

# Integrated Piezoelectric Polymers For Microsensing and Microactuation Applications

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## Abstract

The use of PVDF-TrFE as a material for microsensing and microactuation applications is discussed. PVDF-TrFE is a low modulus polymeric material which can be spin-cast onto wafers or other substrates and which exhibits both piezoelectric and pyroelectric responses after on-chip electrical poling. Micromachining techniques are presented which detail the fabrication of suspended membranes, strings, and cantilever beams from this material. Both sensing and actuation have been achieved with these structures. Qualitative performance of these structures is discussed. Although low modulus organic piezoelectric materials have the potential for enabling relatively large strain piezoelectric actuators, the chemical and process sensitivities of this material may limit its applicability in many processes; careful design of the micromachining processes is necessary in order to successfully realize the desired structures.

## Introduction

Inorganic piezoelectric materials such as PZT or zinc oxide have been used in a variety of microsensor and microactuator applications. Although these materials have a large piezoelectric coefficient, there are also several difficulties associated with their use. Inorganic piezoelectrics can be difficult to deposit, are relatively brittle, and have a relatively high Young's modulus, thus limiting the total strain that can be achieved. Organic materials such as polyvinylidene fluoride (PVDF) can overcome some of these difficulties, at the expense of a lower piezoelectric coefficient and greatly reduced thermal and chemical resistance[1]. For example, due to the low Young's modulus of PVDF, large mechanical deflection with a relatively low applied voltage can be achieved in spite of the lower piezoelectric coefficient. In this work we investigate piezoelectric polymers as potential microsensor and microactuator materials.

Attempts to incorporate PVDF into sensor and actuator structures have been frustrated by the fact that this material must be mechanically drawn in order to achieve a piezoelectric crystal structure [2]. More recently, copolymers of PVDF with trifluoroethylene (PVDF-TrFE) [3] have been developed which crystallize directly into the piezoelectric state without mechanical drawing. This property makes them ideal for spin-casting from solution onto substrates (e.g., silicon) for microsensing and microactuation. After deposition, an in-situ electrical inducement of piezoelectric properties ('poling') [4] is required to achieve the desired piezoelectric response. It should also be noted that this material exhibits a pyroelectric response; that is, a generation of voltage in response to a temperature gradient. This property of PVDF-TrFE has been investigated previously as an integrated sensing material [5,6].

In this paper we discuss our attempts to fabricate more complex micromachined structures from PVDF-TrFE for microsensor and microactuator systems. First, the basic process for spin casting and poling of PVDF-TrFE films on a Si wafer is presented. Second, in order to demonstrate using these films in a simple micromachining process, the fabrication of a suspended piezoelectric membrane is discussed. Third, more complicated suspended 'string' structures of PVDF-TrFE, which can be used not only as a resonant sensor but also as a tool for measurement of the mechanical properties of the film, will be discussed. Finally, a process for actuation using micromachined bimorph cantilever beams is discussed.

### Processing of PVDF Films

In order to achieve micromachined structures using organic piezoelectric materials, it is necessary first to develop a reproducible and effective process for deposition and poling of the piezoelectric material. A variety of solvents and processing conditions were tested to optimize the spin-casting procedure. Single layer films of PVDF-TrFE with thickness of less than 1  $\mu\text{m}$  up to 10  $\mu\text{m}$  can be easily obtained by spin casting from solution in N,N-dimethylacetamide (DMAc). Thicker films can also be obtained by use of multiple layers. By varying the percent solids (and therefore the viscosity) of the polymer solution, a variety of film thicknesses for a given spin speed can be obtained.

Typical conditions for preparation and deposition involve dissolving 30 grams of PVDF-TrFE powder (obtained from Pennwalt) in 100 ml of DMAc and heating until the material is completely dissolved. This solution can be kept for several months with no discernable change in film properties if care is taken to ensure that no evaporation of solvent occurs. In order to obtain high quality films, filtering of the solution to 0.5  $\mu\text{m}$  prior to deposition was necessary. The polymer solution is then spin cast onto a silicon substrate. Typical processing conditions are spin-casting at 2000 rpm for 20 seconds followed by two bake cycles: 15 min at 95  $^{\circ}\text{C}$  followed by 15 min at 160  $^{\circ}\text{C}$ . The thickness of the single layer films produced in this way is approximately 5  $\mu\text{m}$ . By repeating the spin-casting and baking procedure, thicker films with indiscernible boundaries between the film layers can be obtained. The first bake step is for solvent removal, while the second step (which is near the melting point of the material) is performed in order to achieve more uniform thickness, reduce the potential of pinholes in the film, and to fuse multilayer coats. We have observed that in thick and multilayer coated films the probability of pinholes in the film is reduced.

Piezoelectric and pyroelectric properties are induced by thermal poling [7]. The temperature of the film is raised above its glass transition temperature (typically to 80 °C) and an external voltage (approximately 700 V for a 5 μm thick film) is applied to metallized electrodes on both sides of the film, causing the internal dipoles of the material to rotate and align. After 30 minutes the temperature is reduced with the field in place, 'freezing in' the induced polarization and yielding a piezoelectric film. At this point, the spin-cast film exhibits both piezoelectric and pyroelectric properties.

#### Suspended Membranes of PVDF-TrFE

One of the easiest ways to demonstrate the integratability of PVDF-TrFE with micromachining processes is to fabricate a suspended membrane of the film on a Si wafer. Two different methods were used to fabricate suspended membranes. In the first method, the starting material is a two inch <100> single-sided polished silicon wafer. The wafer is coated with PVDF-TrFE solution as described above. The wafer is then placed in a single-sided etching jig [8] which exposes a circular area on the backside of the wafer approximately one inch in diameter. The wafer is then etched using a standard isotropic etch solution (6:1:1 HF:HNO<sub>3</sub>:H<sub>2</sub>O) until the silicon is completely removed. The etch stops nicely on the now-exposed PVDF-TrFE film, which is not attacked. A suspended membrane of material approximately 1.5 inches in diameter and 5 μm thick is thus produced. The films thus produced are transparent and retain their adhesion to the silicon substrate. In order to make electrical contact to the film for subsequent poling and readout, silver paint (Acme E-Kote # 3030) was applied to both sides of the film. The film was then poled as described above, completing the fabrication. A fabrication cross-section is shown in Figure 1.

The structure as fabricated above was connected directly to a Tektronix 2221 oscilloscope (no buffer amplifier between metallized membrane and oscilloscope) in order to qualitatively assess the piezoelectricity and pyroelectricity of the film. Pyroelectricity was assessed using a shuttered incandescent light as a source of changing infrared radiation. An unbuffered response of several volts was observed due to exposure to the heat source. The piezoelectricity of the sample was qualitatively assessed by utilizing the sample as a microphone to pick up generated acoustic waves. Again, responses on the order of several volts were observed.

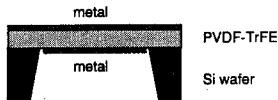


Figure 1. Fabrication cross section of a suspended PVDF-TrFE membrane. The device has been coated with metal on both the front and back sides for poling and assessment of the piezoelectric and pyroelectric responses of the film.

For the second method of suspended membrane fabrication, wafers with silicon membranes were used as a base material for spin-casting of PVDF films; the silicon membranes were then removed to form membranes of PVDF-TrFE. In this process, compatibility with more 'standard' micromachining processes, as well as vacuum deposited electrodes for the films, was demonstrated. For preparing these Si membranes the starting material was a single-sided polished <100> n-type Si wafer two inches in diameter, heavily boron-doped on the front side [9]. A 3500 Å thick oxide film was grown on the wafer. This oxide was patterned using photolithography to open a window in the backside and the wafer was etched in 20 wt% potassium hydroxide solution at 56 °C for 15 hours. This etch stops on the boron-doped layer, forming square silicon diaphragms 8mm on a side and 5µm thick. The masking oxide was then removed in hydrofluoric acid. Next, a layer of Al 1500 Å thick was evaporated on the top, and a layer of PVDF-TrFE was deposited as described above. A second layer of Al was then evaporated in the same manner and of the same thickness as the first layer. Finally, the supporting Si membrane was etched in an 80% CF<sub>4</sub> / 20% O<sub>2</sub> plasma to release the membrane. Electrical connection was then made to the aluminum layers, and the film was poled as described above. Again, the piezoelectric and pyroelectric responses of these films were measured. Responses similar to those for the films fabricated using isotropic etching were observed.

### Resonant String Arrays

Now that it has been shown that PVDF-TrFE can be integrated into a micromachining process, the next step is to move towards more complicated structures. In order to accomplish this we fabricated suspended string arrays of PVDF-TrFE. This experiment was useful not only to demonstrate the compatibility of PVDF-TrFE with more complex micromachining techniques such as photolithography and plasma etching, but also for the potential of in situ measurement of the mechanical properties of the films [10]. Several arrays of polyimide-supported (for mechanical strength) PVDF-TrFE strings with widths of 75 µm-100 µm and lengths of 8 mm were fabricated. The procedure is described below.

Starting with silicon membranes prepared as described above, a layer of polyimide (DuPont PI-2611) was spin-cast and cured using standard conditions to yield an after-cure thickness of approximately 2.5 µm. A layer of aluminum 1200 Å thick was deposited on the polyimide-coated wafer, and a 5 µm thick film of PVDF-TrFE was deposited as described above. A second layer of aluminum 3700 Å thick was then deposited and patterned into a string structure [10]. The second aluminum layer was patterned using PAN etch (phosphoric acid : acetic acid : nitric acid : water 16:1:1:2). The exposed PVDF-TrFE was then plasma etched from the top using a 90% CF<sub>4</sub> / 10% O<sub>2</sub> mixture as the etchant. The bottom layer of aluminum thus exposed was then etched using PAN, and the underlying polyimide was plasma etched in a 5% CF<sub>4</sub> / 95% O<sub>2</sub> mixture until the silicon was exposed. The wafer was then turned over and the silicon membrane was then plasma etched from the back using an 80% CF<sub>4</sub> / 20% O<sub>2</sub> plasma to release the strings. A partial fabrication sequence is shown in Figure 2. It should be noted that due to the resistance of PVDF-TrFE to HF and PAN etching solutions, the above process is self-aligned, needing only one step of photolithography once the Si membranes have been fabricated. Figure 3 shows a

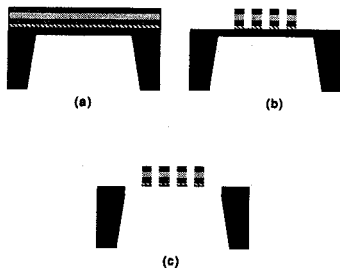


Figure 2. Partial fabrication sequence of polyimide-supported PVDF-TrFE string structures. (a) after coating of multilayer structure; (b) after patterning of strings; (c) after etch of silicon membrane to release strings.

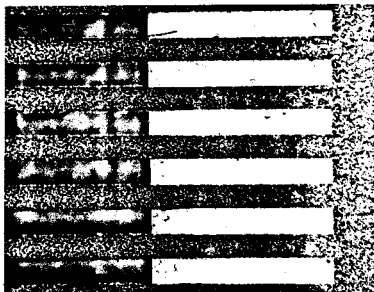


Figure 3. Photomicrograph of fabricated string structures. The strings are shown supported on the substrate (light) at left and suspended over the hole (dark) at right.