Patterning piezoelectric thin film PVDF–TrFE based pressure sensor for catheter application

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Abstract

We report a thin PVDF–TrFE (polyvinylidenedifluoride–trifluoroethylene) copolymer film pressure sensor, fabricated using standard lithography process for cost-effective batch process, film uniformity, and high resolution of polymer patterning. PVDF–TrFE copolymer, a semi-crystalline material, was spin-coated into thin films (1 μm thick) to tap the near β-phase formation. Pressure measurements demonstrated that the thin film (1 μm) show better performance compared to thick film (6 μm) with no electrical poling or mechanical stretching. Thin film devices showed higher β phase formation from Raman spectroscopy measurements, which translate into high piezoelectricity for sensing. The sensors can operate over a broad pressure range of 0–300 mmHg, with fast recovery time of 0.17 s, suitable for real time flow measurements in catheter applications.

1. Introduction

Balloon occlusion of a major blood vessel is commonly used for both diagnostic and therapeutic purposes. Every year, clinicians in the U.S. alone place more than 1.5 million pulmonary artery catheters for the purpose of hemodynamic monitoring [1]. Balloon occlusion of the aorta has emerged as a tool for controlling life-threatening hemorrhage from the pelvis and lower extremities [2]. Currently, the pressure of the inflated balloon is left to the surgeon’s experience or costly contrast based imaging techniques and is not dynamically controlled. Over inflation of the balloon results in a rare but lethal rupture of the occluded artery [3].

Patients with massive bleeding display rapidly changing hemodynamics and blood pressure. Hence the proper inflation pressure for successful occlusion changes with the patient’s physiology. A highly compact pressure sensor would allow development of an interventional catheter that includes multiple points of pressure measurement, including inflation pressure as well as upstream and downstream blood pressure.

Over past decades, many types of microfabricated pressure sensors have been developed, and they can be categorized into three major groups, depending on their operating principles: capacitive, piezoresistive, and piezoelectric sensors [4–6]. Capacitive sensors are most commonly adopted in the clinical setting due to relative simplicity and less expensive fabrication, their high scalability for miniaturization, high sensitivity, and low power consumption, but are mostly applied to low pressures and require complex readout circuitry. Piezoresistive sensors, successfully landed into industry, offer great mechanical stability but they have some drawbacks, for instance, a significant power requirement, large temperature-dependence offset, nonlinearity, long-term instability in dynamic field conditions and impart undesirable stiffness to catheters. Piezoelectric sensors are commonly employed for the measurement of highly dynamic pressures.

The need for a pressure sensor on a catheter is not new and dates back to the 1970s [5,7]. So far, silicon based piezoresistive and capacitive pressure sensors have been employed for this application but with limited success due to above-mentioned reasons. Piezoelectric thin film transducer shows great promise as the implantable and biocompatible pressure sensors, implemented on a catheter for minimally invasive surgery.

In this paper, we design, microfabricate and characterize piezoelectric PVDF–TrFE (polyvinylidene fluoride–trifluoroethylene) based pressure sensor which can be later integrated with catheter for intravascular measurements. Recently, PVDF has gained increasing attention for the development of ultra-compact pressure sensors [8,9]. However, these sensors comprise of thick PVDF...
films with thickness of 10 μm and above. The present study is an extension of our previous work [10] on pressure sensor fabricated from 1 μm thin PVDF–TrFE films.

2. Sensor materials: thin film PVDF

Piezoelectric PVDF, a semicrystalline polymer, may exhibit any of its four phases, α, β, γ, and δ. Amongst these phases, β phase is important since it has largest effective dipole moment [11]. The key to achieving high piezoelectricity of the PVDF polymer is forming β-crystalline phase, which significantly improves sensor and actuator performance.

Fig. 1 shows atomic structure of α-phase PVDF and β-phase PVDF respectively. The crystal structure for β-phase PVDF show how the dipoles are aligned parallel to each other to create surface charge separation under stress or compression. Due to the random orientation of the dipoles in the α-phase, the dipoles cancel out each other resulting in no net surface charges [4]. Untreated PVDF itself cannot have β phase without delicate mechanical stretching or electrical poling processes. Additionally, due to its incompatibility with the standard lithography process, many alternative fabrication methods such as screen printing and shadow mask process [11] have been developed.

Our approach offers a practical option to overcome these limitations, and offers cost-effective batch process with high film uniformity and high resolution of polymer patterning towards enhanced sensor performance using standard lithography fabrication. Further, we hypothesized that, without any mechanical stretching or poling, a thinner film should exhibit higher piezoelectricity compared to a thicker film. The output voltage V produced by a piezoelectric sensor is given by [2]:

$$V = F \cdot \frac{\varepsilon_{33}}{d} \cdot \frac{d}{A}$$

where, F, ε_{33}, are the applied force, appropriate voltage coefficient; d and A are the thickness and area of the film, respectively. Hence, a thicker film should have higher output voltage if the film exhibits good β-phase structure. But a thinner film may have higher crystallinity and hence higher voltage coefficient.

To verify the above, we fabricated two different thicknesses of PVDF films and characterized using Raman spectroscopy and FTIR (Fourier Transform Infra Red) spectroscopy. Samples were spin coated on silicon wafer and the absorbance due to silicon was subtracted from a background spectrum. Raman spectroscopy was done using Renishaw InVia Raman spectroscope using green laser (514.4 nm) with exposure of 30 s.

Fig. 2 showing the Raman spectroscopy peaks for the various PVDF film thicknesses are highly distinct. We notice a clear sharpening in the β-phase crystal phase (840 cm⁻¹) on curing the 1 μm and 6 μm thick PVDF–TrFE films. Further, we notice that the α-phase crystals (800 cm⁻¹) in the PVDF–TrFE films decreases or get eliminated as the film is heated and recrystallized. This phenomenon has also been reported elsewhere [12]. The intensity of the peak from PVDF absorbance (1430 cm⁻¹) remains unaltered, however. Raman spectrum shows mainly the presence of the β-phase crystal domains throughout the films. Less noticeable, however, is the presence of the α-phase crystal structures also. Fourier Transform Infra-Red (FTIR) absorption spectrum for the various PVDF films fabricated was also done in the present study (data not shown). The plots showed similar nature as that from Raman spectroscopy, confirming the presence of beta phase formation in the membrane.

3. Device fabrication

Two different designs of electrodes on PVDF were fabricated: (1) parallel type: electrodes on the same side, where the electrode can be further patterned into dual and quadruple design; and (2) sandwich type: PVDF thin film sandwiched between the electrodes. The PVDF–TrFE lithographic based fabrication process for sandwich structure is illustrated in Fig. 3. Starting with a silicon wafer, photoresist was patterned to define the bottom Al electrode (2000 Å thick) using the lift-off process. PVDF–TrFE was spin coated on the Al-patterned wafer. Then another patterned photoresist was used as a Reactive Ion Etch (RIE) mask to pattern the PVDF–TrFE thin film. The dry etch was performed under 100 sccm oxygen gas environment with 200 W RF power and 5 mT pressure. The PVDF–TrFE thin film etch rate was 150 nm/min. The photoresist mask was etched simultaneously with an etch rate of 100 nm/min and dry etch was continued until the photoresist mask was etched fully. Top Cu electrode (2000 Å thick) was patterned by wet etch and the photoresist mask was removed by dry etch. Using this recipe, we fabricated single, dual, triple and quadruple membrane geometries in the following bottom electrode sizes: 1 × 1 and 1.5 × 1.5 cm². Further, parallel electrode devices were also patterned using just the top mask to pattern the electrodes on one side of the membrane.

Fig. 4 shows film thickness for PVDF–TrFE films that can be prepared versus spin speed. Three different solutions, having
PVDF–TrFE concentrations of 8%, 15%, and 20% w/v in 2-butanone, were prepared. Thickness decreased as spin speed increased. In the present study, we used 8% w/v PVDF–TrFE copolymer with 2000 rpm for 30 s to get 1 μm thickness and 20% w/v PVDF–TrFE at 4000 rpm for 30 s to get 6 μm thickness.

Fig. 5(a) shows SEM images of 20% w/v PVDF–TrFE, showing poor adhesion on the silicon substrate under regular vacuum oven heat treatment and Fig. 5(b) 8% w/v PVDF–TrFE, showing strong adhesion under vacuum oven heat treatment. The film was cured in vacuum oven at 130 °C for 5 h for strong adhesion and near β-phase formation due to the residual stress between the thin film and the substrate.

Fabricated metal-PVDF–TrFE-metal (MIM) structured pressure sensors (dual and quadruple PVDF–TrFE membrane) size of 0.25, 0.5, 1, and 1.5 cm are shown in Fig. 6.

4. Experimental setup

Fig. 7 shows the schematic of the pressure sensor measurement in air chamber. The pressure on the PVDF sensor was determined using commercial pressure sensor (Freescale Semiconductors, MPX2300DT1). Any possible leakages from the chamber were prevented by the use of neoprene o-ring and vacuum grease. Air pressure and flow inside the chamber was manipulated using the multiple outlet valves.
Air flow into the chamber was controlled using a flowmeter (Dwyer instruments) before the inlet and a multiple outlet valve after the inlet. Flow rate combined with the number of open outlet valves were used to generate air pressure inside the chamber in the 0–300 mmHg range. This also happens to be the physiological pressure range over which the PVDF sensor needs to be operational.

The PVDF device was placed at the center of the chamber. The backside of the device was taped to the device holding plate. A commercial pressure sensor (Freescale Semiconductor, MPX2300D1T) was placed on the second plate. Both, the device and the sensor were so placed that the sensing element was perpendicular to the direction of the air flow and hence compression-induced signal from the commercial sensor and the PVDF devices due to air pressure was recorded. The inlet was kept at constant air flow, while the exit of air from chamber was controlled using a multi-stage valve. The two electrodes of the PVDF devices were connected to an external charge amplifier. Charge amplifier setting were always kept on 40 dB gain (100 × amplification), 100 nF feedback capacitor, 0.1–10 Hz bandpass. All data was recorded after 40 dB gain but was scaled to 0 dB before plotting. Outputs from the charge amplifier were connected to a USB-type (6009) Data Acquisition Kit (National Instruments). The output was further filtered using a digital low-pass filter (set to 8 Hz) with infinite impulse response filter set to inverse Chebyshev filter of order three. The chamber plates were sealed using vacuum grease (Dow Corning) and o-ring for the PVDF devices. An actual picture of the chamber with the device in place is shown in Fig. 7. The electrode pads of the PVDF devices were connected to Cu tape through silver print (GC electronics). Wires were then soldered to top of the Cu tape for external connectivity.

5. Results and discussion

The responses upon intermittent external stress applications were immediate and very reliable, having very fast recovery time. Fig. 8 shows experimental results of output voltage for a dual PVDF–TrFE film sensor (1 × 1 cm² bottom electrode surface area) when exposed to impulses of air pressure in the chamber. With exposed to the identical pressure application, similar outputs were observed though the charge amplifier. The two different MIM structures on the same device showed a fast recovery time, 0.17 s and 0.23 s, respectively.

Such recovery times correspond to an efficient resolving frequency of up to 5 Hz. This happens to be in the physiological sampling rates, as most of the physiological phenomenon occurs at 1–3 Hz, corresponding to 72–180 beats per minute.

Fig. 9 shows the hold-and-release output response obtained from a single PVDF pressure sensor fabricated (in blue color; online) corresponding to the pressure the PVDF device was subjected to, inside the chamber. The response obtained from the PVDF devices show the typical dynamic response expected from piezoelectric PVDF films. The pressure inside the chamber was measured using the commercial pressure sensor, indicated by the right vertical axis in Fig. 9. The negative voltage peak corresponds to the compression of the membrane and the positive direction peak corresponds to the relaxation of the membrane. The relaxation response from the PVDF film is a combined function of its spring constant and the damping factor. Response from control devices is shown in red, when exposed to similar pressures. Control devices were assembled in exactly the same manner as normal devices but did not have any PVDF membrane present.

For different magnitudes of pressure inside the chamber, the peak voltage from the PVDF devices were obtained and plotted as shown in Fig. 10. The graph shows a linear response for the PVDF based pressure sensors in physiologically relevant pressure range. Further, we notice that the slope is higher for 1 μm devices compared to 6 μm devices, indicating higher sensitivity from thinner devices. Results indicate that the fabricated pressure sensor shows near β-phase formation in the film even after standard lithography techniques.

Fig. 10a compares the dual membrane design with the quadruple membrane design for 1.5 × 1.5 cm² devices. Only one of the top available electrodes was connected at a given time. The standard deviation for all the data observed was low (<4%). The ratio of slope in the two plots was 2.3 for dual over the quadruple. This ratio of slope was as expected due to nearly double functionally active

Fig. 8. Experimental results of output voltage for pressure sensor having dual PVDF–TrFE film, showing 26% recovery time mismatch between two membranes and 9% repeatability.

Fig. 9. Response from PVDF–TrFE devices on hold-and-release pressures inside the air chamber showing the true dynamic behavior of the piezoelectric PVDF films.
surface area for the dual membrane design compared to the quadrapule membrane design. This ratio of slope was also found to remain the same when the PVDF film was not etched, indicating that it is the area between the electrodes which contributes towards the signal output. In other words, there was no contribution from areas of the PVDF film which were not covered by metal electrodes.

Fig. 10b compares the performance from PVDF devices with Parallel electrodes vs. the sandwich type electrodes. As expected, the sandwich type devices perform better (more than 3 times higher sensitivity) compared to parallel electrodes. This is because the piezoelectric coefficient for PVDF working in compression mode, d_{31}, can be more than two times higher than the lateral stretching mode, d_{33} [13].

Fig. 10c shows the improved performance obtained from a thinner film (1 μm) compared to a thicker (6 μm) PVDF film. We observed nearly 1.7 times higher signal output from the 1 μm PVDF device compared to 6 μm devices, indicative of the higher piezoelectricity of thinner film. This is possible due to the higher surface tension involved in the formation of a thinner film during spin coating, resulting in higher crystallinity in thinner films compared to the thicker films.

6. Conclusion

The low-cost, low-temperature standard lithography fabrication technique is applicable to pattern biocompatible PVDF–TrFE copolymer. The process is fully compatible with existing micromachining fabrication processes without additional mechanical stretching and electrical poling processes. Further, we found that the electrode-patterned surface area only contributes towards the output signal rather than the PVDF area. We achieved better β-phase formation in thin film (1 μm) PVDF–TrFE copolymer compared to the thick film (6 μm) without any electrical poling or mechanical stretching. The demonstrated fast recovery time (0.17 s), biocompatibility, and compact form factor show the great potential for pressure and flow direction measurements as implantable biomedical devices.

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