_8$  treated  $Al_2O_3$  films deposited at 200 °C on PEN substrates.

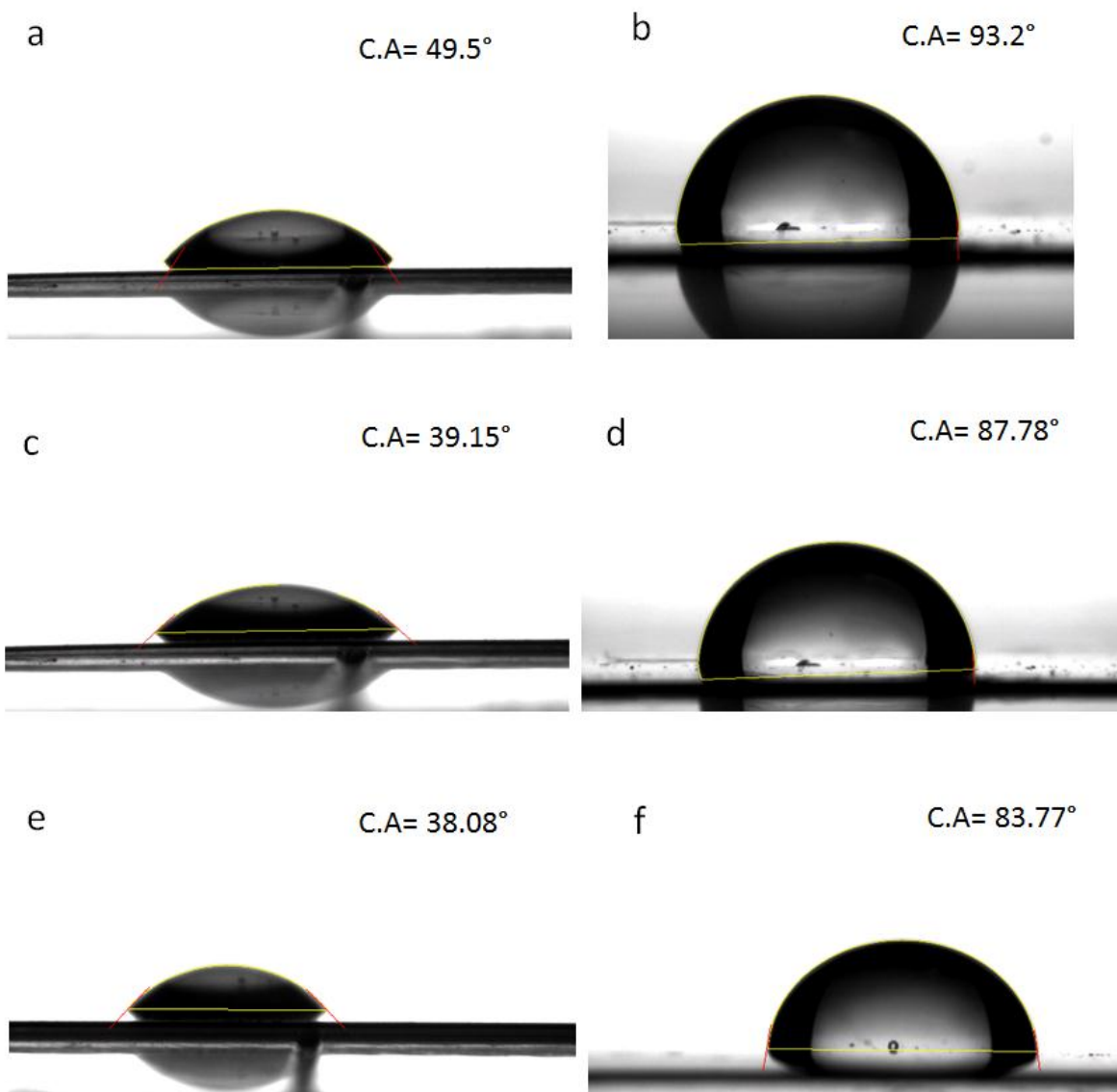


Fig. 5.5: Contact angle images of  $C_3F_8$  untreated and treated  $Al_2O_3$  films deposited at RT (a,b), 100 °C (c,d) and 200 °C (e,f).

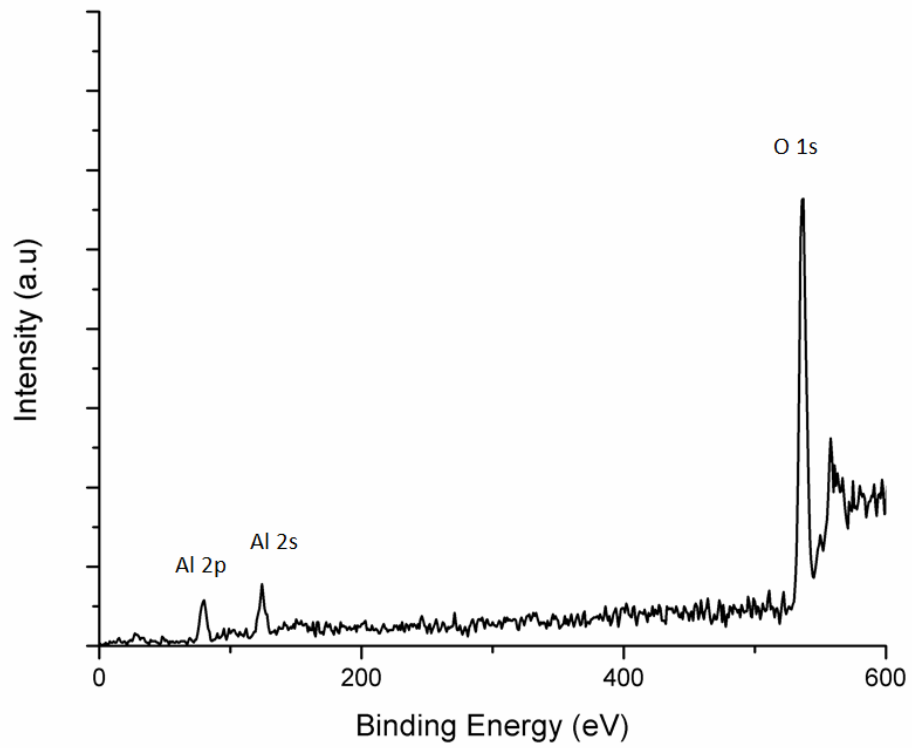


Fig. 5.6: The XPS survey spectrum of  $C_3F_8$  untreated  $Al_2O_3$  films deposited on PEN substrates at  $100\text{ }^\circ\text{C}$ .



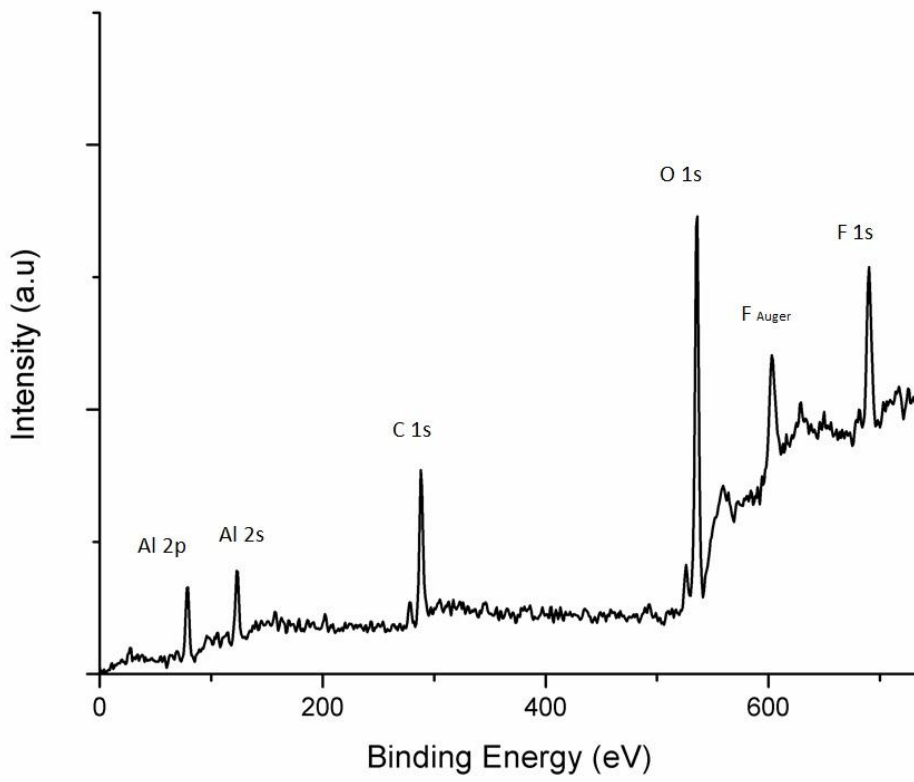


Fig. 5.7: The XPS survey spectrum of  $C_3F_8$  treated  $Al_2O_3$  films deposited on PEN substrates at 100 °C.

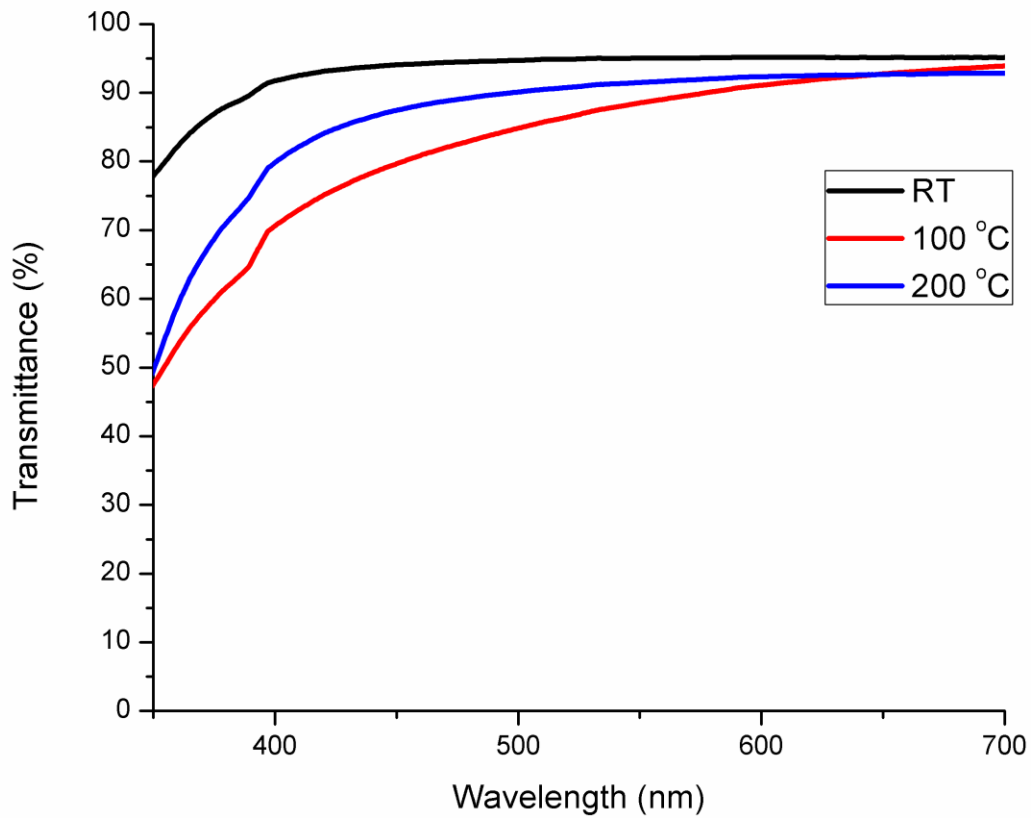


Fig. 5.8: The optical transmission properties of  $C_3F_8$  treated  $Al_2O_3$  thin films deposited on PEN substrates at deposition temperatures of RT, 100 °C and 200 °C.

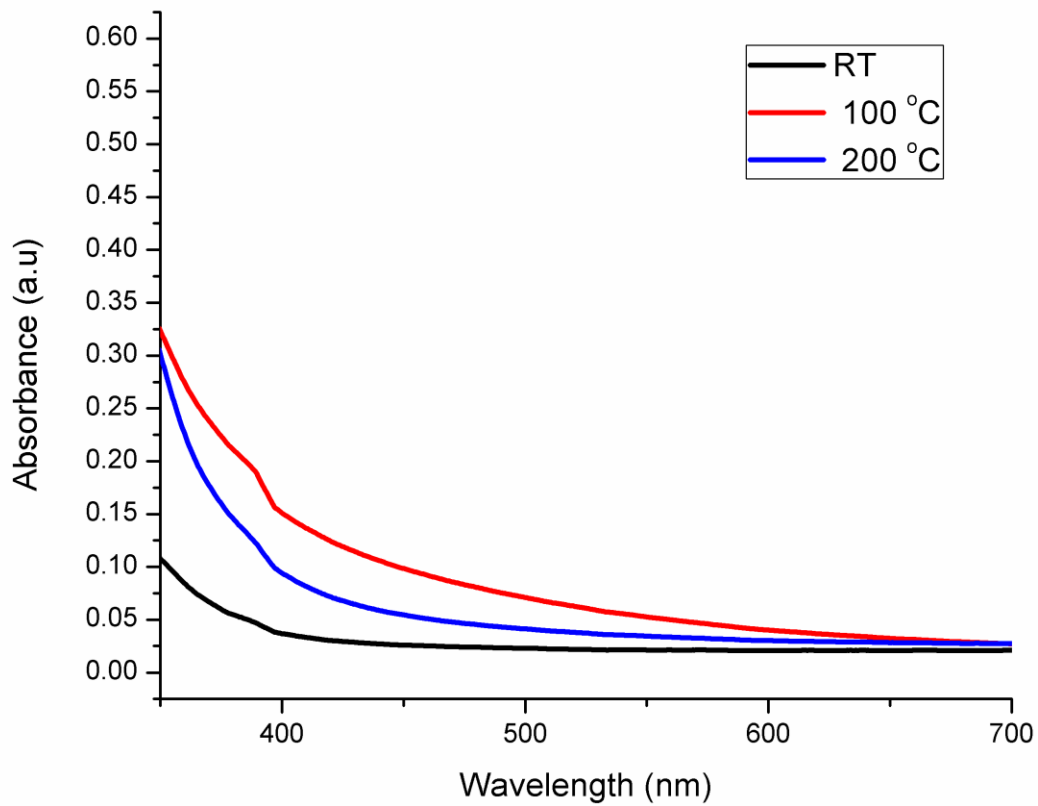


Fig. 5.9: absorbance of  $C_3F_8$  treated  $Al_2O_3$  thin films deposited on PEN substrates at deposition temperatures of RT, 100 °C and 200 °C.

## 6. Executive Summary

This thesis is a comprehensive study of the fabrication of  $\text{Al}_2\text{O}_3$  thin films through the novel technology of atomic layer deposition (ALD) on different kinds of flexible substrates, such as PEN, PET and polyamide. Although many researchers have adopted  $\text{Al}_2\text{O}_3$  ALD as their research topic the analysis is mostly carried out on silicon wafers. The fabrication  $\text{Al}_2\text{O}_3$  thin films through ALD on flexible substrates have gained great importance and reputation in the field of flexible electronics. It has opened a window to great research opportunities in the field of ALD. Therefore this research was conducted to elucidate ALD as a proven method for the successful fabrication of high quality  $\text{Al}_2\text{O}_3$  thin films with excellent chemical, morphological, optical and electrical properties on flexible substrates under different deposition temperatures ranging from room temperature to 200 °C. The thesis also includes the enhancement of hydrophobicity of  $\text{Al}_2\text{O}_3$  film with  $\text{C}_3\text{F}_8$  plasma treatment in order to improve the functionality of the electronic devices and increase their life cycle by reducing the effect of humidity and water vapors transmission.

The thesis first discusses the key strengths and core competencies of ALD in electronics industry. The second chapter involves the detailed discussion of thin films fabrications, atomic layer deposition technology and the broad field of precursors used in this field. The chapter also discusses the applications of ALD and  $\text{Al}_2\text{O}_3$  thin films fabrication through ALD and their applications. The experimental information are presented in chapter three and it involves informations regarding the reactor design of ALD that was used for the  $\text{Al}_2\text{O}_3$  thin films fabrication the precursors and substrates that were used in the experimentation. It also involves the optimized operational parameters that were used for the deposition of thin films and also the characterizations techniques that were used to carefully analyze and study the  $\text{Al}_2\text{O}_3$  thin films. The fifth chapter involves the detailed discussion regarding Enhancement of Hydrophobicity of  $\text{Al}_2\text{O}_3$  film with  $\text{C}_3\text{F}_8$  plasma treatment.

Lastly the results and discussions are presented in detail in the fourth chapter. The ellipsometry results showed that the growth rates of  $\text{Al}_2\text{O}_3$  thin films reached to the maximum values of 1.18Å/cycle,

1.16Å/cycle and 1.17Å/cycle for PEN, PET and polyamide substrates at a temperature of 150 °C. The refractive index was increased from 1.54, 1.55, and 1.53 at room temperature to 1.65, 1.67 and 1.66 at a deposition temperature of 200 °C for PEN, PET and polyamide substrates respectively. The transmittance spectra of the Al<sub>2</sub>O<sub>3</sub> films deposited at room temperature on PEN was more than 90 % in the visible region and decreases to the range of 80 % to 90 % for the films deposited at 200 °C. A much low transmittance was observed for the films deposited on polyamide substrates. The I-V results of Al<sub>2</sub>O<sub>3</sub> thin films with different thickness ranging from 52 Å to 176Å grown at 100 °C on PEN substrates showed that Al<sub>2</sub>O<sub>3</sub> films were highly insulating and a decrease in current was observed with the increase in Al<sub>2</sub>O<sub>3</sub> films thickness and also a decrease in current was observed with the increase in deposition temperature until 150 °C. The surface characteristics of the Al<sub>2</sub>O<sub>3</sub> films deposited on PEN, PET and polyamide substrates were investigated through field-emission scanning electron microscope (FESEM) and NanoView high accuracy 3D nano non- contact surface profiler. The results showed that the surface uniformity increase with the increase in deposition temperature and more uniform particles were formed as the temperature was increased.

The chemical composition and the impurity level of the Al<sub>2</sub>O<sub>3</sub> films deposited on PEN, PET and polyamide substrates at different temperatures of RT, 100 °C and 200 °C were investigated through X-ray photoelectron spectroscopy XPS analysis. The spectra of the films showed only the peaks of O 1s and Al 2p indicating the presence of oxygen and aluminum, respectively. In all spectra of Al<sub>2</sub>O<sub>3</sub> films deposited on PEN substrates at deposition temperatures of RT, 100 °C and 200 °C , the Al 2p and O 1s peaks appeared at binding energies of 74-75 and 531-532 eV, respectively. The energy separation between the peaks is 456- 457 eV and is in agreement with a previous analysis of Al<sub>2</sub>O<sub>3</sub> films. The analysis showed no carbon detection in the films deposited at these temperatures indicating that the carbon concentration is at least below the detection limit of XPS.

The contact angle results showed that the C<sub>3</sub>F<sub>8</sub> plasma treatment has resulted in a major enhancement of hydrophobicity of Al<sub>2</sub>O<sub>3</sub> films and the contact angle was increased from 49.5° to 93.2° with the treatment

for the films deposited at room temperature and increased from 38.08° to 83.77° for the films deposited at 200 °C.

## 7. Conclusions and Future Work

In this thesis successful fabrication of high quality  $\text{Al}_2\text{O}_3$  thin films has been discussed through the novel technology of atomic layer deposition (ALD) on different kinds of flexible substrates, such as PEN, PET and polyamide. The results confirmed that the deposition temperature has a mark effect on the growth rates, film thickness, and surface morphology, electrical and optical properties of the films. The chemical composition was not effected within the selected range of deposition temperature. The results also confirmed that the different substrate material has no major effect on the ALD process and on the quality of the films. The quality of the films deposited on different substrates was almost the same. The growth rates are low at lower temperatures because of thermal activation barriers due to low temperature although there are higher Al-OH and Al- $\text{CH}_3$  surface coverages. The growth rates were decreased when the temperature was raised more than 150 °C. The decrease in growth rates at higher temperature can be explained by decrease in Al-OH and Al- $\text{CH}_3$  surface coverage although the reaction kinetics are more rapid. The increase in refractive index with the increase in deposition temperatures supports the good quality films. The transmittance of the  $\text{Al}_2\text{O}_3$  films deposited at room temperature was more than 90 % in the visible region except for the polyamide substrates. The low transmittance in polyamide substrates is mainly due the the actual nature of polyamide. The  $\text{Al}_2\text{O}_3$  films showed very low absorbance in visible range except the films deposited on polyamide substrates. This decrease in optical transmittance and increase in absorbance can be attributed to the difference in the thickness of the thin films fabricated at different deposition temperatures. The electrical characterizations conclude that the film thickness and the deposition temperatures have a mark effect on the I-V characteristics of the  $\text{Al}_2\text{O}_3$  films. The current is decreased with the increase in film thickness. The deposition temperature indirectly affects the electrical properties by controlling the film thickness. The films grown at low deposition temperatures are of low thickness and results in higher current values as compared to the films grown at higher temperatures with higher thickness of the films. The surface morphology and uniformity of the films was increased with the increase in deposition temperature from RT to 200 °C and also more uniform and fine size particles were

obtained with the increase in temperature and it showed no major dependence upon the substrate material. The X-ray photoelectron spectroscopy XPS analysis concluded that high purity good quality  $\text{Al}_2\text{O}_3$  films with no contaminations and impurities has been produced through the current process of ALD on PEN, PET and polyamide substrates at different temperatures of RT, 100 °C and 200 °C.

The contact angle analysis showed that the  $\text{C}_3\text{F}_8$  plasma treatment has resulted in a major enhancement of hydrophobicity. The reason for major enhancement in case of films deposited at room temperature is the little bit more surface roughness as compared to other samples. The surface roughness for all the films was less than 100 nm therefore the roughness effect on the hydrophobicity can be neglected. This showed that the major factor in the enhancement of hydrophobicity was only the  $\text{C}_3\text{F}_8$  plasma enhanced fluorination treatment.

The XPS spectrum of the  $\text{C}_3\text{F}_8$  plasma treated  $\text{Al}_2\text{O}_3$  films produced at 100 °C showed the peaks of O 1s and Al 2p at binding energies of 74-75 and 531-532 eV, C 1s peak at 285 eV, F auger at 599 eV to 600 eV and F 1s at 685 eV which is in agreement with a previous analysis. These XPS analysis confirmed that the C 1s, F auger and F 1s peaks were originated in the spectrum because of PEF treatment with  $\text{C}_3\text{F}_8$  and concluded that the enhancement in hydrophobicity was the result of  $\text{C}_3\text{F}_8$  PEF treatment.

The  $\text{C}_3\text{F}_8$  plasma treatment  $\text{Al}_2\text{O}_3$  showed good transmittance of more than 90% in the visible range and the films that were deposited at room temperature showed maximum transmittance and the minimum transmittance was recorded for the films deposited at 100 °C. This is because of higher thickness of  $\text{Al}_2\text{O}_3$  films that are produced at maximum growth rates at 100 °C. The absorbance results are showed very low absorbance in visible range and maximum absorbance was recorded for the films deposited at 100 °C and minimum absorbance was recorded for the films deposited at room temperature. This was also the effect of thickness of the films which is the result of deposition temperatures.

As far as the future work and future areas are concerned a lot of opportunities are present the field of ALD. The most latest and advanced trends of ALD are spatial ALD and roll to roll ALD. Also the room temperature ALD has been gaining a lot importance this field. The roll to roll ALD technology has got a



great edge over other trends because it is capable to process various kinds of flexible substrates such as PEN, PET and Polyamide etc. on large scale and this results in very high production at low cost. Apart from the advantages there are some challenges and limitations in roll to roll ALD and one of them is the process temperature. Most of the flexible substrates are sensitive to higher temperatures and get damage if exposed more than a certain period of time. In future this research work can be used as a roadmap for roll to roll ALD of  $\text{Al}_2\text{O}_3$  on PEN, PET and Polyamide substrates and can provide guide lines regarding various important process parameters like deposition temperature and ALD process cycles etc and can also help in room temperature ALD processes.

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