

# Deposition, Processing and Characterization of P(VDF-TrFE) Thin Films for Sensing Applications

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**Abstract**—This work presents wafer level deposition of thin Polyvinylidene Fluoride - Trifluoroethylene P(VDF-TrFE) films by spin coating and their further patterning by dry etching. Uniform and controlled thicknesses were obtained over a large area (4 inch Si wafer) by varying the concentration of solution and the spinner's speed. Absence of any standard method makes it difficult to etch the polymer films from places like pads. A new dry etch recipe, developed for this purpose was used for the selective etching of polymer films. *In situ* polarization of the polymer film has also been addressed.

## I. INTRODUCTION

“Smart materials” like piezoelectric polymers (e.g. PVDF or its copolymer – P(VDF-TrFE)), are of interest in rapidly expanding range of applications (e.g. ultrasonic, MEMS, tactile sensing etc.) as they are tough, flexible and are readily available in the form of thin films. Their close acoustic impedance match to water and living tissues is an advantage in biomedical applications. The work presented here is part of the development of tactile sensing arrays that use piezoelectric polymers as transducers, directly deposited and coupled to the FET devices in touch sensing array [1, 2]. Their ability to generate charge proportional to applied force is used to detect and quantify the contact force. These arrays will be placed on the fingertips of a humanoid robot [3], robotcub] and touch signals from them will be used for object recognition, manipulation and control. Their introduction will ultimately enhance the cognitive capabilities of robot. The design of these tactile sensing arrays - influenced by system constraints (e.g. limited space on the fingertip, fast response, less wires etc.) - is based on ‘sense and process at same place’ concept, shown in Fig.1. Sensing and processing of the sensed data at ‘same place’ is a novel method of improving sensor’s performance.

PVDF is a well-known polymer widely used in piezoelectric polymers based sensors due to excellent

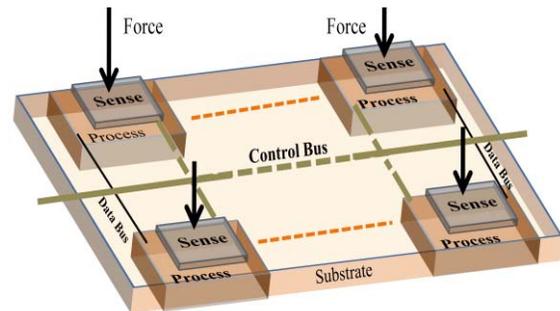


Figure 1. The concept of large area touch sensing array.

features like, flexibility, workability, and fast dynamic response. Unfortunately, it is difficult to use PVDF with the sensors involving conventional microfabrication processes as they need mechanical stretching to transform from the nonpolar  $\alpha$ -phase to the polar  $\beta$ -phase [4]. In other words, mechanical stretching is needed to induce piezoelectric properties into PVDF. For this reason, commercial PVDF films have been widely used in various sensors that involve microfabrication – as in the extended gate approach [5, 6], in which commercial PVDF films are epoxy adhered to the electrodes which act as the extended gates of the FET devices. Though the approach results in a significant improvement in the performance; the presence of epoxy restricts the advantages that it offers [2]. On the other hand, P(VDF-TrFE) – a copolymer of PVDF, has the tendency to crystallize directly in the polar  $\beta$ -phase without any requirement of mechanical stretching. In addition, P(VDF-TrFE) demonstrates a higher level of piezoelectricity than PVDF [4]. The crystalline structure, and consequently the piezoelectric and pyroelectric properties of the polymer film depend on the molecular proportion  $x$  ( $0.6 < x < 0.85$ ) of vinylidene fluoride in P(VDF <sub>$x$</sub> -TrFE <sub>$1-x$</sub> ). Among various compositions of P(VDF-TrFE), the one with 65/35 weight ratio exhibits good ferroelectric response

[4]. For the reasons mentioned above, P(VDF-TrFE), with 65/35 weight ratio, is used in this work.

The successful implementation of touch sensors with the approach described earlier requires specific processing steps that are compatible with the conventional microfabrication techniques. Some of these steps are presented in this work. In the following sections, we present various experiments performed to obtain controlled thickness of the polymer film on a 4 inch silicon wafer; their etching and polarization.

## II. POLYMER FILM DEPOSITION AND PROCESSING

### A. Deposition

The polymer films with uniform thickness are desired for a close match among the responses of various sensors arranged in an array. Following the procedure in [7, 8], thin polymer films with various thicknesses were deposited on Si test wafers (having 0.5  $\mu\text{m}$  Al metal layer) by spin coating the solutions of P(VDF-TrFE) with different concentrations and at different spin rates. The solutions with 10%, 15% and 30% concentrations were prepared by stirring P(VDF-TrFE) pallets in RER500 solvent at 80<sup>o</sup>C for about 30 minutes. The spin-coating was performed in three steps – each with different sets of spin rate and spin time. In first two steps both spin rate and spin time (500 rpm for 2 sec followed by 600 rpm for 8 sec) were kept smaller to allow the solution to spread uniformly over the whole wafer. In the third step both spin rate and spin time were higher to obtain the desired thicknesses. While the spin rate in third step was varied to obtain different thicknesses, the spin time was kept constant (30 seconds) – even though it is also known to affect the thickness of polymer film [7]. The thicknesses of the polymer films - measured with interferometer and profilometer – at various spin rates are plotted in Fig. 2. It can be noticed that for a particular solution concentration, the polymer thickness decreases with increase in the spin rate and that the plot is approximately a straight line. This pattern of thickness variation with spin rate is consistent with values presented in literature [7, 8]. Thin films with 10% and 15% solutions were found to be more uniform than those obtained with 30% solution.

### B. Thermal Treatment

Before evaporating the upper electrode, the polymer films were annealed to enhance the crystallization, to evaporate any left out particles of the solvent and to remove any local stress generated during deposition. The films were annealed up to temperature of 155<sup>o</sup>C (melting point of P(VDF-TrFE)); reaching 155<sup>o</sup>C over a period of one hour and keeping 155<sup>o</sup>C for 10 min and then bringing it down to room temperature in four hours so as to release the stresses slowly. After annealing, the wafers with polymer films were treated with HDMS, and then a 0.2  $\mu\text{m}$  top metal layer was vacuum deposited on films.

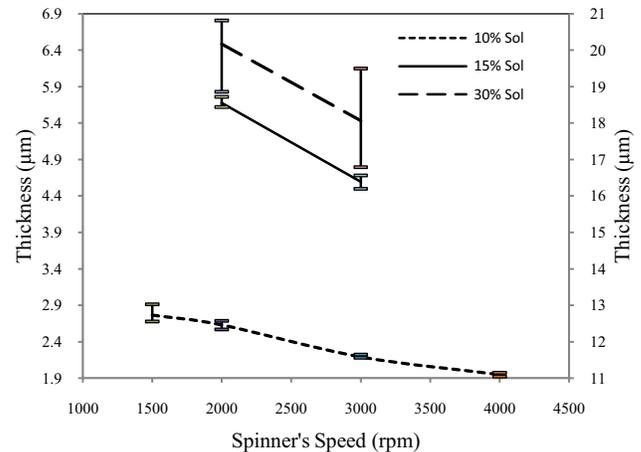


Figure 2. Film thicknesses with different concentrations and spin rate. The deviation from average thickness is lower at higher spinning speeds. Since the polymer thickness was much higher with 30% solution, two scales are used to show the variation clearly.

HDMS treatment improves the adhesion of polymer and metal electrodes. Both, Al/Cr and Au/Cr were used as top metal layer on different wafers to study the adhesion of metal and polymer - which is better in case of Au/Cr, as can be noticed from Fig. 3. The top metal was patterned by standard wet etching procedures for gold and aluminium and it acts as mask during etching of the polymer film.

### C. Etching of The Film

The polymer needs to be etched in order to define various sensing units on the wafer clearly. Same is needed to gain access to the pads on the chip and also to the lower metal electrodes. A number of wet [7] and dry [9] etch methods have been reported in literature for etching of the polymer films. In case of wet etching the edges are not clearly defined, which makes it difficult to polarize the polymer, especially when the thickness of the polymer film is of the order of few  $\mu\text{m}$ . While polarizing the polymer film sparking is experienced close to edges due to poorly defined edges, which can potentially damage the polymer film. Similarly, when the area of polymer film is smaller – as in the touch sensors based on the approach presented in earlier section - the wet etching may result in variations in the effective polymer area and the aspect ratio, thereby, leading to the variations among outputs of a set of sensors. In the absence of any standard dry etch method for P(VDF-TrFE), different approaches were tried in this work. It was observed that dry etch with oxygen (20 sccm) at 20 mBar pressure and He (40 sscm) was sufficient to remove the polymer with a etching rate of 1 $\mu\text{m}/\text{min}$ . Upper metal electrodes acted as the mask for polymer during the dry etching step. Fig. 3 shows the wafer after the dry etching of the film. The SEM photograph of the one of the edges of the polymer film,

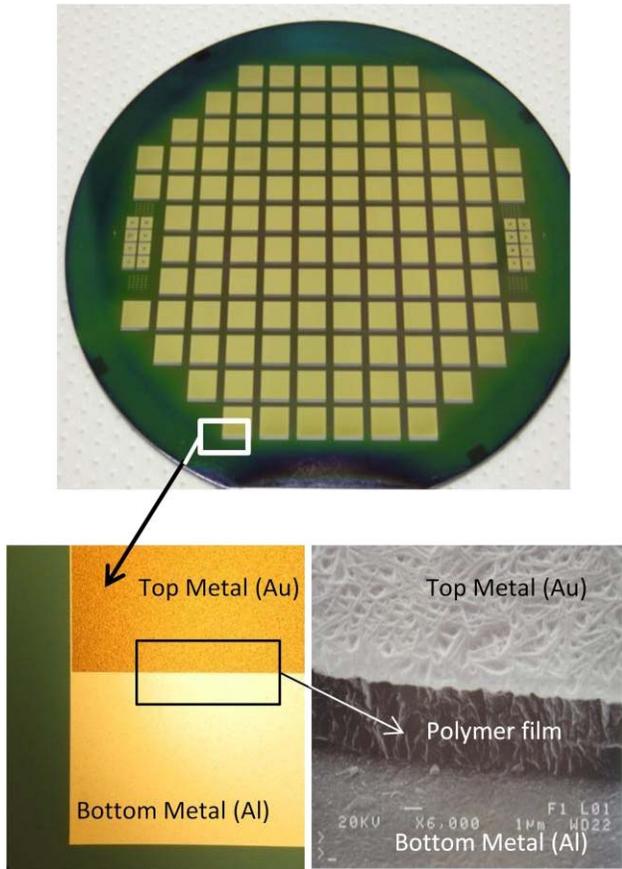


Figure 3. (top) P(VDF-TrFE) thin film deposited on a silicon test wafer with patterned top (Au) and bottom (Al) metal layers. The metal electrodes on two sides of the polymer film were misaligned to connect them to voltage source during poling. (bottom - left) Enlarged view of a section on wafer - after patterning of metal and dry etching of polymer film with new recipe. (bottom right) SEM photograph of the polymer

given in Fig. 3, shows a clear definition of polymer film by dry etching.

### III. POLARIZATION AND CHARACTERIZATION

#### A. Poling

To improve the piezoelectric properties of the polymer films, they need to be polarized. In the event when the sensors – using piezoelectric polymers - are present on a chip, the poling process needs to be done on chip without damaging the devices and readout electronics. Polarization of P(VDF-TrFE) is generally done by applying a high electric field across its thickness. Resulting piezoelectric coefficient depends on the degree of polarization and hence on the strength of electric field. Maximum field strength of  $100 \text{ V}/\mu\text{m}$  is required to polarize P(VDF-TrFE) films. A number of methods like electrode poling (thermal poling) [10], corona poling [11], electron-beam poling [12] have been reported in literature for polarizing piezoelectric polymers. The polarization

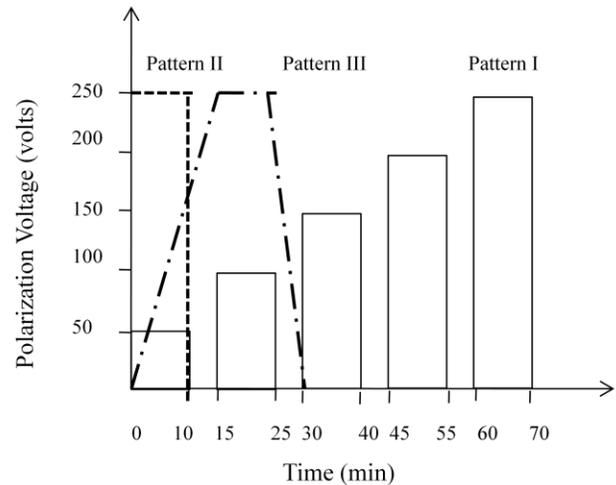


Figure 4. The patterns of applied polarization voltage. In pattern I, 50 volts were applied and was increased by same amount with a short circuit period between two voltage application periods. In pattern II, 250 volt was applied in one step. In pattern III, 250 volt was reached slowly and also reduced in a similar manner.

profiles obtained with corona poling and electron-beam poling are less uniform than with electrode (thermal) poling [13]. Further, there is risk of damaging on chip devices and read out electronics with these methods. On the other hand application of high electric field – as in electrode poling – directly, involves risk of electric and thermal breakdown especially when the thickness of polymer film is not uniform or the likelihood of any imperfection, voids or impurities.

To study these effects, the diced samples (with  $2\text{-}3 \mu\text{m}$  films) were poled at room temperature by directly applying voltage at a rate of  $100 \text{ V}/\mu\text{m}$  across the metals on both sides. The electric field across the electrodes was applied in three different patterns, as shown in Fig. 4. In pattern I, which is similar to that presented in [13], the electric field up to 250 volts – with five steps incremented by 50 volts each time - was applied across the sample with a  $2.7\mu\text{m}$  thick polymer film. In this case, electric field was applied for 10 minutes followed by a 5 minutes short circuit period. The two side of polymer were short circuited to neutralize any access charge. A multi-step poling process like this reduces the chances of electric breakdown. In pattern II, which is similar to standard electrode poling technique, 250 volts were directly applied across polymer for 10 minutes. In pattern III, voltage was slowly increased to a maximum of 250 volts in 15 minutes. After keeping it at its maximum value for 10 minutes, the electric field strength was reduced to zero in 5 minutes. While polarizing the samples with electric field pattern of pattern II, maximum sparking was observed - mainly along edges - and was minimum in the case of electric field with pattern I, thus, resulting in a cleaner sample. Besides this, it is possible to monitor the

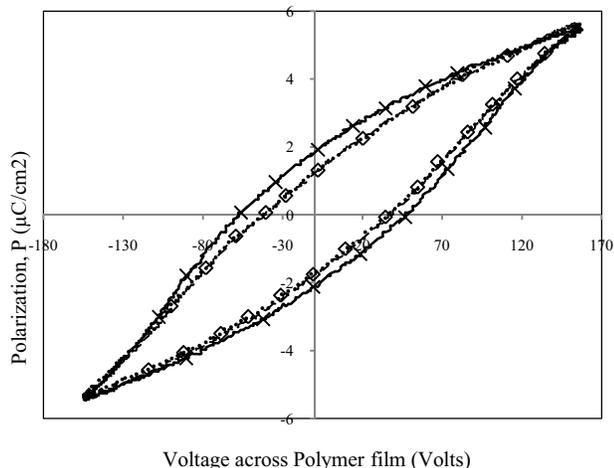


Figure 5. Hysteresis curve (at 10 Hz) showing presence of piezoelectric behavior. — x — corresponds to sample poled by electric field with pattern I; — ◊ — to pattern II and -----to pattern III.

polarization current during poling process, when the electric field is applied with pattern I. This is important to understand and detect the safe voltage limits for the devices and read out electronics on the chip. But, poling of polymer with electric field applied as in pattern I is a time consuming process as compared to others, as can be noticed from Fig. 4.

### B. Measurement

Presence of hysteresis is a necessary condition for any material to be piezoelectric. The polarized samples were tested for the presence of hysteresis loop. The standard Sawyer Tower technique was used to measure the hysteresis among samples poled with different patterns of electric field. The amount of polarization in various samples is compared in P-E plots of Fig. 5. The remnant polarization ( $P_r$ ) for the samples polarized with pattern I is  $1.98 \mu\text{C}/\text{cm}^2$  and that for other samples it is  $1.31 \mu\text{C}/\text{cm}^2$ . It should be noted that the plots are dependent on the frequency of the loop as well as temperature. It can be noticed that pattern I gives better polarization, although a longer poling time is needed with this method. It is known that the remnant polarization ( $P_r$ ) increases, if an electric field is applied to a prepolarized sample [13] and same can be observed in the P-E curve for the sample poled with pattern I of electric field. For the second and subsequent steps the polymer is prepolarized, which could explain the higher remnant polarization ( $P_r$ ) in this case as compared to those from the samples polarized by the electric field of pattern II and III. Thus, a proficient growth is obtained in remnant polarization when the electric field strength in a particular step is higher than that of previous step and this also reduces the risk of electric breakdown.

## CONCLUSION

Various steps in the process of making thin P(VDF-TrFE) film on silicon wafers have been presented. The thicknesses versus spin rate plots are in agreement with the results presented in literature. Etching of the polymer film has been a crucial issue which is solved by dry etching of the polymer films. On chip poling of polymers is a challenging task as there is risk of damaging devices and read out electronics. Among various possibilities, step wise poling has emerged as a better way of *in situ* poling. All the tests presented in this work were performed on dummy silicon wafers and in future these can be repeated on wafers with active devices. The successful implementation of the controlled process presented here, will pave way to the development of tactile sensors having transducer (P(VDF-TrFE) thin films) directly coupled to the gate terminals of FET devices.

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