

# **Research proposal**

## ***Title of the project***

Ferroelectric tunnel junction

## ***Applicant information:***

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## ***Duration of the project***

4 years, starting from September 2010

## ***Estimated funding:***

17k€ per year

## ***Details of Supervisors***

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## ***Equipment and materials***

PVDF polymer – Probe station for measurements – AFM instruments – Alkane thiole – Poly styrene with high molecular weight

### ***Table of estimated costs***

	2010	2011	2012	2013	2014	Total
PhD students	1	1	1	1	1	
Postdocs	-	-	-	-	-	
Technicians	-	-	-	-	-	
Guests	-	-	-	-	-	
Personnel cost	13,000€	38,000€	43,000€	46,000€	32,000€	172,000€
Running Budget	7,500€	15,000€	15,000€	15,000€	7,500€	75,000€
Equipment	-	-	-	-	-	-
Total	20,500€	53,000€	58,000€	61,000€	39,500€	232,000€

## Abstract:

Memories based on tunneling through ultra-thin ferroelectric film can be read out non-destructively. In this research, preparation of defect-free ultra-thin films is a priority. The methods that can be considered for this aim are evaporation of (Vinyledene flouride) (VDF) oligomers, Langmuir-Blodgett film (LB) and spin coating of low concentration (5mg/ml) solution of poly(Vinyledene fluoride-triflouroethylene) P(VDF-TrFE). Studies based on prepared ultra-thin film with VDF oligomer evaporation, showed ferroelectricity down to 60 nm thickness. Hysteresis loops have been reported for P(VDF-TrFE) films with 2, 5 and 30 ML thicknesses prepared by the Langmuir-Blodgett method. The preliminary results obtained for 7 nm thickness with spin coating show a coercive voltage of  $0.35V$ , which that is consistent with the bulk coercive field of P(VDF-TrFE) ( $50MV/m$ ). Moreover, this film has many pin holes. Consequently, all of these three methods will be tested for preparing defect-free ultra-thin films down to a few monolayers. The next step would be ferroelectric tunnel diode fabrication with structure Au/P(VDF-TrFE) or VDF/PEDOT:PSS/Au and tunneling current measurements for applied bias voltages. Finally, the experimental results will be compared with theoretical calculations for tunneling across ferroelectric.

## Introduction:

Information storage is of paramount importance for many applications like radio frequency identification (RFID) tags. Currently the memories applied in RFID tags are based on silicon. Organic electronics in that respect promise low-cost and disposable electronic products. Using organic materials in the fabrication of RFID tags, and in particular the storage memory of the tags, the price of these tags can be reduced to only a few cents, in contrast to 25 cents for silicon-based tags. The tags should be able to retain information. However, no power source is available for refreshing the memory when necessary to prevent information loss. As a result, the target memory for the tags should be non-volatile. Ferroelectric materials show a hysteretic polarization response in the presence of an external electric field. The polarization response of the ferroelectric can be used for digital storage, i.e. the different polarization directions of the material, up and down, can be used to store “0” and “1”, respectively. The ferroelectric polarization is stable upon removal of the external field. Therefore ferroelectric materials are ideal for non-volatile memory applications [1-3].

Ferroelectrics have intrinsic dipole moments such that in the pristine state, the dipoles have random orientations that cancel each other out. Thus, the net polarization of the material is zero. To align the dipoles, an electric field that is larger than a threshold (coercive) field, is required. As shown in Figure.1.a, at fields higher than the coercive field all of dipoles will be aligned with the external electric field, hence a net polarization is induced. The induced polarization is partially maintained when the external field is turned off, as the so-called remnant polarization. The “0” and “1” binary state can be assigned to the ferroelectric, according to the direction of the

remnant polarization. A simple technique to measure the remnant polarization and coercive field of a ferroelectric is shown in Figure.1.b [1-3].

Inorganic ferroelectric materials like barium titanate ( $\text{BaTiO}_3$ ) and lead zirconate titanate ( $\text{Pb}(\text{Zr,Ti})\text{O}_3$ , PZT) have been investigated for memory applications. Highly sophisticated and high temperature processing, however, impedes the application of the inorganic ferroelectrics in disposable products due to fabrication costs. Organic ferroelectric materials are a strong candidate to lower the costs. The random copolymer of poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) is a very well studied organic ferroelectric. P(VDF-TrFE) has properties like relatively high remnant polarization, short switching times, thermal stability, radiation tolerance, non-flammability, stiffness and resistance to harsh chemicals [1-3].

Memory devices based on ferroelectrics can be realized using capacitor, field effect transistor and diodes. In a capacitor, a layer of ferroelectric is sandwiched between two electrodes. Information is stored in the form of polarization charges on capacitor plates. Ferroelectric field effect transistors (FeFET) utilize ferroelectric materials as the gate insulator instead of a normal insulator. Information storage in FeFETs is based on the change in the resistance of the conducting channel up on polarization of the ferroelectric. In the diode design, a phase-separated blend of organic ferroelectric and organic semiconductor is sandwiched between bottom and top electrodes. Upon polarization of the ferroelectric the resistance of the diode is modulated.

All these devices have the promising feature of nonvolatile storage. However, there are several notable drawbacks associated with each device. In the capacitor, the read-out operation of the memory is performed by applying a field higher than the coercive field of the ferroelectric and monitoring current transients. Thus, the read-out process is destructive. The FeFETs, although they have non-destructive read-out, suffer from an elaborate device structure that limits realization of high-density memories. Blend diodes have non-destructive read-out operation and a simple device structure; however they are limited when down-scaling the device area due to the specific phase separated morphology of the storage medium. Therefore there is still a need for a memory device that combines all the aspects of non-volatility, non-destructive read-out and scalability down to small device area.

To fulfill that necessity, a new memory device, the Ferroelectric tunnel diode has been the focus of recent research. Ferroelectric tunnel diodes are based on an ultra-thin ferroelectric layer (a few nanometers) between two metal electrodes. Due to the small thickness of the ferroelectric, electrons can tunnel from one electrode to the other. The magnitude of the tunnel current in the diode is influenced by the polarization direction of the ferroelectric material. Hence the current shows bistability. The first hurdle that needs to be overcome is to produce an ultra thin ferroelectric film. Growing ultra-thin films of inorganic ferroelectric has been proven very challenging. Furthermore, as mentioned above this is a costly process. Organic ferroelectrics are promising candidates again due to the variety of low-cost processes that are available to achieve ultra-thin films.

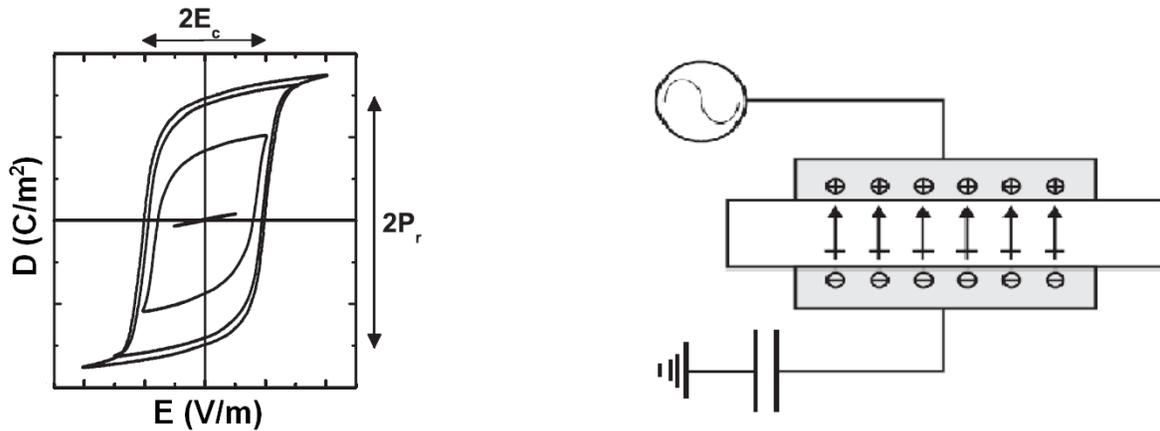
There are several important questions that should be answered first:

1. What is the appropriate range of thickness for the tunneling effect?
2. How are the ferroelectric properties influenced for ultra-thin films?
3. How can device behavior be explained?

It has been shown that ferroelectricity persists in organic ferroelectric P(VDF-TrFE) for films as thin as a few nanometers which corresponds just a few monolayers of P(VDF-TrFE). The remnant polarization and coercive field both show an increase compared to that of the bulk material. Organic ferroelectric diodes, however, have yet to be demonstrated.

In this project we propose to make the first ultra-thin ferroelectric films by conventional low-cost techniques based on which an organic ferroelectric tunnel diode could be fabricated. Further, we will attempt to understand the device behavior based on current theories of tunneling across ferroelectrics.

The outline of the proposal will be as follows: first, we present a brief theory on tunneling effects in organic ferroelectrics. Then, we will consider experimental methods which can be used to prepare ultra-thin films of P(VDF-TrFE) or ferroelectric small molecules. We will use oligomers of VDF as small ferroelectric molecules in this research. The focus will be to make defect-free ultra-thin film of organic ferroelectrics. Then, the ultra-thin films will be integrated into a device structure by introducing contacting electrodes. In the next part of proposal, we present our preliminary results on film preparation and device characterization, as well as some recent data from the literature, all which strongly supports our concept of a functional organic tunnel diode. In the last section of the proposal, a project time line is given.



**Figure. 1** (a) Displacement current versus applied electric fields showing hysteresis loops for a ferroelectric capacitor measured with a Sawyer-Tower circuit. In the bigger loops, the ferroelectric reached saturation polarization at high fields. (b) A sinusoidal voltage signal is applied to a ferroelectric capacitor. The displacement charge is measured via voltage buildup on a reference capacitor that is connected in series. The voltage drop over the reference capacitor is minimized by using a large reference capacitor. Figures from [15].

## Theory:

Electron tunneling through a thin layer of insulator has been extensively studied. This effect can be explained by quantum mechanics and is based on the dual wave-particle properties of electron. When two metals are separated with a very thin layer of insulator or vacuum, tunneling of electrons will occur through the barrier from the Fermi level on one electrode to the another one. This effect is a direct consequence of overlap of the wave functions of electrons in both metals.

In Figure. 2, a diagram of the band model for metal-insulator-metal junctions is shown. A very thin layer of insulator with thickness  $t$  is sandwiched between two electrodes,  $M_1$  and  $M_2$ . For the ultra-thin film (a few nm), we expect to see tunneling effects through insulator according to the wave properties of electrons. In this diagram,  $E_F$  is a Fermi level,  $\chi$  is the electron affinity and  $d$  is the barrier thickness.  $\Phi_1$ ,  $\Phi_2$  are the barrier heights of the bottom and top electrodes, respectively. In this diagram, a bias voltage is applied on one electrode while another electrode is grounded. The Fermi level of electrode under positive or negative bias voltage moves upward or downward, respectively. The difference between two Fermi levels causes migration of electrons through the narrow barrier from filled state of one electrode to empty state of another one [12-13].

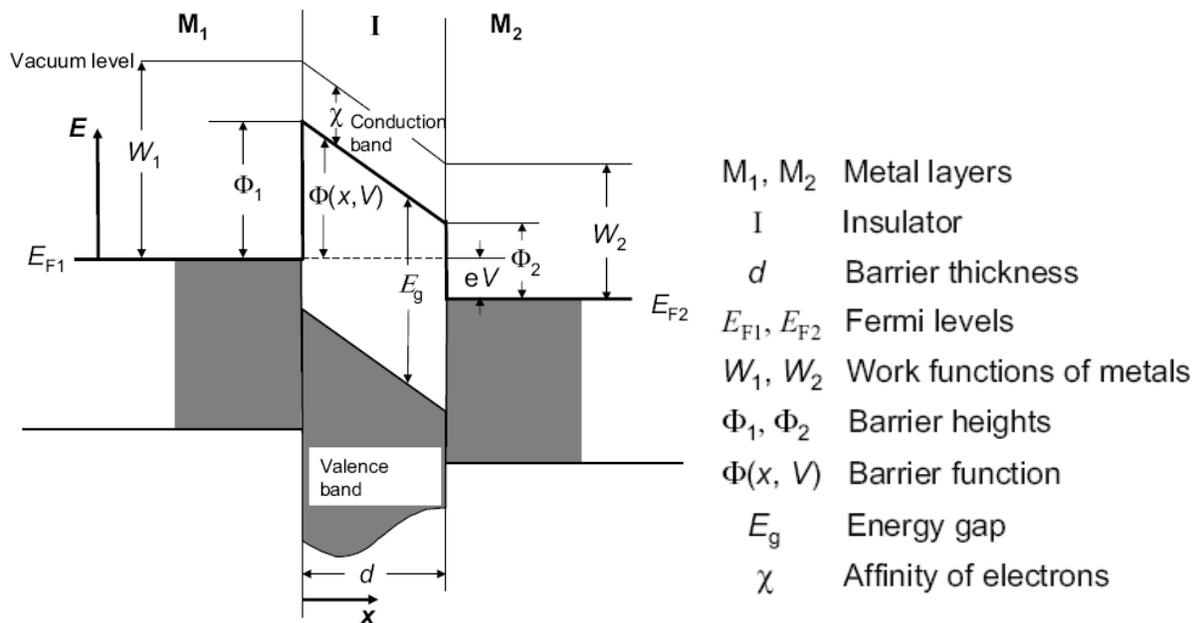
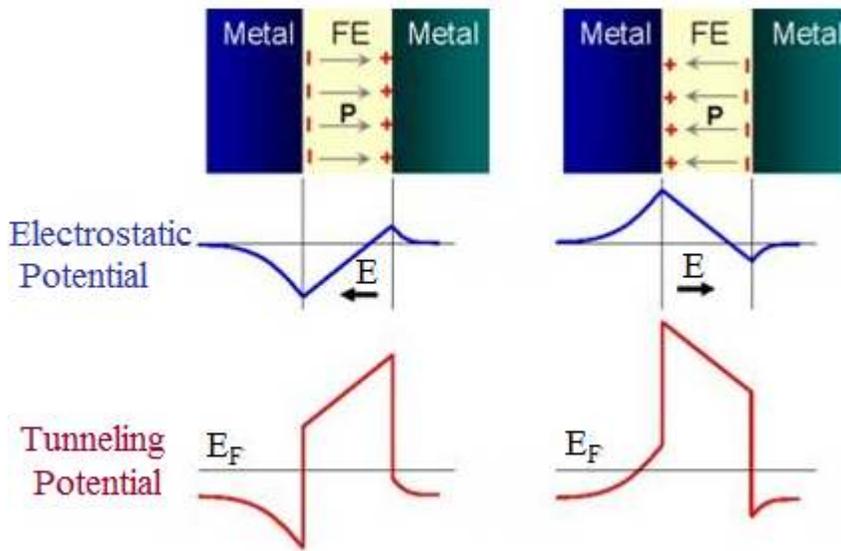


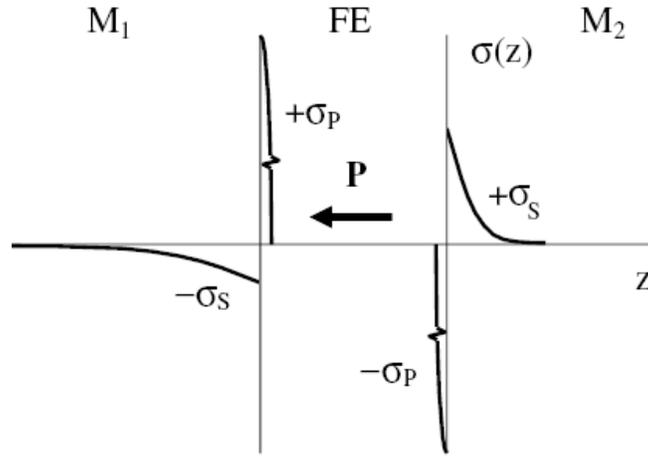
Figure. 2. Band diagram model for metal- insulator- metal configuration [16]



**Figure..3.** Electrostatic and tunneling potential in a FTJ for two opposite polarization orientations [13]

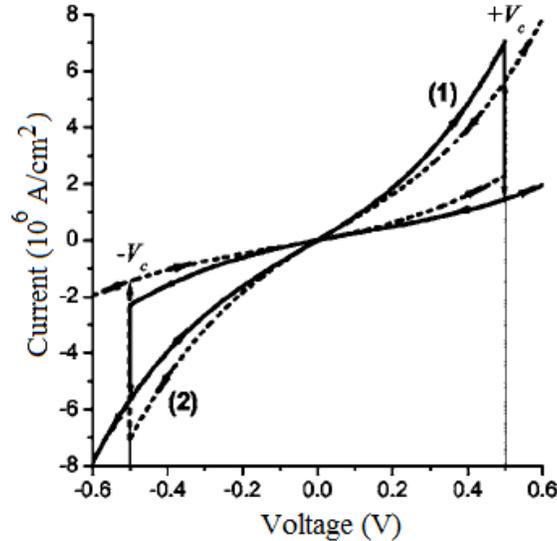
Now we consider a thin ferroelectric layer in place of the thin insulator. Figure..3 shows an ultra-thin ferroelectric sandwiched between two different metals ( $M_1$  and  $M_2$ ) with different in Fermi energy levels up to  $0.1V$ . Electrostatic and tunneling potential in two polarization direction has been sketched in metal-ferroelectric-metal structure. Small difference in Fermi energy level of two metal electrodes results in tiny built-in potential inside the ultra-thin ferroelectric layer in MFM structure. Therefore, coercive voltage will be shifted downward. Charge distribution in metal-ferroelectric interface has been shown in Figure.4 for one polarization direction. Negative polarization charges of the ferroelectric,  $\sigma_p$ , at the interface with one metal ( $M_1$ ) plate, induces charge distribution,  $\sigma_s$ , at this metal.  $M_1$  and  $M_2$  have different Thomas-Fermi screening length. The  $\sigma_s$  induced on the metal electrodes at the metal-ferroelectric interfaces therefore leads to creation of two different screening lengths. The screening of the ferroelectric polarization causes variation of electrostatic potential across the junction in two different polarization states.

When different metal electrodes are applied to contact the ferroelectric, the difference in the screening length of the metals creates an asymmetry in potential profile across the ferroelectric layer upon ferroelectric polarization. The resulting tunneling current is affected by the changes in the screening length in different polarization states. The resistance of the tunnel junction consequently changes by several orders of magnitude, leading to giant electro resistance (GER) [14].



**Figure..4.** Charge distribution in metal-ferroelectric interface at Metal-ferroelectric-Metal structure [13]

Figure..5 shows theoretical current versus bias voltage characteristics of the asymmetric ferroelectric tunnel junction presented in Figure. 3. The mean barrier height of two electrodes in this plot has been changed by about 0.1eV between the two polarization states [12].



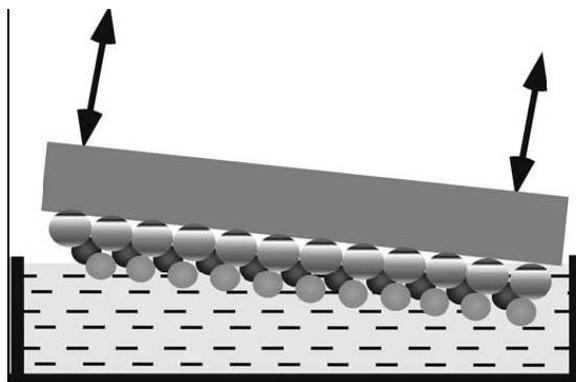
**Figure..5.** Current – voltage curves of asymmetric ferroelectric tunnel diode in when source of depolarization is (1) on biased electrode and (2) on grounded electrode[12]

## Experiments:

As mentioned in the last section, the desired thickness of the ferroelectric layer is on the order of a few nanometers. Ferroelectricity in P(VDF-TrFE) copolymer down to a few monolayers has been reported. Ferroelectric properties of P(VDF-TrFE) ultra thin films with thickness of 2, 5 and 30 ML have been shown recently by Bune, *et al.* In this research, ultra-thin films of P(VDF-TrFE) will be formed by three techniques as discussed in the following.

### 1- Langmuir- Blodgett method

In this method, uniform molecular monolayer (ML) can be deposited on a substrate. A solution of P(VDF-TrFE) with a very low concentration will be dispersed on water surface. Because of the highly hydrophobic properties of P(VDF-TrFE), a very thin layer of P(VDF-TrFE) will be formed on top of the water as a liquid sub phase. By dipping the substrate vertically or transferring it horizontally to the water surface, a monolayer will be formed on the substrate as shown in Figure. 6. During deposition, the surface PVDF layer dispersed on water surface will slowly be compressed by two closing barrier. To get multilayer P(VDF-TrFE) structures, deposition is repeated until the targeted thickness is achieved. The thickness of each P(VDF-TrFE) monolayer is about 0.5nm [4-8].



**Figure..6.** Horizontal LB film deposition with putting a substrate in slight angle on the water

### 2- Using VDF oligomers

The second method for the preparation of ultra-thin films of vinylidene fluoride (VDF) is to evaporate VDF oligomer on to the substrate. The fabrication of defect-free ultra thin film VDF

has been reported by Xu *et al.* VDF oligomer thin film with 60 nm thickness have been made in to capacitors. Here the attempt will be to prepare defect-free ultra-thin films (thickness less than 5 nm) by evaporation of VDF oligomers. The parameters that have been used for preparing of 60 nm VDF film will be optimized for thickness to achieve less than 5nm defect free thin films [9-11].

### 3- Spin coating of P(VDF-TrFE) from solution

Spin coating P(VDF-TrFE) is another way to achieve ultra-thin films. In this method, ultra-thin P(VDF-TrFE) film will be made down to few nanometers by adjusting the solution concentration, spin coating condition, temperature and finally testing suitable solvents for spin coating.

## Preliminary results:

It has been shown that P(VDF-TrFE) ultra-thin films prepared by Longmuir-Blodgett method exhibit bistability in current versus bias voltage measured for 2, 5 and 30ML. However, the coercive fields in the range of 0.5-1GV/m with very low switching time were reported [4-8]. Here we need to prepare the experimental setup and investigate these effects. In our opinion, the reported values can be improved by optimizing of the process and using different contact electrodes.

Measurements on VDF thick layers of about 500 nm showed a remnant polarization of  $130 \text{ mC/m}^2$  and coercive field on the order of 120 MV/m. Lowering the film thickness to about 60 nm does not affect the remnant polarization but reduces the coercive field. Both non-ferroelectric and ferroelectric phases are simultaneously present in thin films of VDF oligomer. Here the evaporation process needs to be optimized in order to enhance the presence of the ferroelectric phase [9-11].

So far our focus has been on ultra-thin spin coated films. Figure..7 shows atomic force microscopy (AFM) topography and phase image of P(VDF-TrFE) ultra-thin film with a thickness of about 7nm on a gold-coated glass substrate. The major hurdle to creating contacts to an ultra-thin film can be easily overcome by introducing a conducting polymer buffer layer. Therefore we optimized the device configuration as the following Au/P(VDF-TrFE)/PEDOT:PSS / Au, PEDOT: PSS. Tunnel diodes were consequently fabricated with the P(VDF-TrFE) film shown in Figure. 7. The current-voltage characteristic of the device is presented in Figure. 8.

Figure..8 illustrates hysteresis loops for current density versus voltage in positive bias voltage in device with structure Au/P(VDF-TrFE)/ PEDOT:PSS / Au. This Figure. can prove ferroelectric properties of P(VDF-TrFE) layer with 7 nm thickness as well as bistability of the device. Figure..8 shows the switching voltage of this device is about 0.35 V for 7 nm thickness film. This is consistent with the coercive field 50MV/m for bulk P(VDF-TrFE) reported on literature. The true origin of the bistability is still ambiguous. Since P(VDF-TrFE) ultra thin film are not

pinhole free, the bistability could be attributed to penetration of the PEDOT particles into the pinholes. Then the origin of the bistability would be improved injection into PEDOT due to polarization of ferroelectrics.

To monitor the true tunneling current we need to first create a pinhole free layer or fill up the pinholes with other insulating materials. The former is achieved by adjusting the spin coating parameters and the latter is achieved by molecules that self assemble on the bottom electrode, hence preventing direct contact between PEDOT and Au. Here alkanethiols are one option to fill up the pinholes.

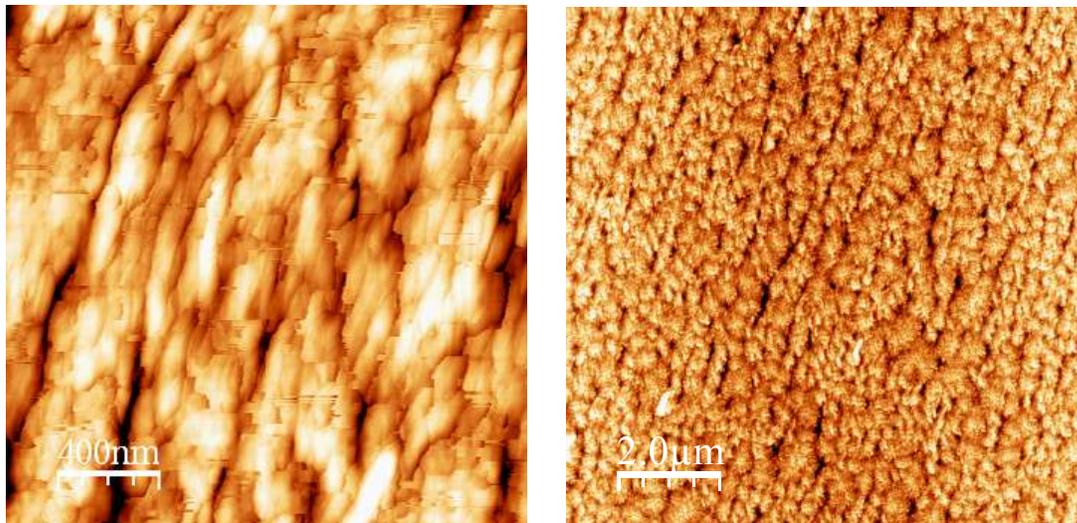
## Project Timetable:

**First year:** Establishing the experimental setups and optimizing of the processes mentioned in the experimental section. Moreover, efforts will be also focused on adapting the different models proposed for tunneling across inorganic ferroelectrics to for the organic ferroelectric material.

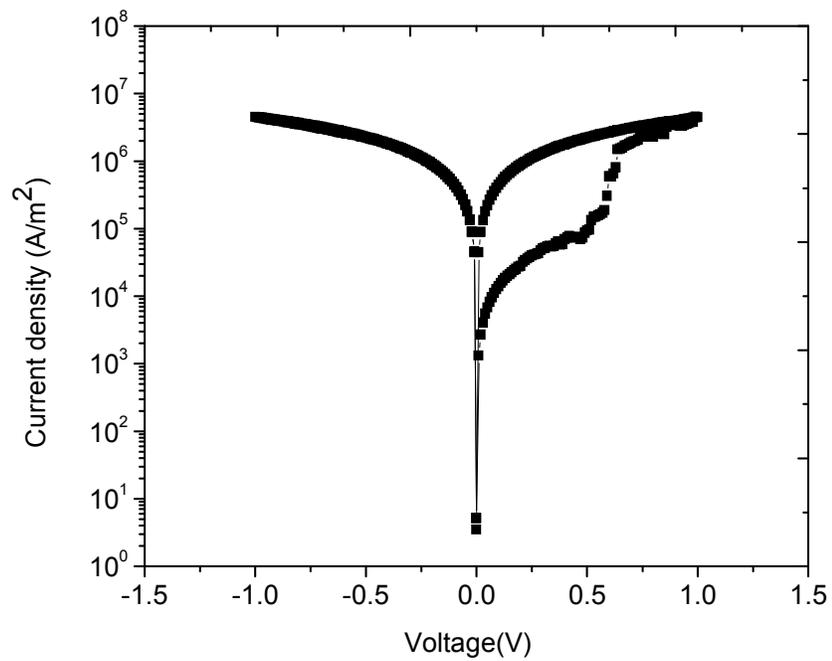
**Second year:** Attempts will be focused on making ultra-thin films of P(VDF-TrFE) and VDF oligomers. Full characterization of the morphology and parameters affecting film formation will be done during this year. At the end of the year defect free films will be ready to be integrated into devices.

**Third year:** Ferroelectric tunnel diodes will be made based on the device structure metal / P(VDF-TrFE) or VDF / PEDOT: PSS / metal. Full electrical characterization will be performed. Efforts will be on developing a solid understanding of the experimental measurements with the developed theory.

**Fourth year:** Finalizing data analysis and writing up reports will be the focus of this year. At the end of this year the PhD candidate is expected to hand in his/her results in the form a PhD thesis.



**Figure..7.** AFM topography image of P(VDF-TrFE) ultra-thin film with 5mg/ml concentration and 7nm thickness in  $2 \times 2 \mu\text{m}^2$  and  $10 \times 10 \mu\text{m}^2$



**Figure.8.** Current density versus bias voltage for ultra-thin P(VDF-TrFE) film (7 nm) with structure Au/P(VDF-TrFE)/PEDOT: PSS/Au on photo resist coated silicon substrate

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