Fabrication Optimization and Characterization of PVDF-TrFE Based Pressure Sensors

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Introduction

Optimization of Organoid Grippers

3D culture and electrophysiological recording of human organoids are important issues when studying the working functions of human neural systems and developing organoid intelligence (OI). To enable a stable, biocompatible, and chronic recording of organoids, 'organoid grippers' are thought to be an suitable device. As a type of MEMS that holds the organoid during cell culture and signal recording, organoid grippers are being widely studied to improve its functionality in terms of causing less damage to the cell and collecting wide-spread, accurate signals. Currently, there is an ongoing study that deals with a magnetically-controlled foldable organoid gripper. This device exhibits six leaflet-shaped structures that grasp the whole surface of the organoid. Here, it is possible to optimize this MEMS by adding a pressure sensor to ensure its stable holding of the organoid. By adding pressure sensors to each leaflet, the contact pressure between the organoid and the sensor would be generated into a certain amount of voltage, allowing us to detect how well the organoid is held by the gripper. Considering the significance of this sensor in the sense that it could vastly improve the reliability in organoid studies via organoid gripper, detailed study focused on this pressure sensor in a bigger scale was conducted. In this study, a thin film of a biocompatible, piezoelectric material PVDF-TrFE was utilized for this sensor. Throughout the experiment, sensor fabrication parameters including solvent, film thickness, and patterning were optimized, along with the sensitivity characterization of the final device.

Main Idea

Piezoelectric Properties of PVDF-TrFE

Utilizing the piezoelectric property of PVDF-TrFE was the key idea of this study. Possessing a piezoelectric property means that it can generate an electric charge in response to applied mechanical stress. This phenomena can be effectively utilized in pressure sensors, and among such materials, PVDF-TrFE is widely-used due to its high sensitivity, biocompatibility, flexibility, etc. PVDF-TrFE, as same as PVDF, has five different phases depending on the orientation of the monomers, $(-CH_2-CF_2-)_n$. As depicted in Fig.1, the most common phase or α phase, shows random orientation of dipoles, resulting in charge canceling. On the other hand, β phase has all monomers aligned in one direction, resulting in high polarity and piezoelectric effects. Here, since PVDF-TrFE has a set of hydrogen atoms of PVDF replaced to fluorine atoms, polymers can directly crystallize into a structure similar to the beta phase of PVDF. The main focus of this study is based on generating the β phase by optimizing its thickness or baking conditions and utilizing it as a pressure sensor.

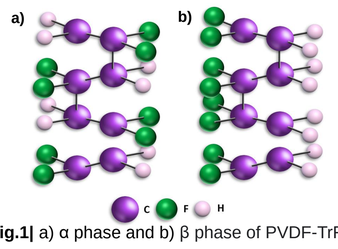


Fig.1| a) α phase and b) β phase of PVDF-TrFE.

Experimental Methods

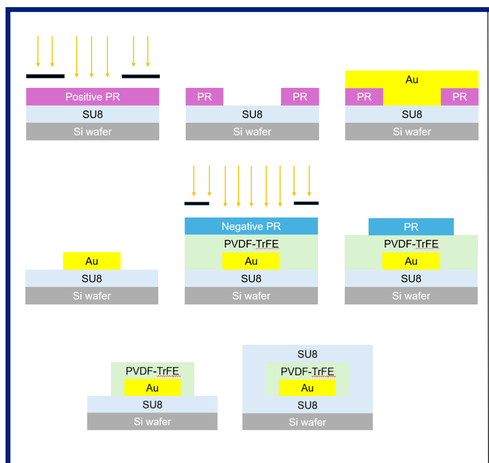


Fig.2| Device Fabrication Process in Cross Section View

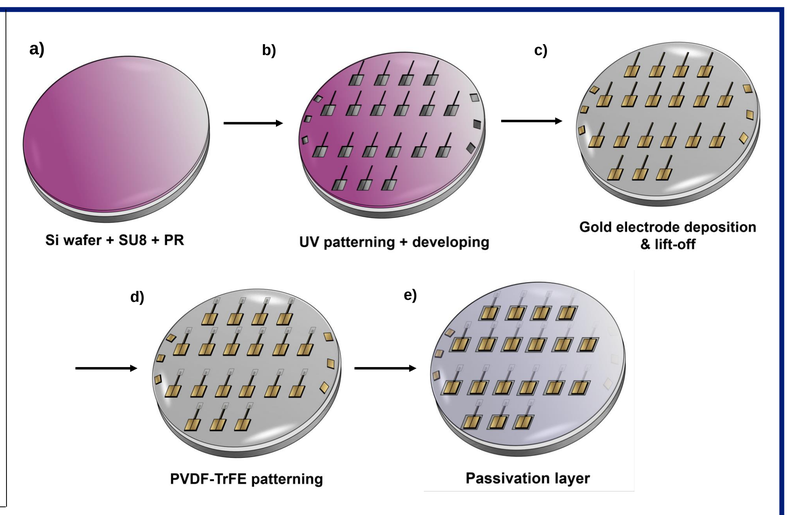


Fig.3| Device Fabrication Process in Top View

a) Passivation Layer deposition. A negative PR (SU8) was spin coated on Si wafer as bottom passivation layer. SU8 was baked, exposed by UV, and went through PEB.
b) PR deposition and patterning. Two positive PRs (LOR 3A, S1805) were spin coated, baked, and patterned by UV.
c) Electrode deposition and lift-off. Au was deposited via thermal evaporator and stripped off by lift-off process using acetone and mr-rem.
d) PVDF-TrFE deposition and patterning. PVDF-TrFE was coated and cured after plasma treatment for surface adhesion. Patterning was made by RIE etching through etching mask using DNR. Mask was removed after.
e) Passivation Layer deposition and patterning. SU8 was deposited and patterned to passivate the PVDF-TrFE. Electrodes were exposed for proper connection with wires and oscilloscope.

Results

1. Solvent Optimization

To dissolve PVDF-TrFE in a liquid, it is favorable to use polar solvents since they can align the PVDF-TrFE dipoles to have maximum charge. Most typically used solvents are DMF(Dimethylformamide) and MEK(2-Butanone), which have many previous studies proving their effectiveness in forming beta phases of PVDF-TrFE. The result was tested also in this study via XRD. Testing DMF first, the solvent was later changed to MEK regarding its limitations in viscosity, thickness, and solubility.

	DMF	MEK
concentration	8%, 10%, 15%, 20%	8%, 10%, 15%
advantages	high quality coating in 10%	high quality coating and moderate visocsity in all concentrations
	faster etching rate	not dissolved in mr-rem, IPA
		moderate thickness
disadvantages	excessive viscosity in 20%	slower etching rate
	dissolved by all acetone, mr-rem, IPA	dissolved by acetone
	insufficient thickness	

Table 1| Advantages and Disadvantages of using DMF and MEK based on experimental results.

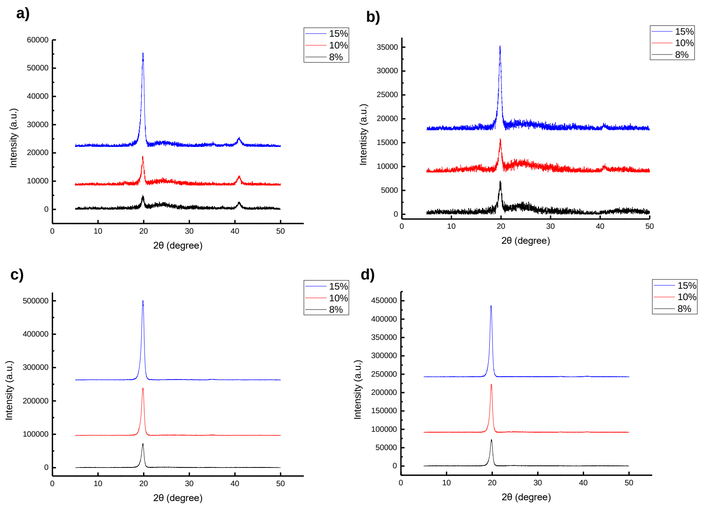


Fig.4| XRD Results with different solvent type, spin coating rpm, solution concentration. a) DMF solvent spin coated in 1000 rpm, b) DMF solvent spin coated in 4000 rpm, c) MEK solvent spin coated in 1000 rpm, and d) MEK solvent spin coated in 4000 rpm. Peak values in 20 degrees show successful formation of β phases in all solutions.

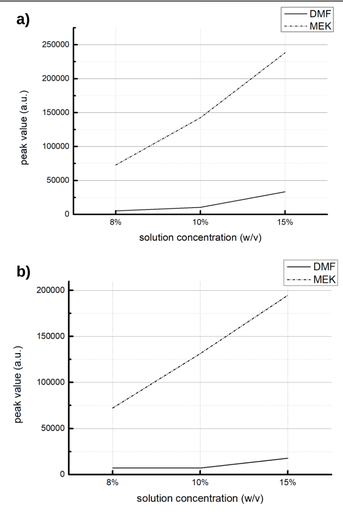


Fig.5| Trend of peak value with different solution concentration a) MEK and DMF spin coated in 1000 rpm and b) 4000 rpm. Peak value increases with concentration.

2. Thickness Optimization

The PVDF-TrFE film needs sufficient thickness to sense pressure and print out a piezoelectric response. At the same time, an overly-thick film would be inappropriate for device application, considering that the patterned electrode would be in microscale. In this sense, it is important to deposit the PVDF-TrFE film in an adequate thickness of about a few micrometers. To do so, thickness of different concentration and spin coating rpm of solutions using MEK were measured via SEM. Considering that 15% w/v solution is overly thick, and that 10% w/v solution thickness relatively decreases regularly, 10% w/v was chosen to be fabricated for the following procedures.

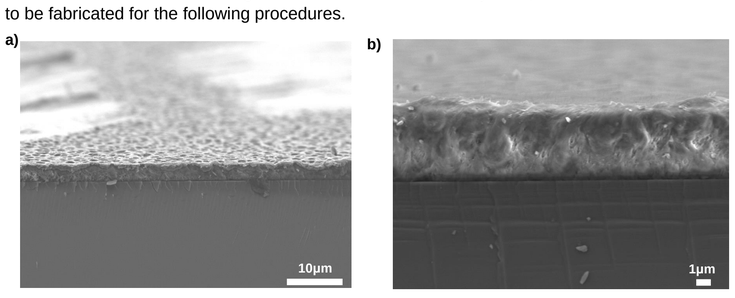


Fig.6| SEM of PVDF-TrFE film deposited on Silicon Wafer. Side view of sliced wafer coated with PVDF with each conditions of a) MEK 8% w/v 1000rpm and b) MEK 10% 1000rpm.

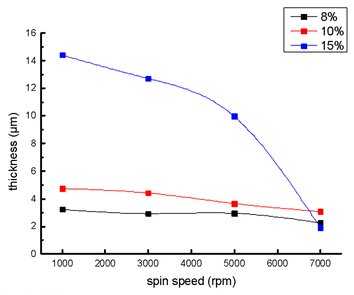
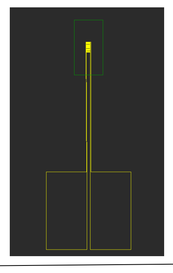


Fig.7| Film thickness with different concentration and spin coating rpm. Thickness decreases with increasing rpm and shows a drop around 5000 rpm.

3. Patterning / Etching Optimization

1) PR lift-off	PR dissolved by pvdf - X
2) PR RIE etching	Slow RIE etching rate - X
3) Ni mask lift-off	PVDF-TrFE dissolved by acetone - X
4) Ni etchant etching	Pattern unsustained -X
5) Optimized PR RIE etching	Modification of RIE recipe / PVDF-TrFE thickness 1000 rpm, O2 +CF4

Table 2| Patterning method optimization



PVDF-TrFE needs to be patterned onto the electrode of the device for piezoelectric effect detection as drawn in fig. 8. Limitations of each patterning method was realized and was optimized in the order as shown in table 2.

Fig.8| PVDF coating pattern (green) on gold electrode (yellow) schematic on CAD

MEK 10%
1000, 3000, 5000 rpm
O_2 50W etching (20 min)

↓

MEK 10%
1000, 3000, 5000 rpm
O_2+CF_4 150W etching
(20 min)

↓

MEK 10%
1000, 3000, 5000 rpm
O_2 150W etching (20 min)

Fig. 9| RIE recipe optimization. O_2 150W recipe showed the highest etching rate of all.

$$\left[(C_2H_2F_2)C_2HF_3\right]_n + F + e \rightarrow CF_2^+ + HF + e \quad (1)$$

$$\left[(C_2H_2F_2)C_2HF_3\right]_n + O + e \rightarrow CF_2O + CO + CO_2 + HF + e \quad (2)$$

$$CF_2O \rightarrow CO + 2F \quad (3)$$

Etching rate may be optimized by CF_4 due to the decomposed fluorine atoms, which are responsible for reactive etching for PVDF-TrFE. Concentration of fluorine atoms can be improved by the addition of oxygen.

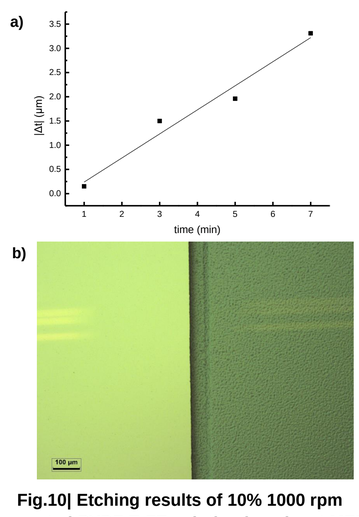


Fig.10| Etching results of 10% 1000 rpm coated PVDF-TrFE solution in solvent MEK. a) Etching rate with recipe of O_2 150W is calculated as 497 nm/min. (thickness (t)) b) Etching boundary picture. Left section is etched.

Expected complete etching time for 10% w/v solution is calculated as 9.5 min. It is shown that microscale etching is possible via RIE.

4. Final Device

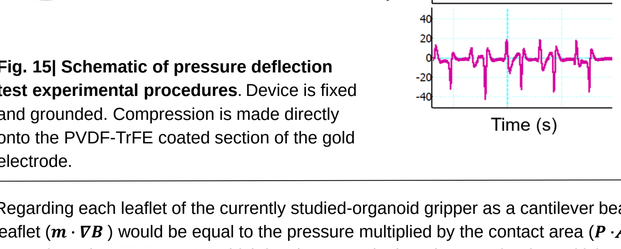


Fig. 11| Cross-section schematics of device. Each SU8, Gold, PVDF-TrFE are stacked before wire connection.

Fabricated device shows a structure (one electrode section magnified) as depicted in fig. 11. PVDF-TrFE is patterned directly onto the electrode for which it is the location to collect pressure stimulation. By consequently following additional steps in fig.12, the device can be characterized, connected to external examination devices. Device is shown in fig. 13, and fig. 14 shows the electrode section of the device. Thickness of electrode is 30 μm with separation distance of 10 μm.

Separation of fabricated wafer into individual pieces

↓

Copper tape

↓

Wire connection (soldering)

↓

Ag connection of electrode and wire

Fig. 12| Final device fabrication process

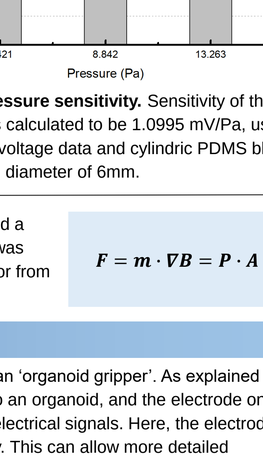


Fig. 13| Image of device

Fig. 14| OM Image of final device

5. Pressure deflection test / sensitivity

To test the pressure deflection, the device was connected to an oscillator. By gaining pressure on the PVDF-TrFE site of the device by stacking cylindric PDMS blocks, the piezoelectric response was visualized as an instant spike in the graph of the oscillator. Device was fixed to reduce mechanical noises, and an additional amplifier was utilized for detailed signal detection. Compression via PDMS block and ground connection was done for minimalizing effects of static electricity. Average of five peak values as shown in fig.16 were used to calculate the sensitivity of the sensor in fig.17.

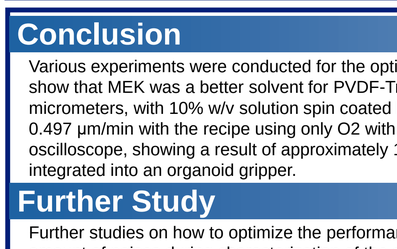


Fig. 15| Schematic of pressure deflection test experimental procedures. Device is fixed and grounded. Compression is made directly onto the PVDF-TrFE coated section of the gold electrode.

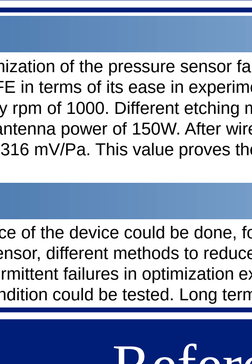


Fig.16| Output voltage differentiation in response to increasing pressure. Each in response to stacking of one, two, three PDMS blocks in order from top to bottom.

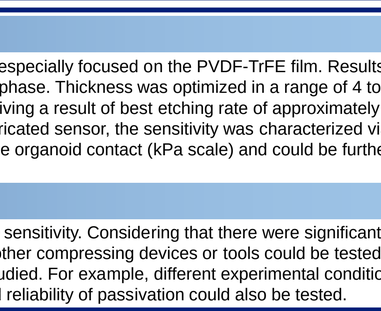


Fig.17| Pressure sensitivity. Sensitivity of the device was calculated to be 1.0995 mV/Pa, using the output voltage data and cylindric PDMS block data: 0.5N, diameter of 6mm.

Regarding each leaflet of the currently studied-organoid gripper as a cantilever beam, the magnetic force required to fold a leaflet ($\boldsymbol{m \cdot \nabla B}$) would be equal to the pressure multiplied by the contact area ($\boldsymbol{P \cdot A}$). By calculation, the force required was approximately 1.75E+04 Pa, which is a larger scale than the examined sensitivity (1.0995 mV/Pa) of the pressure sensor from this study. Therefore, the sensitivity of this sensor is sufficient for organoid grasp detection.

$$\boldsymbol{F = m \cdot \nabla B = P \cdot A}$$

6. Device Integration

Fig.18| Schematic of organoid gripper. Six leaflet-like structures (blue) with integrated electrodes (yellow) are holding the organoid (red).

This pressure sensor can be integrated to a broader device, an 'organoid gripper'. As explained in the introduction and fig.16, the leaflets of the device can grip onto an organoid, and the electrode on each leaflet could generate compression made when contact into electrical signals. Here, the electrode would be fabricated in a much smaller scale than in this study. This can allow more detailed information about organoid gripping in terms of how firmly the organoid is held. This may enable more detailed control in stably culturing organoids as their size grow.

Conclusion & Further Study

Conclusion

Various experiments were conducted for the optimization of the pressure sensor fabrication optimization, especially focused on the PVDF-TrFE film. Results show that MEK was a better solvent for PVDF-TrFE in terms of its ease in experiment and formation of β phase. Thickness was optimized in a range of 4 to 5 micrometers, with 10% w/v solution spin coated by rpm of 1000. Different etching methods were tested, giving a result of best etching rate of approximately 0.497 μm/min with the recipe using only O2 with antenna power of 150W. After wire connection of the fabricated sensor, the sensitivity was characterized via oscilloscope, showing a result of approximately 1.316 mV/Pa. This value proves the sensor ability to sense organoid contact (kPa scale) and could be further integrated into an organoid gripper.

Further Study

Further studies on how to optimize the performance of the device could be done, focusing on its pressure sensitivity. Considering that there were significant amount of noises during characterization of the sensor, different methods to reduce noise such as using other compressing devices or tools could be tested. In addition, trials to find the possible reasons for intermittent failures in optimization experiments could be studied. For example, different experimental conditions such as ambient nitrogen condition or vacuum condition could be tested. Long term stability of device and reliability of passivation could also be tested.

Reference

[1] Sharma, Tushar, et al. "Patterning piezoelectric thin film PVDF–TRFE based pressure sensor for catheter application." *Sensors and Actuators A: Physical*, vol. 177, Apr. 2012, pp. 87–92, https://doi.org/10.1016/j.sna.2011.08.019.
[2] Jiang, YongGang, et al. "Reactive ion etching of poly(vinylidene fluoride-trifluoroethylene) copolymer for Flexible Piezoelectric Devices." Chinese Science Bulletin, vol. 58, no. 17, June 2013, pp. 2091–2094, https://doi.org/10.1007/s11434-013-5836-9.
[3] Mao, Duo, et al. "Ferroelectric properties and polarization switching kinetic of poly (vinylidene fluoride-trifluoroethylene) copolymer." Ferroelectrics - Physical Effects, 23 Aug. 2011, https://doi.org/10.5772/17147.
[4] Shaik, Habibuddin, et al. "Towards β-phase formation probability in spin coated PVDF thin films." Journal of Polymer Research, vol. 24, no. 3, 9 Feb. 2017, https://doi.org/10.1007/s10965-017-1191-x.