UNIVERSITY OF CALIFORNIA SAN DIEGO

Sculpting Surfaces: Investigating Pressure and Solvent Effects in Langmuir-Blodgett Thin Film Engineering

A thesis submitted in partial satisfaction of the requirements for the degree Master of Science in

Materials Science & Engineering

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The thesis of Pranjali Ravindra Khajanji is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

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List of Abbreviations

DMSO: Dimethyl Sulphoxide

Cyclopentanone: CP

D+A: 40% DMSO+ 60% Acetone binary solvent system

D_5: DMSO sample at 5 pressure

D_7: DMSO sample at 7 pressure

CP_5: Cyclopentanone sample at 5 pressure

CP_7: Cyclopentanone sample at 7 pressure

D+A_5: 40% DMSO+ 60% Acetone at 5 pressure

D+A_7: 40% DMSO+ 60% Acetone at 7 pressure

LB: Langmuir Blodgett

PVDF-TrFE: Polyvinyl Difluorine Triflouro Ethylene polymer

AFM: Atomic Force Microscopy

PFM: Piezoresponse Force Microscopy

MW: Memory Window

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ABSTRACT OF THE THESIS

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This research aims to examine the impact of pressure and solvent choice on the deposition of Langmuir-Blodgett (LB) thin films, to improve the engineering of thin film surfaces. This study delves into

the complex relationship between processing parameters and the characteristics of ferroelectric polymer (PVDF-TrFE) thin films. PVDF-TrFE is a well-known ferroelectric polymer and several attempts have been made to enhance the ferroelectric properties.

The evaluation of different solvents, such as Dimethyl Sulfoxide (DMSO), Cyclopentanone, and DMSO with Acetone binary solvent system, was conducted by testing under varying pressure settings. This research investigates the intricate impacts of these factors on the structure, thickness, and surface roughness of films, using methodologies such as atomic force microscopy (AFM), Piezoresponse Force Microscopy (PFM), and Ellipsometry. The study's results provide interesting observations: the binary solvent system of DMSO and Acetone emerges as a promising candidate, as it demonstrates improved evaporation that promotes the creation of a smoother and more consistent film.

Furthermore, the impact of fluctuations in pressure on the properties of films highlights the need for carefully regulated processing parameters in shaping surface features. The study findings have broader implications that go beyond the realm of fundamental thin film engineering. These implications have the potential to be applied in several domains, including semiconductor device production, and memory technologies. This work makes a valuable contribution to the field of materials science and nanotechnology by providing a comprehensive understanding of the fundamental processes that drive the deposition of LB films.

I Introduction

1.1 Background and Context:

Incorporating cutting-edge memory technologies is crucial for improving the performance of semiconductor devices in the fast-changing realm of electronic materials. This study centers on the novel technique of using Langmuir-Blodgett layer deposition on ferroelectric polymers. Ferroelectric polymers have distinct characteristics that make them very suitable for memory applications, since they may demonstrate spontaneous electric polarization. Langmuir-Blodgett film deposition techniques can be used to make customized thin films on ferroelectric polymer substrates.[1] These techniques are accurate and can be changed easily. Learning more about the complicated relationship between the deposited films and ferroelectric properties will lead to the creation of semiconductor devices with better memory. This work enhances our fundamental comprehension of material behavior and has substantial potential for increasing the design and performance of electronic systems that require a large amount of memory.

1.2 Motivation for the research:

The endeavor to enhance semiconductor technology is a fundamental aspect of contemporary engineering research, establishing the basis for breakthroughs in electronics, communications, and computers. Exploring the incorporation of ferroelectric polymers, particularly PVDF-TrFE, into semiconductor devices is a state-of-the-art research direction. This study aims to maximize the capabilities of memory engineering through the utilization of Langmuir-Blodgett (LB) film deposition techniques. This method provides a distinct way to improve the performance and functionalities of semiconductor memory devices.

Ferroelectric polymers, such as PVDF-TrFE, have exceptional characteristics, including elevated spontaneous polarization, short switching times, chemical durability, low fabrication costs, and compatibility with the environment.[2,3] These attributes provide them with very favorable candidates for nonvolatile memory applications. Comprehending and using the innate powers of ferroelectric polymers has the potential to completely transform the field of semiconductor memory technology. The utilization

of Langmuir-Blodgett film deposition processes brings a new aspect to the incorporation of ferroelectric polymers into semiconductor devices.[4] LB deposition provides exceptional accuracy in terms of layer thickness, crystallinity, and orientation, surpassing conventional techniques.[4] Precise control at this level is crucial for customizing the characteristics of the ferroelectric films, eventually impacting the performance and dependability of semiconductor memory components.

The main goal of this study is to design memory devices that have improved functions. The LB deposition technique may greatly enhance uniformity and alignment, leading to a reduction in flaws and enabling more precise patterning. This addresses the difficulties commonly encountered with traditional deposition processes. Additionally, the capacity to manipulate memory components at reduced voltages is a pivotal breakthrough that has the potential to result in energy-efficient and high-performance semiconductor systems. The findings of this research can influence several industries, ranging from consumer electronics to new fields such as the Internet of Things (IoT) and artificial intelligence. Enhanced performance and reduced energy usage are crucial for the ongoing advancement of electronic systems. The results of this study add to the overall objective of developing semiconductor memory technology and pushing the limits of what can be accomplished in modern engineering. Our objective is to utilize Langmuir-Blodgett film deposition on PVDF-TrFE to explore novel opportunities in memory engineering, hence introducing groundbreaking advancements that have the potential to revolutionize the field of electronics and computers.

1.3 Research Objective and Hypotheses:

The experiment can be characterized by its prospective research aims and hypotheses.- The goals of the research:

- *Conduct a study on the viability of Langmuir-Blodgett film deposition*: To assess the feasibility of utilizing Langmuir-Blodgett (LB) film deposition as a method for applying ferroelectric polymers, namely PVDF-TrFE, onto semiconductor substrates.

- *Improve the performance and capabilities of semiconductor memory devices*: To investigate the possible enhancements in the efficiency of semiconductor memory devices by using ferroelectric polymers. Direct your attention to attaining consistency, regulated thickness, and improved crystal structure.

- *Assess the influence of LB deposition on the characteristics of the film*: To investigate the impact of LB deposition on the crystalline orientation, thickness, and uniformity of ferroelectric polymer films. Evaluate the benefits of LB deposition compared to traditional approaches.

- *Optimize Operating Parameters for LB Deposition*: To determine the most efficient values for pressure, temperature, and time in LB deposition to get the desired film properties on semiconductor surfaces.

- *Evaluate Low-Voltage Operation*: To examine the viability of running memory components at reduced voltages, and the overall efficiency of semiconductor devices.

Hypotheses:

- The utilization of the Langmuir-Blodgett deposition technique can lead to the production of ferroelectric polymer films that exhibit enhanced uniformity in comparison to films formed by traditional techniques.

- Enhanced Crystalline Orientation by LB Deposition: LB deposition has the potential to enhance the crystalline orientation of ferroelectric polymer films, hence improving their electrical characteristics.

- Achieving lower voltage operation is possible. The semiconductor memory devices that utilize LB-deposited ferroelectric polymers can operate reliably at reduced voltages while maintaining high-performance levels.

- The utilization of the Langmuir-Blodgett deposition technique enables the accurate arrangement of ferroelectric polymer films, resulting in fewer imperfections and facilitating the creation of more intricate features in semiconductor memory components.

1.4 Significance of the Study

This research holds great importance in the field of semiconductor technology. The application of ferroelectric polymers, particularly PVDF-TrFE, presents a new method for improving the functionalities of semiconductor memory devices. The study intends to enhance the performance metrics of memory devices, such as data retention, switching rates, and overall reliability, by utilizing novel Langmuir-Blodgett (LB) film deposition processes. The inquiry into low-voltage functioning is in line with the crucial goal of advancing energy-efficient semiconductor technologies, which is a serious issue in contemporary electronics. In addition, the study investigates the influence of LB deposition on accurate patterning, offering valuable insights into its potential as an innovative technique for producing consistent and well-aligned polymer films. In addition to immediate technological gains, this discovery has the potential to include environmentally beneficial components in the electronics sector. Consequently, the study's influence goes beyond only improving memory and includes factors related to the environment, ultimately adding to the long-term viability of future semiconductor advancements. This study offers practical strategies for enhancing device performance and shaping the trajectory of materials science applications in the field of electronic engineering.

1.5 Scope and limitations

This study involves a thorough investigation of Langmuir-Blodgett (LB) methods for depositing films on ferroelectric polymers, notably targeting PVDF-TrFE, with the main objective of improving semiconductor memory systems. This study examines the complexities of LB deposition, exploring its capacity to tackle issues of data preservation, switching rates, and general dependability of memory devices. The research encompasses the investigation of low-voltage operation, with a particular focus on energy-efficient semiconductor technology. In addition, the study investigates the influence of LB deposition on

accurate patterning, offering useful insights into its suitability for producing consistent and well-aligned polymer films. Nevertheless, specific constraints are recognized. The study's scope may be limited by variables such as the distinctive properties of PVDF-TrFE, the complexities of LB deposition procedures, and potential obstacles in attaining general industrial acceptance. Furthermore, the research may not include all semiconductor memory technologies, but will mainly concentrate on the specified objectives. An important difficulty arises in accurately managing the LB deposition process to attain homogeneous and well-aligned films, guaranteeing the constant replication of the required characteristics throughout the semiconductor substrate. Controlling the thickness of the film at the nanoscale level and dealing with any fluctuations in crystallinity provides additional challenges. Additionally, the study encounters the difficulty of balancing the necessity for low-voltage operation to enhance energy economy with the requirement for dependable data preservation and swift switching rates in semiconductor devices. The applicability of the results to various semiconductor technologies and the possibility of the entire industry adopting LB deposition procedures also present difficulties, necessitating a detailed comprehension of the special characteristics of PVDF-TrFE and the wider semiconductor field.

II. Literature Review

2.1 Overview of semiconductor memory devices

A semiconductor memory device is an electronic storage media that utilizes semiconductor technology to store and retrieve digital information. These devices are essential elements in electronic systems, enabling the storage of data for a wide range of applications, including personal computers, cell phones, embedded systems, and large-scale data centers. Semiconductor memory devices may be categorized into two primary groups: volatile memory (VM) and non-volatile memory (NVM).[5] Volatile memory, such as DRAM and SRAM, experiences data loss upon power off. In contrast, non-volatile memory, such as Flash memory, Read-Only Memory (ROM), and new technologies like Phase Change Memory (PCM) and Resistive Memory (ReRAM), is capable of preserving data even in the absence of

power.[6] These devices are essential for storing, retrieving, and processing data in many electronic devices and applications.

The evolution of computers from their early days to the present reflects a revolutionary transformation driven by technological advancements. Although computers have experienced substantial changes in size and design, the essential components that enable their functioning, such as microcontrollers, have remained unchanged. Microcontrollers, as demonstrated by contemporary microprocessors, possess a central processing unit (CPU) for executing tasks, together with Random-Access Memory (RAM) and Read-Only Memory (ROM).[7] RAM enables rapid retrieval of essential data for executing applications, and its contents are cleared when power is lost. On the other hand, ROM is responsible for storing crucial system settings and parameters that cannot be changed and remain unchanged even in the event of power loss. RAM and ROM, which are the two primary forms of semiconductor memory, have essential functions in computer operation.

Categories of Volatile Memory:

- *Dynamic RAM* (dRAM) is a type of memory that has a large capacity. It employs cells that consist of two cooperating MOS transistors. However, it requires cyclical refreshing because of leakage.

- *Static RAM* (sRAM) is a type of memory that is faster than dynamic RAM (dRAM). It uses static flip-flops to store data and is frequently utilized for CPU or hard disk data caching.

Categories of Non-Volatile Memory:

- *Programmable ROM* (PROM): It can be programmed with data only once, permanently securing vital system information.

- *Erasable Programmable ROM* (EPROM) enables the erasure of cell content by UV irradiation, which facilitates the development of subsequent non-volatile memories.

- *Electrically Erasable Programmable ROM* (EEPROM): Facilitates electrical erasure, streamlining the process of cleaning and enabling multiple erasures.

- *EEPROM FLASH* is an upgraded iteration of EEPROM that allows for the simultaneous erasing of whole memory sectors, resulting in quicker erasure. It is separated into two types: NOR flash and NAND flash.

Innovative Memory Types:

- PCM (Phase-Change Memory) is a kind of memory that can switch between crystalline and amorphous structures using electrical power. It offers the advantages of high write cycles, longer durability, and quick read/write speeds.

- FRAMs, also known as Ferroelectric Random-Access Memories, make use of the ferroelectric effect to store data. They provide fast operation, low energy consumption, and long-lasting durability.

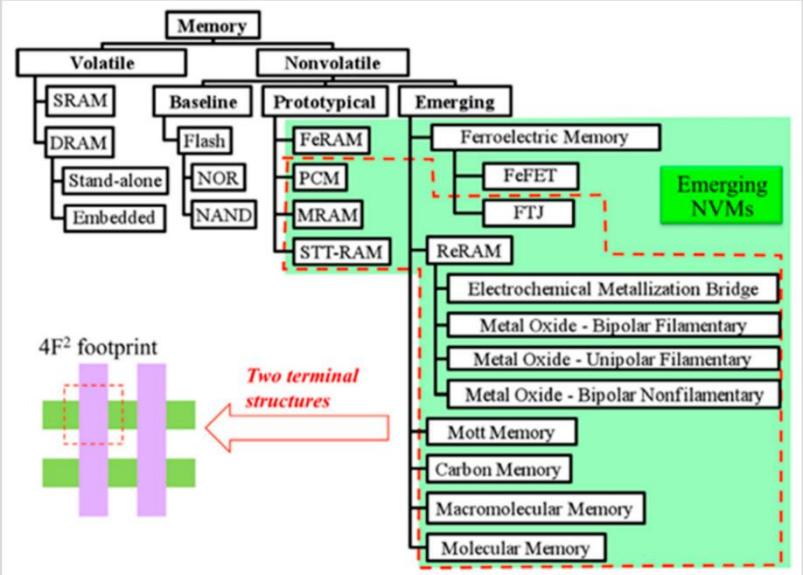

Figure 1: Memory Taxonomy. Many emerging non-volatile memories are in simple two-terminal devices and suitable high-density crossbar arrays. (Ref- 6)

Applications of Semiconductor Memories:

Flash memories are extensively utilized in memory cards, USB drives, and SSDs, whilst RAMs and ROMs are essential components of many computer units, automation systems, control systems, and home products.

Advancements and Future Outlook of Memory:

Technologically evolved operating systems benefit from the ongoing enhancement of memory, which is marked by improved speed and capacity. Memories have advanced from computer systems with megabytes of RAM to those endowed with gigabytes, becoming more cost-effective. The continuous progress in memory technology shows potential for ever more effective solutions, influencing the future landscape of electronic gadgets and computers.

2.2 Introduction to ferroelectric polymers

Ferroelectric polymers are a specific type of polymers that demonstrate ferroelectricity, which is a feature distinguished by the existence of a lasting electric polarization that may be reversed by the application of an external electric field.[8,9] The ability to reverse the polarization is what sets ferroelectric materials apart from non-ferroelectric materials. Polyvinylidene fluoride (PVDF) and its copolymers, frequently including trifluoroethylene (TrFE) or other monomers, are extensively researched ferroelectric polymers.[1] The molecular structure of these polymers enables the alignment of molecular dipoles, leading to a macroscopic polarization in the material.[10]

Ferroelectric polymers are utilized in diverse electronic gadgets, and they have special significance in nonvolatile memory technologies. The polarizations of these devices exhibit bistability, enabling their utilization in memory systems that may retain information without requiring a constant power source. Ferroelectric memories have the intriguing ability to retain information even after the electric field is no longer present, thanks to the remanent polarization. Ferroelectric polymers possess notable characteristics such as inherent polarization, durability, and the capacity to transition between several polarization states. These characteristics render them highly important in the advancement of sophisticated electrical gadgets and memory systems.

Ferroelectric crystals, which possess a permanent electric polarization that can be altered by an external electric field, serve as a crucial basis for the advancement of nonvolatile memory systems.[9,11] Ferroelectric crystals have a polarization-electric field hysteresis loop, similar to the hysteresis loop seen in ferromagnetic crystals.[12] This loop allows for the existence of two stable states. The inherent dual stability of ferroelectric polarization, especially in thin films, has been utilized for the development of nonvolatile memory, an increasingly progressive technology with applications in smart cards and cache chips. Typically, ferroelectric memories utilize perovskite ferroelectrics such as lead zirconium titanate (PZT) or strontium barium titanate (SBT).[13,14] Perovskite memory devices have been produced, successfully addressing issues such as film deterioration (also known as "fatigue") and the need for high-temperature annealing.[15] Although these devices have benefits, they use a readout system that destroys because of leakage problems.[16]

A promising alternative can be found in ferroelectric vinylidene-fluoride (VDF) polymers, such as polyvinylidene fluoride (PVDF) and its TrFE copolymers.[2] VDF copolymers are distinguished by their prominent features, such as substantial spontaneous polarization, remarkable stability, and rapid switching times, making them very suitable for nonvolatile memory.[17] Due to their high resistivity, they have little leakage and are thus well-suited for use in ferroelectric field-effect transistors (Fe-FETs). Contrary to perovskites, VDF polymers do not necessitate high-temperature processing, hence guaranteeing compatibility with other chip components.[18] The current study is focused on the commercialization of straightforward cross-point destructive-readout memories that are built using VDF copolymers. Although ferroelectric polymers provide benefits such as cost-effectiveness, chemical stability, and simplicity of processing, certain configurations still face the difficulty of short data retention durations. Current endeavors are centered on tackling these obstacles and promoting the incorporation of ferroelectric polymers into advanced nonvolatile memory systems.

Ferroelectric polymers, particularly polyvinylidene fluoride (PVDF) and its copolymers, have become a significant field in electronic materials research.[1] Originally acknowledged for their piezoelectric

and pyroelectric characteristics, these polymers, especially when combined with trifluoroethylene (TrFE), exhibit a distinct blend of structural density, chemical durability, and a significant permanent polarity.[2] Ferroelectric polymers are crucial components in electronic memory systems due to their simplicity of manufacture and compatibility with various materials and techniques. Polyvinylidene fluoride (PVDF), with its unique and varied crystalline structures, exhibits a wide range of interesting and useful properties. PVDF is known to crystallize into five distinct polymorphs (α, β, γ, δ, ε) which are determined by factors such as chain conformations, molecular packing, electric poling, and mechanical drawing.[19,20] Although α does not exhibit macroscopic polarization, it is significant in other phases such as β, γ, and δ phases. The β phase exhibits an orthorhombic structure with a conformation of all-trans molecules, which results in the maximum polarization/dipole moment of 0.13 C/m^2.[21] The increased spontaneous polarization of the β phase renders it a superior material for piezoelectric and ferroelectric applications. Trifluoroethylene (TrFE) has three fluoride atoms per monomer, which can combine with PVDF to improve the all-trans conformation in the β phase by copolymerization.[21] Due to the greater size of the fluoride atom compared to the hydrogen atom, it causes a more significant steric hindrance. This leads to a fairly high remanent polarization, which facilitates the generation of large device contrast. Additionally, the low dielectric constants of fluoride contribute to the reduction of operating voltages. PVDF and its copolymers are appealing for several reasons[17]:

- They possess the same fundamental conformational structure as PVDF.
- They may be readily deposited by the process of evaporation.
- Langmuir-Blodgett (LB) deposition may be suitable for them due to the ability to modify the chain lengths and termination groups, CF_3 and I, to regulate the characteristics and functioning of the film formation.
- Due to their monodispersed nature, these molecules have a higher tendency to crystallize. Consequently, they are expected to exhibit fewer chain-folding flaws and lamellar structures compared to PVDF and its copolymers.

- They have maintained reversible polarization patterns of 65 nm or less.

- The termination points of the chain might serve as inherent locations for the formation of new nuclei, so enhancing the rate at which nucleation occurs. This would result in quicker switching since the distance required for propagation would be limited to only 5 nm. They should have the capability to achieve extremely high bit densities, as evidenced by atomic force microscope (AFM) investigations of rewritable bits as tiny as 65 nm.

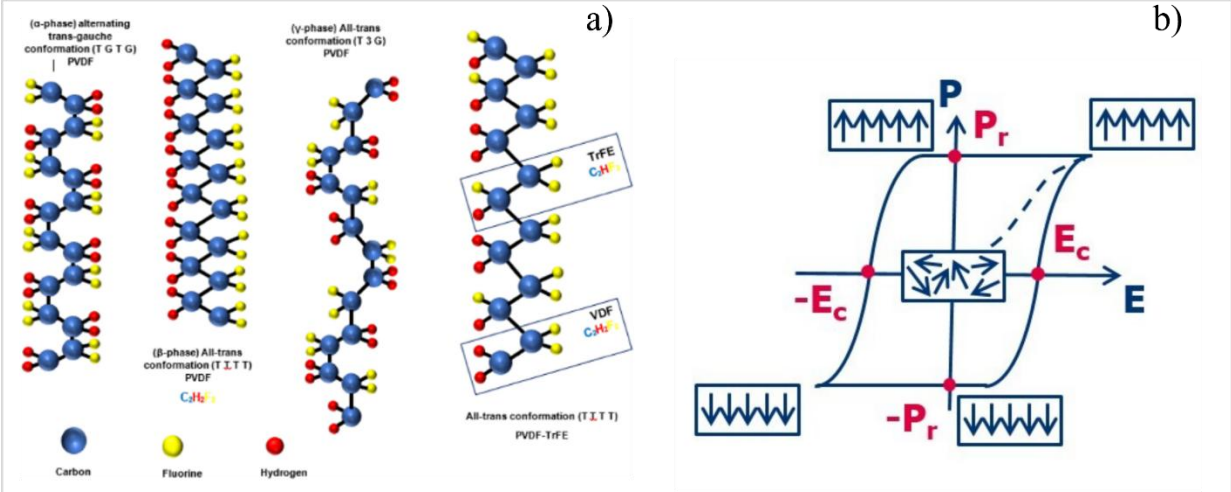

Figure 2: a) Molecular structure of PVDF-TrFE in different configurations.[10] b) Ferroelectricity hysteresis as observed in polymers[12]

The investigation of ferroelectric polymers in memory devices has significantly contributed to the advancement of cutting-edge technology. Metal-ferroelectric-insulator-semiconductor (MFIS) diodes and ferroelectric-field-effect-transistors (FeFET) are important memory structures that utilize P(VDF-TrFE) layers.[22,23] These devices utilize the switchable molecular dipoles present in the ferroelectric polymer, enabling the preservation of recorded data even when power is not available. The polymers' low-temperature manufacturing, cost-effectiveness, and chemical stability make them very desirable for memory applications.

In addition to conventional memory devices, ferroelectric polymers are being utilized in other cutting-edge technologies such as negative capacitance devices, organic photovoltaic cells, and

multiferroic tunnel junctions.[24, 25] Manipulating and harnessing the distinct characteristics of ferroelectric polymers enables progress in the field of organic electronics. Current research efforts aim to enhance memory performance measures, including switching time, voltage needs, and endurance, to broaden the scope of electronic memory applications.[26] Ferroelectric polymers are increasingly important in the development of electronic memory systems. These polymers have flexible features that will support the creation of novel and energy-efficient technologies in the future.

2.3 What and why Langmuir-Blodgett film deposition techniques

The Langmuir-Blodgett (LB) technique is a precise approach used to deposit molecular monolayers onto solid surfaces.[27] This method capitalizes on the capacity of certain chemicals to create very thin layers on the surface of a liquid subphase, usually water. Liquid-liquid interface deposition entails the transfer of these monolayers from the liquid surface onto a substrate using either vertical or horizontal techniques.[28] Through iterative repetition, LB films are systematically constructed with precise thickness and certain structural properties.

- **Molecular-Level Precision:** - LB deposition offers exceptional precision at the molecular level, enabling the creation of homogenous and precisely designed films. The accuracy of these measurements is essential for applications in ferroelectric memory devices since the thickness and arrangement of layers have a direct influence on the performance of the device.
- **Structural Control:** LB methods allow for precise manipulation of film structure by modifying several factors throughout the deposition process, such as subphase conditions like temperature, pH, and compression. Having control over the film structure is crucial for maximizing the ferroelectric characteristics of the materials that are deposited.
- **Two-Dimensional Ferroelectricity:** The use of LB-deposited films of ferroelectric polymers has uncovered distinct two-dimensional ferroelectric properties. This finding has unveiled novel prospects

for the design and execution of ferroelectric memory systems, presenting distinctive attributes compared to conventional three-dimensional ferroelectric materials.

- **Highly Ordered Films:** LB deposition yields films that exhibit a high degree of planarity and order, as seen by methods like as Scanning Tunneling Microscopy (STM). The presence of an organized arrangement significantly enhances and maintains the ferroelectric characteristics, which is essential for ensuring the dependable functionality of memory devices.
- **Scalability and Manufacturing Potential:** LB deposition possesses inherent scalability, rendering it very ideal for industrial operations. Although there are issues such as film replenishment that need to be resolved, LB systems are already accessible for laboratory purposes and may be expanded to accommodate bigger wafers. The possibility of using continuous replenishment systems makes LB deposition feasible for large-scale manufacturing.
- **Environmental Friendliness:** The process of depositing ferroelectric polymers using the LB technique utilizes ecologically benign resources, with water being the predominant substance involved. The copolymers employed are non-toxic and have received approval from the FDA. Additionally, the minute quantity of solvent utilized may be retrieved through the process of evaporation.

To summarize, LB film deposition processes provide a blend of molecular accuracy, structural manipulation, and distinctive ferroelectric characteristics that render them very well-suited for use in ferroelectric memory systems. LB deposition is a potential approach for furthering the development and manufacture of novel ferroelectric memory systems due to its flexibility to customize film properties, scalability, and environmental concerns.

2.4 Critical analysis of existing literature

The current challenge lies in the switching mechanism of Polyvinylidene fluoride (PVDF) and its copolymers, which has generated conflicting results in the literature. Recent research have introduced diverse models to elucidate the dynamics of switching, hence augmenting the intricacy of comprehending

the process. Researchers proposed that the Nucleation-Limited-Switching (NLS) model accurately characterizes the switching dynamics seen in P(VDF-TrFE) films.[29] Contrarily, others employed piezoresponse force microscopy (PFM) to suggest an alternative process, termed non-Kolmogorov-Avrami-Ishibashi (non-KAI), which involves constrained domain expansion.[30,31,32] Scientists also advocated for the suitability of the Interface-Mediated Switching (IFM) paradigm in explaining the two-stage switching behavior seen in thick P(VDF-TrFE) films.[33,34]

The wide range of time intervals for ferroelectric switching dynamics, which spans from picoseconds to seconds, makes it challenging to definitively determine the underlying process. The microscopic process consists of nucleation, followed by forward domain growth, and subsequent sideways growth.[31] The process of nucleation and the subsequent growth of domains usually takes place within a time frame of 1 picosecond to 1 nanosecond. However, the sideways expansion of domains can extend over many nanoseconds to seconds or even longer, depending on several variables both inherent and external to the system. The synthesis process is made more complex by the presence of defects and structural disorders, which serve as nucleation centers and pinning sites for the migration of domain walls.[31] These issues underscore the complex characteristics of ferroelectric switching in PVDF and copolymers.

III. Theoretical Framework

3.1 Principles/Requirements of Langmuir-Blodgett Film Deposition

The Langmuir-Blodgett (LB) film deposition method is a flexible technology that produces precisely organized thin films with regulated molecular configurations.[35] The technique depends on the spontaneous organization of amphiphilic molecules at the boundary between air and water, resulting in the creation of single layers that can be moved onto solid surfaces. This section will provide an introduction to the essential principles and requirements that govern the LB film deposition.

I. **Amphiphilic Molecules and Langmuir Trough**

Amphiphilic molecules are substances that have both hydrophilic (water-loving) and hydrophobic (water-repelling) properties. The Langmuir trough is a device used to study the behavior of these molecules at the air-water interface. Amphiphilic compounds, which have both hydrophilic and hydrophobic components, have a significant impact on the deposition of LB films. The molecules are meticulously placed onto the water's surface, creating a Langmuir monolayer.[36] The Langmuir trough, normally made of Teflon, functions as the experimental device for regulating the water surface area, enabling accurate manipulation of the monolayer.[37,38] The trough also facilitates the monitoring of surface tension and pressure, which are crucial factors in the LB film deposition process.

LB films employ molecules that possess both hydrophilic (attracting water) and hydrophobic (repelling water) components. These molecules possess a dual nature that enables them to spontaneously arrange themselves at the interface between air and water.[39] The Langmuir trough is a Teflon container designed to regulate the surface area of water that may be accessed by the monolayer. It enables the quantification of surface tension and pressure while creating a regulated setting for film deposition. The monolayer at the interface between air and water may be further modified using a moveable barrier, which enables precise control over the area occupied by each molecule. The Langmuir monolayer may be transferred onto a hydrophilic surface using an upward stroke and onto a hydrophobic surface using a downward stroke. A dual-compartment trough facilitates the concurrent processing of two distinct materials, while a controlled dipping sequence permits the assessment of layer structure at a molecular scale.

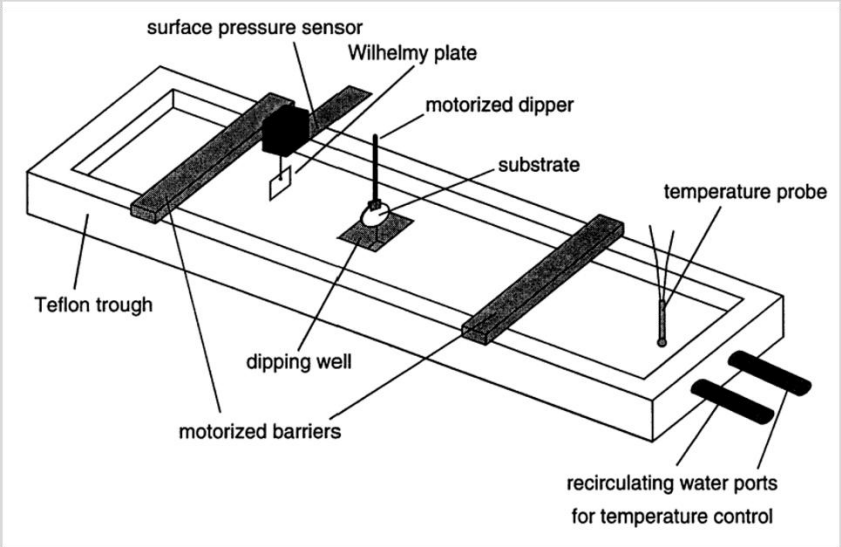

Figure 3: A schematic diagram of a typical Langmuir-Blodgett trough[37]

II. Monolayer Formation and LB Film Deposition

The fundamental LB approach comprises two primary steps-

(a) Preparation of a monolayer film that floats on the surface of water at the air-water interface (known as a Langmuir film)[38]

(b) Deposition of this formed Langmuir film on a solid substrate, also known as an LB film.[39]

The LB film deposition technique starts by precisely depositing a diluted solution of amphiphilic molecules onto the surface of water. The molecules disperse spontaneously to create a monolayer, while the volatile solvent evaporates, resulting in a stable molecular configuration.[37] The LB film deposition process entails the sequential passage of a solid substrate across the contact between air and water. Deposition involves the deliberate alignment of molecules, leading to the formation of a multilayer coating with distinct structural properties. Amphiphilic molecules are added to the water surface in a diluted solution, drop by drop, with caution.

The molecules disperse spontaneously to create a Langmuir monolayer, and the solvent evaporates, resulting in the formation of the monolayer. LB multilayers are formed by sequentially guiding a solid substrate across the interface between air and water. During deposition, the molecules orient themselves

with the polar headgroups attaching during the upward movement and the tails attaching during the downward movement, resulting in the formation of a multilayer film.[39]

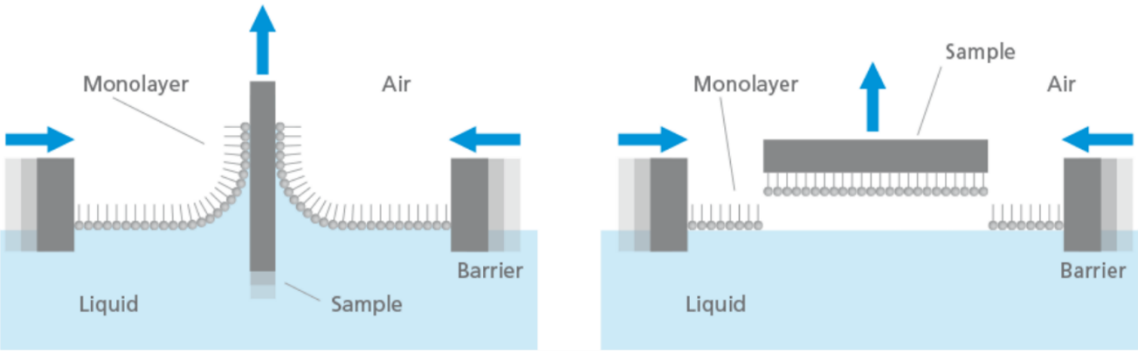

Figure 4: Langmuir Blodgett deposition (left) and Langmuir-Schaefer deposition (right)[39]

During deposition, the surface pressure is maintained at a predetermined and constant value. The Langmuir monolayer may be deposited onto a solid substrate using multiple techniques, such as X-type, Y-type, and Z-type deposition.[39] The transfer of the first layer (Langmuir film) onto the substrate depends on whether the substrate is hydrophilic or hydrophobic, and this transfer occurs when the substrate is elevated or lowered via the interfacial film. If the films are exclusively deposited onto the solid substrate during the downward stroke, the manufactured LB films are referred to as X-type films. If the films are applied onto the substrate by both upward and downward movements, the deposition is of the Y-type. Consequently, if the films are present only on the solid substrate during the upward stroke, the films are classified as Z-type films.[39] The process of depositing a multilayer film involves repeatedly lowering and raising the substrate via the floating layer. The Y-type deposition film exhibits a structure where the heads are aligned with each other and the tails are aligned with each other. The Y-type deposition is frequently employed in the LB method.[39] However, in some instances, the floating monolayer is transferred exclusively either during the immersion (X-type deposition) or the emersion (Z-type deposition) of the substrate. The deposition of LB films is influenced by several factors including the pH and temperature of the subphase, humidity, deposition speed, deposition pressure, layer number, and contact angle between the substrate and floating layer during deposition.[40]

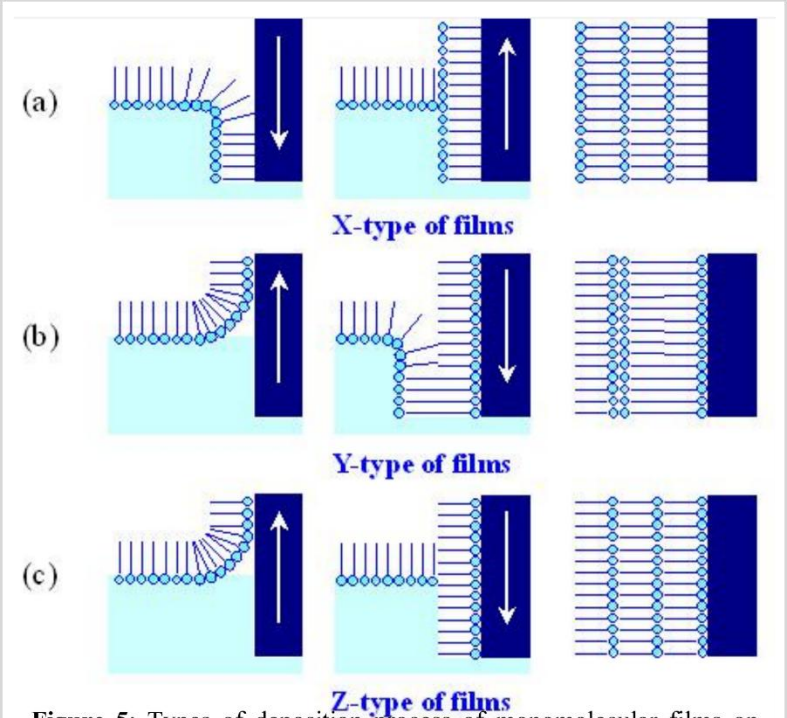

Figure 5: Types of deposition process of monomolecular films on solid substrates[39]

S

III. Surface Tension, Pressure Measurement, and Transfer Ratio

Surface tension is a crucial factor that is observed throughout the process of LB film deposition. The hydrophilic plate's passage through the air-water interface is utilized to measure the force exerted and then determine the surface tension. Surface pressure, which is the discrepancy between the actual surface tension and the surface tension of the naked subphase, offers valuable information on the stability of the film.[41] The transfer ratio (TR) is defined as a diagnostic metric that indicates the reduction in surface area of a monolayer after deposition.[42] The measurement of surface tension involves evaluating the force exerted on a hydrophilic plate as it moves over the boundary between air and water. Surface pressure (π) is the quantitative measure of the deviation between the real surface tension and the surface tension of the bare subphase.

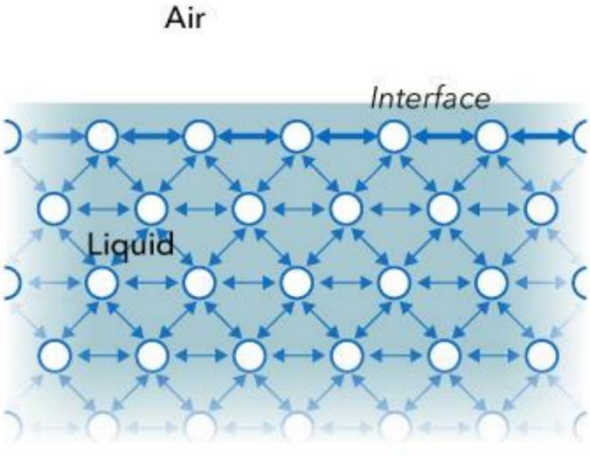

Figure 6: The forces acting on the liquid molecules near and at the surface[41]

IV. Temperature and Speed Control

Temperature regulation is crucial for ensuring stability during the development of LB films. The rate at which the substrate is pulled out under control impacts the effectiveness of LB transfer, enabling appropriate water drainage. The interaction of temperature, velocity, and other variables determines the ultimate properties of LB films. Accurate temperature regulation is essential to maintain stability while the film is being formed. The withdrawal velocity of the substrate during deposition is meticulously regulated to provide effective water drainage, hence improving the effectiveness of LB transfer.

The substrate removal rate during deposition is a critical factor influencing the quality of Langmuir-Blodgett (LB) films. Superior films are achieved by gradually removing the substrate, facilitating efficient water drainage from the film. The strength of the interaction between the molecules' headgroup and the substrate determines the precise rate at which this process is limited. Significantly, when the first layer is applied during the downward stroke, the transfer process becomes less responsive to substrate characteristics, as long as the substrate is hydrophobic. The process of making substrates hydrophobic is commonly accomplished by first depositing a self-assembled monolayer.

Notably, the transfer ratio, especially when the first layer is applied during the upward stroke, can be influenced by the surface pressure of the Langmuir monolayer before transfer. However, this sensitivity is associated with the level of affinity between the headgroups of molecules and the substrate.

The successful deposition that occurs during the upward movement following the first layer deposition depends on the efficient removal of water, and the maximum rate of deposition is governed by the hydrophilicity of the headgroup.[37] Controlling the pace at which the substrate is removed and taking into account the strengths of the interactions between molecules and the substrate are essential elements for creating LB films of high quality.

3.2 Factors affecting LB deposition

Various techniques are available for applying thin organic films onto solid surfaces, such as thermal evaporation, sputtering, electrodeposition, molecular beam epitaxy, adsorption from solution, Langmuir-Blodgett (LB) technique, and self-assembly.[43] Out of these methods, the Langmuir-Blodgett technique is particularly notable as a very promising method for creating thin films because of its distinct benefits such as accurate manipulation of monolayer thickness, uniform deposition across extensive surfaces, and multilayer structure creation.[44] The LB approach has the advantage of being compatible with a diverse array of solid substrates. The ability to deposit monolayers on a wide range of surfaces makes this technology very versatile and widely applicable. Given these benefits, it is crucial to investigate the mechanisms that influence LB deposition. This entails comprehending the effects of variables like temperature, pressure, and molecular interactions, as well as the consequences of substrate qualities. A detailed analysis of these aspects will offer valuable insights for refining the LB approach to achieve customized thin film development.

1) Surface pressure:

Surface tension is a quantification of the force that holds molecules together at the boundary between two substances. The molecules within a liquid have mutual attraction. The molecular interactions inside a liquid are in equilibrium, resulting in equal forces of attraction acting in all directions.[36] Surface-free energy refers to the surplus energy found at the surface and can be measured as energy per unit area. This scenario may be alternatively described as having either line tension or surface tension, which is defined as a measurement of force per unit length. The prevailing units for surface tension are dynes per

centimeter or millinewtons per meter. These units are of equal value. The surface serves as the boundary between two fluids. If the experiment incorporates a gaseous phase, it is called a surface tension measurement. An interfacial tension measurement refers to an experiment conducted when two liquids are examined. Regardless of the scenario, the more compact fluid is designated as the heavy phase, while the less compact fluid is designated as the light phase. Solids can also possess surface-free energy at their interfaces, however, it is not feasible to directly determine its value using the procedures employed for liquids.[37] Polar liquids, such as water, have robust intermolecular forces, resulting in elevated surface tension. Any component that diminishes the intensity of the contact will reduce the surface tension. Therefore, raising the temperature of the system will decrease the surface tension.

As previously stated, the air/water interface contains additional free energy that arises from the disparity in conditions between the molecules at the surface and those in the bulk.[37] The interfacial free energy may be determined by measuring the surface tension, represented by the symbol γ. The surface tension of water at 20°C is around 73 mN/m, which is significantly higher than that of other liquids.[45] This high value makes water an excellent subphase for monolayer investigations. A commonly employed method for conveying an amphiphile to the surface involves dissolving it in a volatile non-polar solvent that is not soluble in water and subsequently depositing it onto the surface using a microsyringe.[46]

The solution soon expands to encompass the entire accessible region. Upon evaporation of the solvent, a single layer of molecules is created. When the accessible surface area for the monolayer is extensive, the distance between neighboring molecules is significant, resulting in weak interactions between them. The monolayer may be seen as a two-dimensional gas. Given these circumstances, the monolayer has minimal impact on the surface tension of water. When the barrier system reduces the surface area of the monolayer, the molecules begin to exert a repulsive force on one another.

The surface pressure, denoted as Π, is a two-dimensional equivalent of pressure. It is defined as the difference between the surface tension, γ, in the absence of a monolayer and the surface tension, γ0, with the monolayer present.[36]

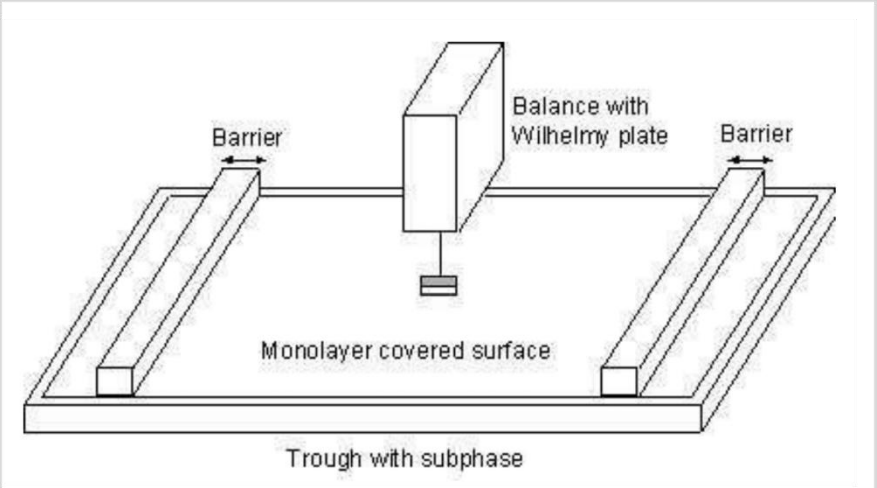

Figure 7: A Langmuir film balance with a Wilhelmy plate electro-balance measuring the surface pressure and barriers for reducing the available surface area[36]

2) The Langmuir Film Balance:

The trough containing the subphase is often constructed from Teflon material to effectively prevent any seepage of the subphase beyond its boundaries.[39] The trough is temperature-regulated by flowing water in conduits positioned beneath the Teflon trough. The surface area of the trough may be altered by moving obstacles across its surface. The barriers are constructed from Delrin, a hydrophilic substance, and possess sufficient weight to effectively prevent any seepage of the underlying monolayer.[40] Both the surface pressure and the mean molecular area are constantly measured throughout the compression process.

The mean molecular area may be calculated by measuring the displacement of the barriers and using the known dimensions of the trough. The Wilhelmy plate method is used to measure the surface pressure. This approach involves measuring the force resulting from surface tension on a suspended plate that is partially submerged in the subphase. The force is subsequently transformed into surface tension, measured in mN/m or dynes/cm, using the plate's size.[39] The plate is frequently characterized by its slender profile and composition of platinum, however alternative materials like as glass, quartz, mica, and filter paper can also be employed.[41] The plate experiences downward pressures from gravity and surface tension, while upward buoyancy is caused by the displacement of water. The equation for the net downward force

on a rectangular plate, with dimensions lp, wp, and tp, made of material with density ρp, submerged to a depth hl in a liquid of density ρl, is as follows:

The equation may be expressed as $F = \rho p g l p w p t p + 2\gamma(tpwp)(\cos\theta) - \rho l g t l w l h l$, where γ represents the liquid surface tension, θ is the contact angle of the liquid on the solid plate, and g is the gravitational constant. The surface pressure is subsequently calculated by quantifying the variation in force (F) exerted on a motionless plate when comparing a pristine surface to the identical surface coated with a monolayer. If the plate is fully saturated with the liquid (i.e. $\cos\theta = 1$), the surface pressure may be determined using the following equation:

By employing an extremely thin plate, sensitivity may be enhanced. The force is calculated by monitoring the variations in the mass of the plate, which is directly linked to a very sensitive electrobalance.[37] The monolayer can also be maintained at a consistent surface pressure by a computer-controlled feedback system that links the electro-balance and the motor controlling the motions of the compressing barrier. This is beneficial when creating LB films, especially when the monolayer is applied over a solid substrate.

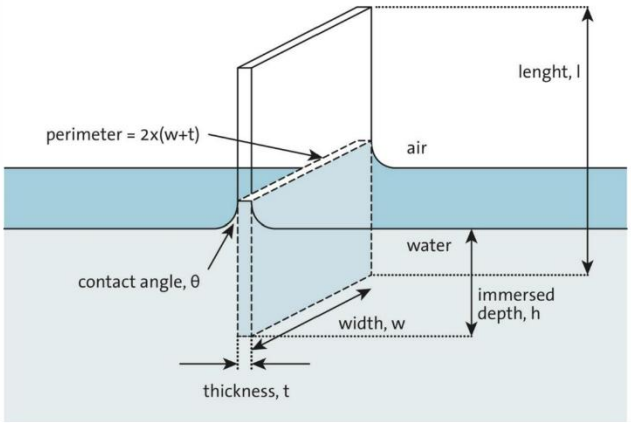

Figure 8: A Wilhelmy plate partially immersed in a water surface[39]

3) Surface Pressure Area Isotherm:

Amphiphilic monolayers are characterized by measuring the surface pressure about the average molecular area. This process yields a significant indication called a surface pressure-area isotherm.[27] This isotherm is created by compressing the monolayer film at a constant velocity and measuring the surface pressure, all while maintaining a constant temperature. The resultant isotherm displays well-delineated sections or phases, providing insight into the behavior of the monolayer when subjected to compression.

Important Stages in Isotherms[28]:

- Gaseous Phase: Monolayers originally arise in the gaseous phase (G). Applying pressure to the monolayer causes it to change into the liquid-expanded condition (L1).
- Liquid-Expanded State (L1): Continuing to compress the L1 phase leads to a transformation into the liquid-condensed state known as L2. This transition is influenced by the length of the hydrocarbon chain and the cohesive/repulsive forces.
- Liquid-Condensed State (L2): As the density increases, the monolayer transitions into a solid state (S). The intermolecular attraction strengthens as the length of the molecule chain increases, resulting in the condensation of the isotherm.
- Solid State (S): Further compression of the monolayer in the S state can cause it to undergo a collapse, resulting in the formation of three-dimensional structures. Collapse is characterized by a sudden reduction in surface pressure or a horizontal discontinuity in the isotherm of liquid monolayers.

The monolayer's phase behavior is controlled by the amphiphile's physical and chemical characteristics, subphase temperature, and composition. Ionizable amphiphiles generate repulsive forces that oppose phase transitions.[44] Understanding these isothermic phases and critical points is vital for designing amphiphilic monolayers for specific applications, providing precise control over their characteristics.[47]

4) Anomalies in Langmuir-Blodgett Layers: Chemical Slant and Flow-Driven Orientation

When anisotropy arises on the surface plane of Langmuir-Blodgett (LB) films, it is mostly caused by molecule tilt.[48] Because the tail projects onto the surface plane, it serves as a molecular director, giving

the film a directed quality because of molecular tilt. Anisotropic molecular packing is typically the result of this tilt. Furthermore, anisotropic packing may arise even in the absence of tilt due to particular close-packing constraints imposed by molecule geometries.

Two primary causes of macroscopic anisotropy in LB films are epitaxial growth on the substrate or the layer above it, and flow-induced orientation within the Langmuir trough.[49] A flow within the monolayer is started by adding or removing the substrate. This flow modifies the architecture of associated domains in the Langmuir monolayer by displacing molecules in the LB film and creating a complicated pattern. It causes the molecules to orient preferentially, which frequently results in extended macroscopic domains that are parallel to the direction of dipping.[49]

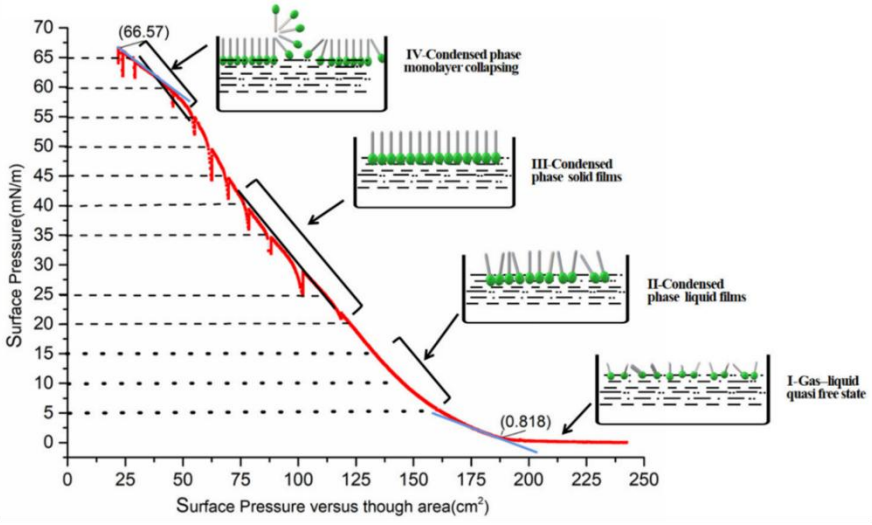

Figure 9: π–A isotherm and the LB film formation of P(VDF-TrFE) Solution (0.01%) with ultra-pure water subphase. [47]

The film is oriented at the molecular level as demonstrated by dichroic ratios seen in infrared spectra. During the precursor Langmuir monolayer phase, the dipping direction or other generated flows are correlated with the anisotropic azimuthal distribution of molecule tilt.[50] The anisotropic properties of LB films are largely determined by the interaction between molecule tilt and flow dynamics.

Other than these parameters that affect the LB monolayer film formation are[51]-

- Van der Waals interaction: Short-range forces (ΓVDW ∝ r−6) which are directly proportional to the number of carbon atoms in the hydrocarbon chain for the saturated hydrocarbon and thus depend upon the presence of double bonds or functional groups like methyl group or other substituents in the chain.
- Electrostatic interaction: Present in Ion – Ion (Γii ∝ r−1), Ion – Dipole (Γid ∝ r−2), or Dipole-Dipole (Γdd ∝ r−3)
- Subphase composition: pH, temperature, type or nature of the materials in the subphase

3.3 Mechanisms of Film Evolution & challenges

During the nucleation stage of thin film formation, vapor atoms or molecules condense and then undergo surface diffusion. They are driven by both self-energy and the thermal energy of the substrate, causing them to move. These entities establish persistent places on the substrate, continually assimilating neighboring particles, resulting in the slow development of a film. Methods such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning probe microscopy (SPM), and field-ion microscopy (FIM) have successfully seen this activity.

Thin film deposition on crystal substrates may be classified into three primary growth modes:

- The growth model known as Layer-by-Layer Growth Model, often referred to as the Frank-Van der Merwe Model, is characterized by the sequential deposition of atomic or molecular layers on a substrate. This phenomenon happens when the wetting angle (θ) approaches zero, leading to the formation of two-dimensional layers with less strong bonding between them. This phenomenon is frequently observed in materials that have a uniform composition, as well as in certain combinations of materials with different properties, such as semiconductor and oxide epitaxial growth.[52]
- Island Growth Model (Volmer–Weber Model): Occurs when the wetting angle (θ) is above zero, resulting in the formation of three-dimensional nucleus islands with robust intermolecular bonding.

This method frequently yields polycrystalline thin films with an uneven surface, especially when used with substrate-film combinations that are not uniform.[53]

- The Stranski-Krastanov model is an intermediary step that occurs between layer-by-layer and island development patterns. Thin films first undergo two-dimensional layer-by-layer development, which then transitions to three-dimensional island growth as a result of stress-induced impacts after the two-dimensional growth phase.[54]

Epitaxial growth is a widely used and appealing approach for film growth, where a continuous single-crystal layer is formed on a crystalline substrate by layer-by-layer development. This procedure is very suitable for attaining films of exceptional quality, particularly for semiconductor and oxide materials.

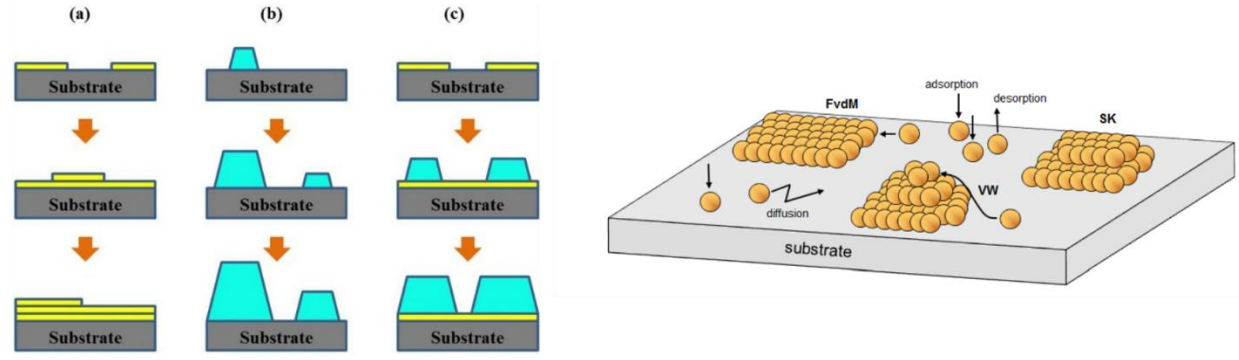

Figure 10: Schematic representation of the known film growth models depending on the free energy contributions. a) Frank-Van der Merwe Model b) Volmer–Weber Model c) Stranski-Krastanov model. The spheres can be either atoms/nanoparticles (NPs). When NPs approach a substrate either adsorption, desorption or diffusion occurs.[52,53,54]

3.4 Fundamental concepts of ferroelectric polymers

Since the 1970s, crystal structures and phase transitions of ferroelectric polymers—in particular, Polyvinylidene Fluoride (PVDF) and its copolymers—have been the subject of much research. To fully use the potential of these materials in a variety of applications, this understanding is essential. Determining the operating speed of devices and designing purposeful materials requires an understanding of the dynamics of polarization switching.

Three successive processes are involved in the universal mechanism of polarization switching: sideways growth, forward domain growth, and nucleation. This mechanism, first described by Fatuzzo,

starts with the electric field creating tiny nuclei at grain boundaries or interfaces. These nuclei ultimately form domains as they travel forward, and finally they extend sideways, resulting in a complete reversal of polarization across the sample.

Extrinsic switching, which is typified by domain nucleation and growth, is shown to be the predominant switching mechanism in ferroelectric thin films. With increasing temperature (T) and electric field (E), this activated process shows an exponential increase in the switching rate (reciprocal switching time $1/\tau$).[55] For most ferroelectrics, extrinsic coercive forces, which are usually measured at 50–60 Hz, vary from 0.01 to 10 MV/m.[56] The coercive fields of thin films, especially those made using the Langmuir-Blodgett (LB) technique, are higher and can approach 500 MV/m.[56] For fields of 100 MV/m, the propagation velocity of domain barriers is projected to be 10 m/s, implying quick switching in some situations.[57]

For applications like as NV-RAM, however, the very slow switching seen in certain LB films presents difficulties, possibly because it inhibits nucleation and domain development at lower film thickness. Studies suggest that the main consequence of introducing nucleation by defect production, such electron irradiation, would be the material's transformation into an amorphous state.

Controlling nucleation and domain dynamics may be achieved by synthetic manipulation and nanoscale patterning. The performance of switching is influenced by patterning by localized heating, chemical modification, or fault structures; on the other hand, nucleation may be selectively promoted through synthetic manipulation, for as by inserting molecular units or blocks. These tactics seek to improve ferroelectric materials' switching determinism and speed, which are essential for maximizing their performance in a range of applications.

The mechanism underlying the dynamics of domain-derived polarization switching is clarified by several quantitative models. The homogeneous nucleation and subsequent domain development hypothesis is put forth by the Kolmogorov–Avrami–Ishibashi (KAI) model.[30] The nucleation-limited switching (NLS) model was presented by Tagantsev et al. in which switching and nucleation happen region by region and

take longer than domain wall motion.[29] P(VDF-TrFE) and ultra-thin PVDF films demonstrated an inherent mechanism that differs from standard nucleation and growth processes.

To summarize, the basic principles of ferroelectric polymers include a thorough comprehension of phase transitions, crystal structures, and the complex dynamics of polarization switching. The design and functionality of devices made with these materials may be optimized with the use of this information.

3.4.1 The KAI Model

The Kolmogorov-Avrami-Ishibashi (KAI) model is based on the assumption of homogeneous nucleation and infinite domain development in an infinite medium.[58] It was initially developed for evenly polarized single crystals and epitaxial films. This model finds practical use in some circumstances, especially for fast-switching processes in ceramics, despite its limits in correctly describing polarization switching in ferroelectrics with limited size and polycrystalline films or bulk materials.[59]

$$\mathrm{P(t)} = 2P_s\left\{1 - \exp\left[-\left(\frac{t}{t_0}\right)^n\right]\right\},$$

$$\mathrm{I(t)} = 2P_s\frac{n}{t_0}\left(\frac{t}{t_0}\right)^{n-1}\exp\left[-\left(\frac{t}{t_0}\right)^n\right],$$

With parameters like Ps (spontaneous polarization), t0 (typical switching time), and n (a value between 1 and 3, defining the rate of nucleation and dimension of subsequent growth), the KAI model defines the reversed polarization (P(t)) and switching current density (I(t)). Notably, for physical importance, n must equal or exceed 1.

Recent research, such as that conducted on P(VDF-TrFE) films, indicates that the polarization reversal seen in these films is consistent with the conventional KAI process. This discovery is consistent with the model's effective use in the explanation of fast-switching phenomena in inorganic ceramics. All things considered, the KAI model is still a useful resource for comprehending the kinetics of polarization switching in certain ferroelectric materials and combinations.

3.4.2 NLS Model

An alternative scenario, the Nucleation-Limited Switching (NLS) model, was created in response to the limitations of the Kolmogorov-Avrami-Ishibashi (KAI) model. This model is especially well adapted to describe longer-duration polarization switching processes, such as those seen in some ferroelectric thin films where the nucleation time is much longer than the domain wall motion time.[29]

$$P(t) = 2P_s \int_{-\infty}^{\infty} \left\{ 1 - \exp\left[-\left(\frac{t}{t_0} \right)^n \right] \right\} F(\log t_0) d(\log t_0)$$

where F(log t0) is the distribution function of log t0 and meets the following normalizing condition-

$$\int_{-\infty}^{\infty} F(\log t_0) d(\log t_0) = 1$$

The ferroelectric film is assumed by the NLS model to consist of many areas that independently nucleate and switch. An improved formulation of the NLS model that includes a distribution function of switching times (log t0) is used to represent the time-dependent polarization. For thin-film ferroelectrics and bulk ferroelectrics, the value of parameter 'n' is assumed to be 2, and the equation requires an integral over the distribution function. To characterize the random electric field distribution, several research have suggested several distribution functions, including Gaussian and Lorentzian.[59]

The NLS model has been effectively utilized by researchers, such as Mao et al., to match the region-by-region polarization reversal in polycrystalline P(VDF-TrFE) thin films. The polarization reversal behavior in the time domain has been effectively described by the NLS model, offering important insights into the switching dynamics of ferroelectric materials.[60]

3.4.3 Intrinsic Switching

Studies on ultra-thin PVDF and P(VDF-TrFE) films has shown different switching dynamics that differ from the nucleation and domain wall motion predicted by the KAI and NLS models.[56] Specifically, studies on films made using the Langmuir-Blodgett (LB) process have shown this. Due to these models' insufficiency for extremely thin films, the Landau-Ginzburg-Devonshire (LGD) theory-based phenomena known as intrinsic (homogeneous) switching was proposed.

The LGD theory states that ultra-thin ferroelectric films have an internal coercive field (Ec), indicating that polarization switching happens only when Ec is exceeded by an external electric field (E).[61] Highly correlated dipoles in the crystal switching coherently or not at all are the characteristic that define this intrinsic switching phenomena. The predicted value of Ec in the absence of nucleation is large, often on the order of 100 MV/m for ferroelectrics.[56] P(VDF-TrFE) LB films exhibit intrinsic switching, as noted by Ducharme et al., who also showed that the coercive field rises with decreasing thickness initially until saturating below a threshold thickness of 15 nm.[56]

Because the films are so thin, the coercive voltage during intrinsic switching is limited to 5 V. Simulations by Paramonova et al. revealed a critical thickness of 3–6 nm and a coercive field of 500–2500 MV/m.[34] According to the LGD theory, the Gibbs free energy (G) is a function of temperature (T), spontaneous polarization (P), and the external electric field (E). The resultant normalized steady-state P(E) hysteresis loop clarifies the dynamics of polarization switching under various external electric field circumstances by displaying stable, metastable, and unstable phases.

Following the discovery of intrinsic switching in ultra-thin P(VDF-TrFE) LB films, Gaynutdinov et al. carried out further studies with PFM to confirm the presence of intrinsic switching at the nanoscale while reducing the impact of electrodes. Confirming the validity of the intrinsic switching mechanism required this experimental evidence. In addition, intrinsic switching in pure PVDF ultra-thin films was observed by Tian et al. Later research expanded the use of intrinsic switching to ultra-thin ferroelectric $BaTiO_3$ films and ultra-thin epitaxial $PbTiO_3$ films. The combined data highlights intrinsic switching's frequency and importance in a variety of ultra-thin ferroelectric films.

3.5 Relevant theories and models in semiconductor electronics

In comparison to solvent-based manufacturing, Langmuir-Blodgett (LB) deposition of copolymer films offers benefits including adherence to a variety of surfaces, chemical stability, low-temperature processing, and compatibility with a range of patterning techniques. When it comes to producing

homogenous films as thin as a nanometer, LB deposition works better than solvent approaches, which is especially advantageous for integrated polymer-semiconductor technology.

Compared to spun copolymer films, LB copolymer films have improved chain and crystalline alignment, as well as excellent crystallinity. These films exhibit promise for high-performance nonvolatile memory with a consistent (110) crystal orientation, particularly as device dimensions reduce.[62] As flaws are reduced, finer patterning is made possible, and memory components that operate at lower voltages can be created, the advantages of LB films become increasingly apparent.

Data preservation without power has been shown by the development of a bistable nonvolatile memory element based on the Metal-Ferroelectric-Insulator-Semiconductor (MFIS) structure.[63] Because the MFIS structure is easier to assemble than FeFET devices, it makes it easier to test important interactions between the depletion/accumulation layer of the semiconductor and ferroelectric film polarization.[22] The ferroelectric PVDF (70%) with TrFE (30%) LB sheet, silicon oxide insulating layer, and aluminum electrode that make up the MFIS memory components show promising properties.[44]

The influence of polarization hysteresis on the gate-voltage range is shown via polarization hysteresis loops with different amplitudes. Stable polarization states are responsible for the observed polarization levels, even when they are lower than the nominal value.

To optimize device behavior, several pertinent theories and models are essential in the field of semiconductor electronics for ferroelectric-based memory devices. The following are some important theories and models:

1) Models of Ferroelectric Hysteresis:

Landau-Ginzburg-Devonshire (LGD) Theory: Explains how temperature, electric field, and spontaneous polarization relate to each other in ferroelectric materials. It is essential to comprehend hysteresis behavior and the ferroelectric phase transition.

2) Models of Switching Dynamics:

In an endless medium, the Kolmogorov-Avrami-Ishibashi (KAI) model postulates homogeneous nucleation and infinite domain growth. It sheds light on the kinetics of polarization switching in

ferroelectrics. The Nucleation-Limited Switching (NLS) model postulates that the film is composed of several independently nucleating and switching areas. It fits well with the explanation of time-consuming switching processes in ferroelectric thin films.

3) Mechanisms of Polarization Switching:

Tagantsev and Fatusso proposed the three-step switching mechanism, which entails nucleation, succedent sideways growth, and forward domain growth in the polarization switching process.

4) Models of Domain Wall Motion:

These explain the domain wall motion dynamics in ferroelectric materials using the Miller-McWhorter model. It takes into account how charge carriers and the domain wall interact.

5) Models of Charge Trapping:

The Sawyer-Tower Model is a popular tool for studying the trapping and de-trapping of charges at interfaces in ferroelectric memory. It aids in the comprehension of polarization endurance and retention.[64]

6) Models of CMOS Integration:

Models for Interface Engineering: Models about interface engineering and compatibility are essential when taking into account the integration of ferroelectric materials with CMOS technology. Comprehending the ferroelectric layer's interaction with semiconductor components is necessary for this.

7) Models for Device Operation and Reliability:

- Models for Read and Write Operations: Explain how ferroelectric-based memory devices are read from and written to.
- Dependability Frameworks: Examine ferroelectric memory's long-term dependability while taking retention and fatigue into account.

8) Models of Ferroelectric Tunnel Junctions:

Models of Tunneling Electroresistance (TER): To comprehend the TER effect employed in nonvolatile memory, investigate the tunneling phenomena in ferroelectric tunnel junctions.

In semiconductor electronics, comprehending and utilizing these theories and models is essential for ferroelectric-based memory device design, optimization, and performance prediction. To have a thorough

understanding of the intricate behavior of these devices, engineers and researchers frequently combine different models.

IV. Experimental Methodology

4.1 Overview of materials and equipment

Silicon wafers were obtained from University wafer. The p-type silicon wafer each had thickness of 280 microns, and ohmic resistance of 0.001-0.005. The solvents DMSO, Acetone and Cyclopentanone were procured from Sigma Aldrich. PVDF-TrFE polymer used in this research is a product of Arkema Piezotech sold by PolyK Technologies. This blend had a composition of VDF/TrFE 70/30 mol, Tm of 152 °C and Tc in the range of 90-105 °C.

4.2 Detailed description of Langmuir-Blodgett film deposition process

The fabrication of devices was performed using KSV-NIMA system which included KSV NIMA trough type 611, and NIMA dipper type D1L. PVDF-TrFE 1% weight solution was made in DMSO, 40% DMSO+ 60% Acetone, and Cyclopentanone. Ultrapure water was poured onto the LB trough. The pressure was monitored by the Wilhelmy plate/ Whatman filter paper was first calibrated. The surface pressure was continuously monitored for 20 minutes till the value was stabilized to a surface pressure of approximately 5 mN/m and 7 mN/m. Later, approximately 250 µL of PVDF-TrFE solution was pipetted out on the surface. The silicon substrate was then dipped using the dipper attachment into the trough. After waiting for roughly 15 minutes to evaporate the solvent the movable barriers are compressed till the surface pressure reaches the desired values of 5 and 7 mN/m. The substrate was then deposited with nano-films by slowly moving the dipper up in a controlled way. Finally, the Silicon with PVDF-TrFE substrate was removed and allowed to dry for few minutes. The substrates were then annealed at 135 ºC for 30 minutes.

4.3 Fabrication and characterization of semiconductor memory devices

The devices were then characterized for further studies. The microstructure and surface morphology were measured with Atomic Force Microscopy (AFM) and Piezoresponse Force Microscopy (PFM) were performed on Park NX20. The morphology was first examined by AFM in non-contact mode.

For understanding the ferroelectric properties, piezoelectric force microscopy (PFM) was performed. Each sample was swept from -1V to +1 V at seven different locations for PFM spectroscopic studies. DC voltage bias was applied on the sample substrate and the AC voltage bias 1V-10V was applied on the PFM probe, Gold cantilever. AFM scans were performed using Si cantilever to understand the surface topography and the roughness of surfaces. The thickness was obtained by J.A.Woolam M-2000D Ellipsometer over the angle range 45°~90°.

V. Results and Discussion

5.1 LB Film Characterization-

- Atomic Force Microscopy (AFM):

It was observed that lower surface pressure may be advantageous for sensitive thin films to get uniform and defect-free film growth. Higher surface pressure tends to promote over-stacking of the molecules leading to the formation of clusters. However, DMSO+Acetone solvent system provided smoother surfaces thin films. This could be attributed to better dispersion of the polymer molecules in this solvent system.

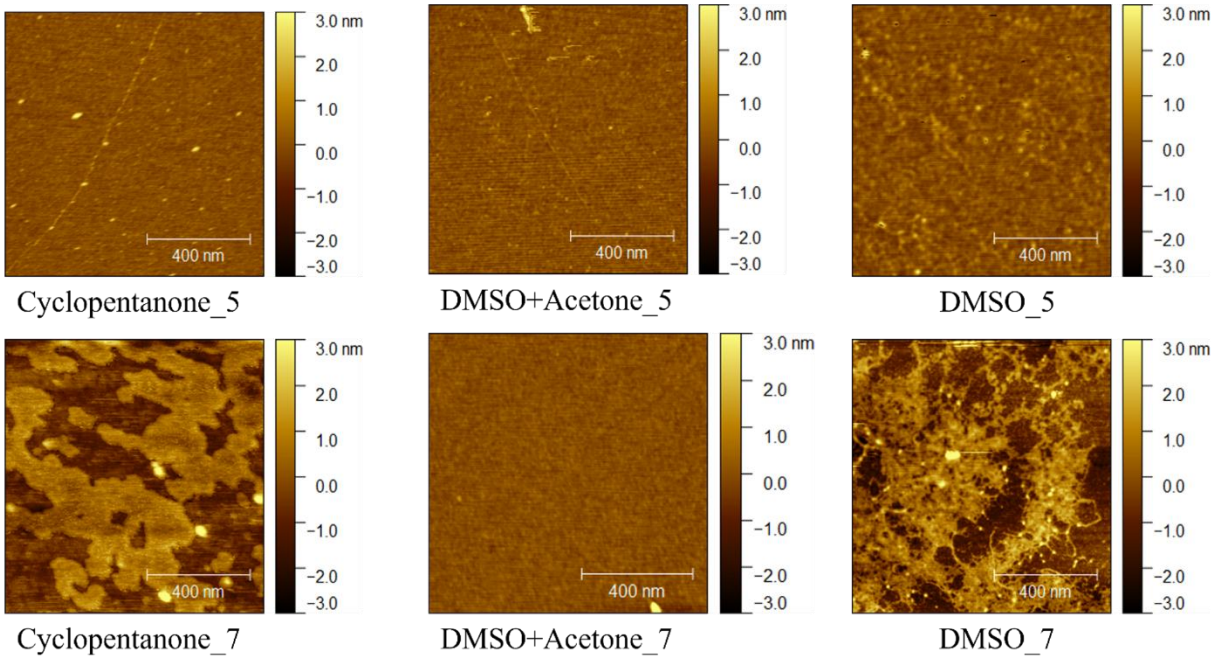

Figure 11: AFM scans as observed using park NX20 system

The roughness values were also plotted as a function of solvents and was compared to understand the effect of solvent systems on LB deposition. It was observed that DMSO+Acetone system led to smoother thin film surfaces. Cyclopentanone at 5 pressure value also had low roughness which can be also observed from AFM scans as depicted in Figure 11.

Graph 1: Comparison of roughness values

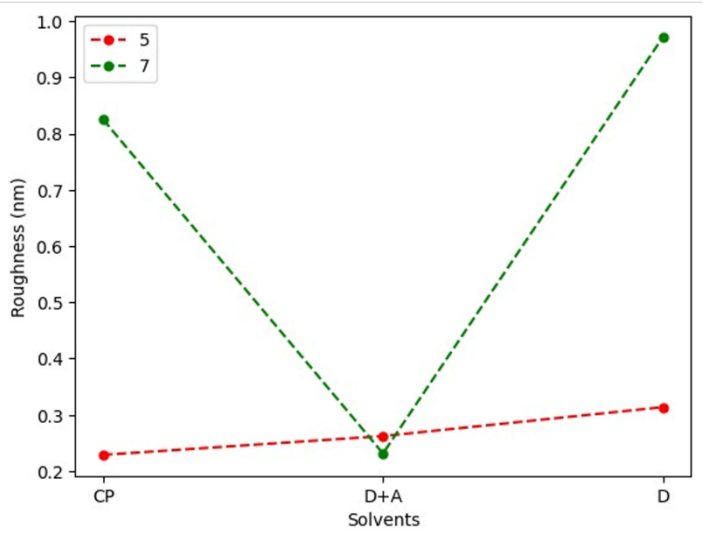

Table 1: Comparison of roughness values

Solvent	Roughness (nm)
DMSO 5	0.31
DMSO+Acetone 5	**0.26**
Cyclopentanone 5	0.23
DMSO 7	0.97
DMSO+Acetone 7	**0.23**
Cyclopentanone 7	0.82

- Piezoresponse Force Microscopy (PFM)

The PFM spectroscopy was performed on each sample. The phase vs bias and amplitude vs bias plots were obtained. The Phase vs Amplitude plots showed the hyteresis curves for all of samples. However, in DMSO+Acetone system the hyteresis were more pronounced. The Ps/Pr ration from the plots were calculated to understand the squareness of the loops. The DMSO+Acetone system at both pressure values had the best Ps/Pr ratio; out of which D+A_5 sample had Ps/Pr ration ~1 showing more ideal ferroelectric characteristics. Hysteresis loops in ferroelectric materials represent the relationship between polarization (P) and electric field (E) during the process of polarization switching. They exhibit a symmetric shape, showing the reversibility of the polarization process under an alternating electric field. The width of the hysteresis loop indicates the speed at which the material can switch its polarization under an applied electric field. Squareness of loops is found for DMSO+Acetone solvents, indicating better polarization switching characteristics, and exhibiting more stable and reliable data storage. The shift in the loops could be

attributed to residual charges present in the system, either on the surface of the sample or within the experimental setup. These charges can lead to an offset in the hysteresis loop.

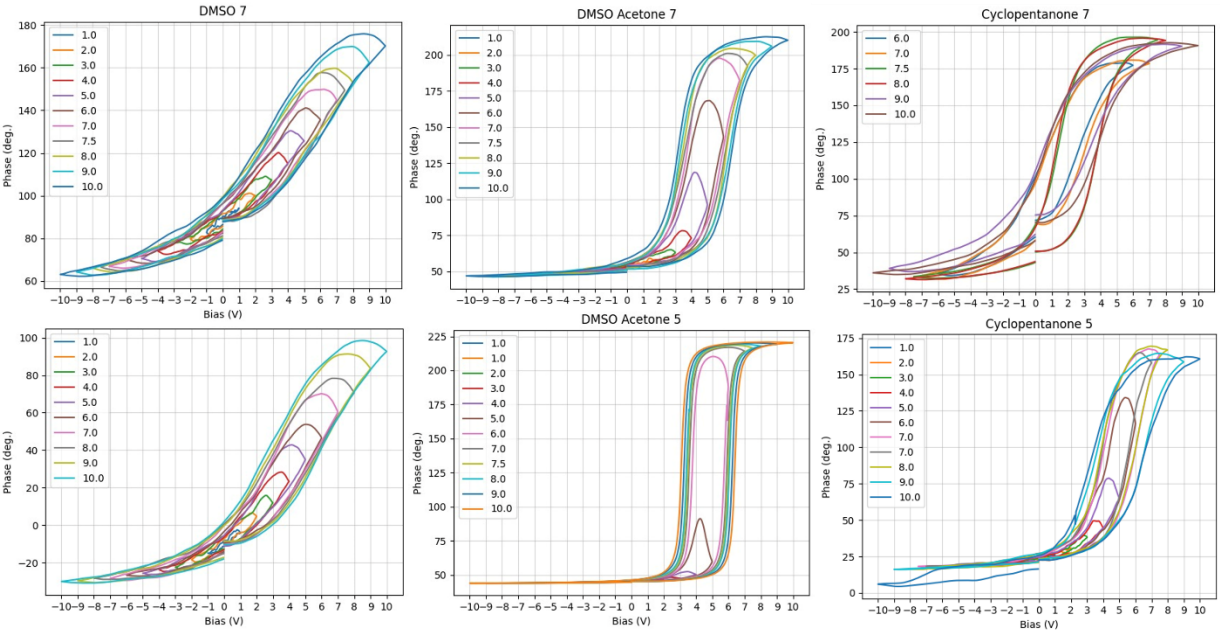

Figure 12: PFM Phase vs Bias plots for different samples. Every sample was swept at 10 different voltages.

The amplitude vs bias plots were also studied to understand if the flipping of polarization, a typical characteristic of ferroelectric materials was observed. From the PFM spectroscopy, a comparison of memory widow and squareness of loop gave better understanding of the relationship of solvents on ferroelectric properties. This behavior of DMSO+Acetone system could be attributed to segregation of the β phase of the PVDF-TrFE polymer. These devices have MW of ~3V, indicating its potential for applications in non-volatile memory storage.

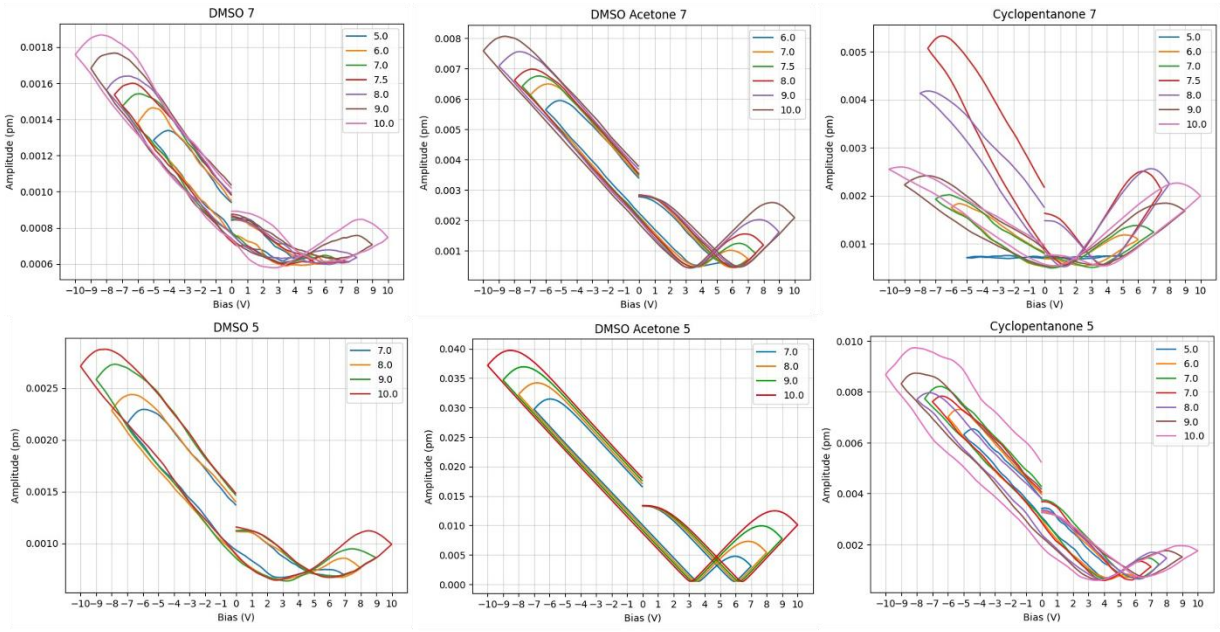

Figure 13: PFM Amplitude vs Bias plots for different samples. Every sample was swept at 10 different voltages.

Graph 2: Comparison of memory window and squareness of loops

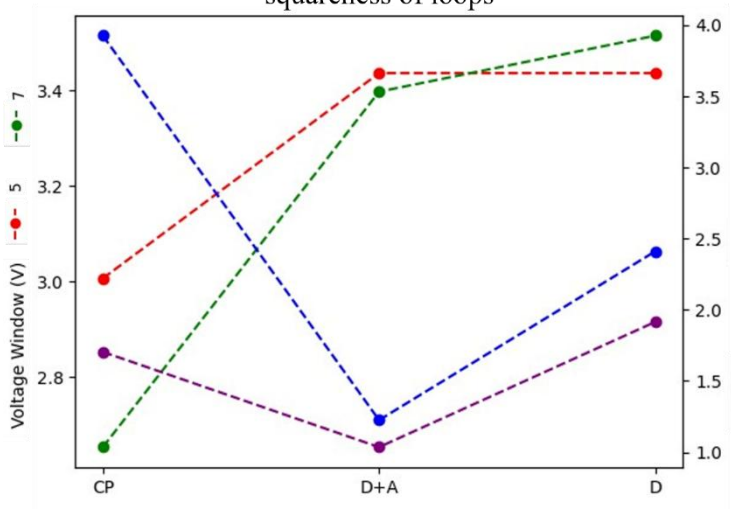

Table 2: Comparison of memory window and squareness of loops

Solvent	MW	Ps/Pr
DMSO 5	3.43	1.91
DMSO+Acetone 5	**3.43**	**1.03**
Cyclopentanone 5	3.00	1.70
DMSO 7	3.51	2.41
DMSO+Acetone 7	**3.39**	**1.22**
Cyclopentanone 7	2.653	3.92

- Ellipsometry (Thickness measurements):

The Ellipsometry data was plotted and compared to understand how the solvents affected the LB deposition. It was observed that the DMSO+Acetone solvent mixture consistently produces thinner films, highlighting its potential for precise control over film thickness compared to other solvents. The thickness of the films at 5 pressure units is probably thinner than it is at 7 pressure units. This is due to the fact that

thinner and more uniform films are often formed during LB deposition when lower pressure is applied. In contrast to films deposited at higher pressure (7 pressure units), where the increased pressure may lead to thicker and possibly less uniform films due to enhanced molecular packing and stacking, the smoother surfaces observed at 5 pressure units suggest that the molecules are more evenly distributed and aligned, resulting in a thinner and more homogeneous film.

Graph 3: Comparison of thickness values

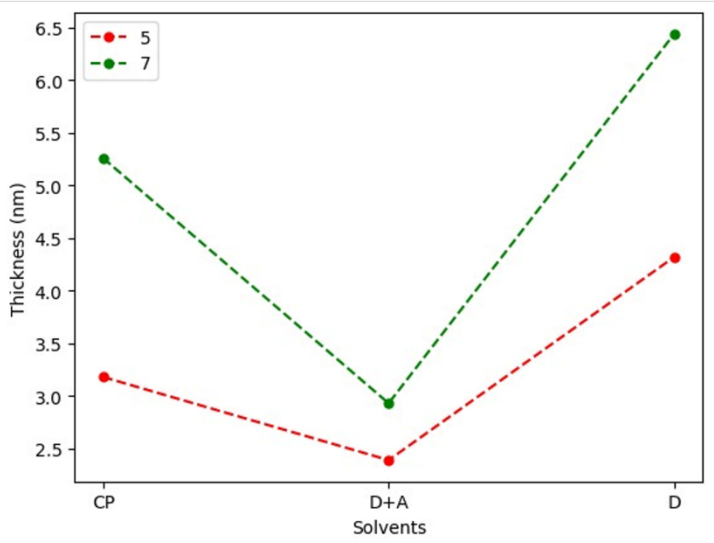

Table 3: Comparison of thickness values

Solvent	Thickness (nm)
DMSO 5	4.32
DMSO+Acetone 5	**2.39**
Cyclopentanone 5	3.18
DMSO 7	6.44
DMSO+Acetone 7	**2.93**
Cyclopentanone 7	5.26

5.2 Discussion of key findings-

To understand the superior behavior of DMSO+Acetone solvent system, the focus was shifted to theory. In chemical terms, solvents can be describe in terms of Hansen's parameters which were coined by Charles Hansen 1967. It is a way of predicting whether one substance dissolves another. Hansen described the solubility parameters for solvents based open the three molecular forces that govern dissolving polymers in different medium. The solubility parameters are δD for Dispersion (van der Waals), δP for Polarity (related to dipole moment), and δH for Hydrogen bonding. These three parameters are treated like Vector for a point in three dimensional space called as the Hansen space. The distance between polymer and solvent is given by the relationship:

$$D_{S-P} = \sqrt{4 * \left(\delta_{d,P} - \delta_{d,S}\right)^2) + \left(\delta_{P,P} - \delta_{P,S}\right)^2 + \left(\delta_{h,P} - \delta_{h,S}\right)^2}$$

The London dispersion forces between molecules are described by the dispersion parameter (δd), which indicates how well a solvent can dissolve nonpolar compounds. Polar Parameter (δp): Indicates the solvent's capacity to dissolve polar compounds by reflecting the dipole-dipole interactions among molecules. The hydrogen bonding parameter (δh) shows how molecules interact with one another and indicates whether a solvent may dissolve compounds that can form hydrogen bonds. Understanding the solvation behavior of various solvents and forecasting solvent-solute interactions can both benefit from an understanding of Hansen's parameters. One may ascertain solvent compatibility, solubility, and the probability of successful procedures like film deposition by comparing the solvents' Hansen's parameters with those of the solute or substrate.

Table 4: A descriptive chart of boiling points and Hansen's parameters for different solvents with respect to PVDF-TrFE

Species	Density (g/cm3)	Melting /Boiling Temperature (◦C)	Dipole Moment (Debye)	Hansen's parameters			
				δ_d	δ_p	δ_h	D_{S-P}
PVDF-TrFE	1.9	150		17.2	12.5	9.2	
DMSO	1.1	189	3.96	18.4	16.4	10.2	4.68
DMSO+ Acetone	0.91	109.2	3.31	16.66	12.8	8.28	1.45
Acetone	0.79	56	2.85	15.5	10.4	7.0	4.56
Cyclo-pentanone (CP)	0.95	131	2.87	17.9	11.9	5.2	4.28

The compatibility or resemblance between a solvent system and the target material, namely the PVDF-TrFE polymer, may be determined by examining the lowest HSP (Hansen Solubility Parameter) distance or Ra (HSP distance). A smaller HSP distance indicates a higher degree of similarity between the solvent system and the PVDF-TrFE polymer in relation to its solubility property. The previous statement suggests that the solvent system exhibits enhanced capacity to dissolve and engage with the polymer, resulting in enhanced solvation, spreading, and uniformity of the polymer solution throughout the LB deposition procedure. From a practical perspective, a reduced HSP distance or Ra value signifies enhanced compatibility between the solvent and polymer, leading to the deposition of thin films that are smoother, more uniform, and free from defects. Hence, it is advantageous to use a solvent system that exhibits the shortest (HSP) distance to the desired polymer in order to attain the highest possible film quality and device performance. The DMSO+Acetone solvent system has a strong dispersion component and nearly equal distribution of polar and hydrogen bonding components, making it a suitable solvent for PVDF TrFE. The presence of a strong dispersion component implies favorable solubility, whilst the presence of balanced polar and hydrogen bonding components indicates compatibility with the polymer. The nearer two molecules in this 3D space, the more likely they will dissolve into each other. For our study, the ranking for better solvents was found to be: DMSO+Acetone > Cyclopentanone > DMSO.

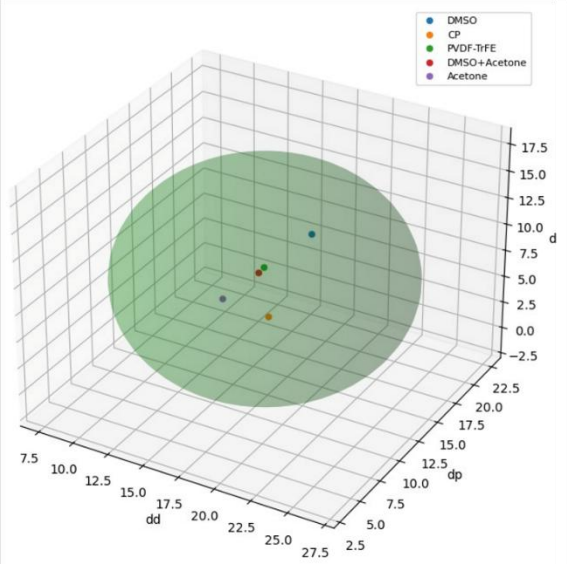

Figure 14: Hansen's space showing the compatibility of different solvents for PVDF-TrFE

5.3 Addressing the parameters that affect LB deposition-

The Langmuir-Blodgett (LB) deposition method is a highly versatile approach utilized in the production of thin films, allowing for precise modification of both structure and characteristics. The LB deposition process is influenced by multiple factors, such as the selection of solvent, surface pressure, qualities of the substrate, and conditions in which the deposition takes place.

- Selection of Solvent: The selection of solvent has a substantial influence on the development of LB films. Importance is given to solvents that possess suitable volatility, polarity, and surface tension. Various solvents exhibit distinct interactions with the substrate and molecules at the interface between air and water, hence influencing the process of film spreading and transfer onto the substrate. The uniformity, thickness, and shape of a film are determined by the rates of solvent evaporation and the interactions with the monolayer at the interface between air and water.

- The influence of surface pressure on LB deposition is significant since it governs the compression of the monolayer. The attainment of homogenous molecular packing and required film properties requires the development of optimal surface pressure conditions. Insufficient or excessive compression can result in the occurrence of imperfections, the creation of several layers, or suboptimal adherence to the substrate.

It is essential to comprehend and enhance these characteristics in order to get LB films of superior quality that include unique characteristics suitable for diverse applications, such as sensors, electrical devices, and biological coatings.

VI. Conclusions

6.1 Summary of Key Findings:

The significance of solvent selection in LB deposition is shown by the higher performance of the DMSO+Acetone solvent combination in comparison to Cyclopentanone and DMSO. The improved compatibility and interaction between the solvent mixture and the PVDF-TrFE polymer may be inferred from the closer alignment of Hansen's parameters and the smoother surface exhibited in AFM scans. The significance of controlling pressure during LB deposition is underscored by our research findings. The

utilization of lower pressure values led to the creation of films of higher quality, as indicated by the lowered roughness found in AFM scans. This highlights the need of accurately optimizing deposition settings in order to attain the necessary film properties. It is important to comprehend the influence of solvent selection and deposition pressure on film characteristics in order to enhance the efficiency of LB deposition procedures in practical applications. Researchers may improve the performance and consistency of thin films for electrical and optoelectronic devices by choosing suitable solvents and regulating deposition settings. This leads to progress in semiconductor technology.

6.2 Research Contributions:

The present investigation enhances our understanding of LB deposition methods and their application in the field of engineering thin film surfaces. Through a comprehensive analysis of the complex interplay between processing parameters and film characteristics, significant insight has been acquired on the enhancement of LB deposition for diverse applications. The results provide valuable insights for academics and engineers who aim to create customized thin films with desired characteristics.

6.3 Constraints and Prospects for Subsequent Investigation:

Despite the noteworthy results, this investigation possesses certain constraints. The primary aim of the experiment was to examine the impact of solvent selection and pressure variation, while disregarding other potential parameters that may influence the deposition of LB. Subsequent investigations may delve into supplementary variables, including substrate characteristics, deposition conditions, and further treatments, in order to augment the quality and efficacy of the film. Furthermore, expanding the scope of the research to examine the application-specific characteristics of films deposited with LB will yield significant insights into their practical applicability across several domains.

VII. Recommendations

7.1 Practical applications of the research

The results of this study include several practical implications across diverse domains. Thin film surfaces with better characteristics, such as increased ferroelectricity and decreased surface roughness, may

be created using optimal LB deposition processes in semiconductor device production. Tailored thin films exhibit potential for use in non-volatile memory devices, whereby precise modification of film properties is essential to get optimal device functionality. Moreover, the knowledge acquired from this research can guide the creation of sophisticated surface coatings for many industrial uses, such as sensors, actuators, and biological devices.

7.2 Suggestions for further studies

Furthermore, doing research on the scalability of LB deposition processes for the purpose of large-scale manufacturing applications will yield advantageous outcomes for industrial deployment. Furthermore, broadening the scope of the investigation to encompass additional ferroelectric polymers and innovative deposition processes may result in additional progress in the field of thin film engineering.

7.3 Recommendations for industry or technology development

Based on the empirical evidence presented in this study, a number of suggestions may be put up for the advancement of industry or technology. The use of the optimized LB deposition processes reported in this work has the potential to enhance the fabrication of high-performance memory devices for semiconductor manufacturers, resulting in enhanced reliability and lifetime. In addition, there is a strong emphasis on fostering collaboration between academic institutions and industry partners in order to effectively translate research findings into tangible and applicable solutions. It is advisable to allocate resources towards research and development endeavors that specifically target LB deposition technology. This strategic investment is crucial for fostering innovation and expediting the integration of modern thin film engineering methodologies across diverse industrial domains.

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