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Reactive ion etching of poly (vinylidene fluoride) and its optimization

Hirofumi Miki, K. Morimoto, T. Tamaki and S. Tsuchitani

***Abstract*— A new fabrication process technology for the β-poly(vinylidene fluoride)(PVDF) based high resolution skin sensor devices is proposed using reactive ion etching. Fluorine-containing feed gas X (X denotes CF_4, CHF_3 and SF_6) and O_2 were investigated for the first time to optimize the composition of gas mixture for a high etch rate in β-PVDF microstructure fabrication process. PVDF etch rate in pure feed gas X is very low compared to that of pure O_2. At the condition of 100 W/13.56 MHz of RF power and 20 Pa of process pressure by keeping the total feed gas constant at 48 sccm, 285 nm/min of etch rate was achieved in the pure O_2 only, and it is 8 times higher than that of pure CF_4 or CHF_3, and about 4 times higher than that of pure SF_6. By mixing the fluorine-containing gas X to the feed of O_2, the etch rate could be increased further. The optimized feed composition was around 75~80 vol % of O_2 concentration to achieve the highest etch rate. In the feed of CF_4+O_2, as high as 770 nm/min of etch rate could achieved, and it is about 3 times higher than that of pure oxygen, and even 22 times higher than that of x-ray photo-etching. Having 70/130 μm of line & space PVDF microstructure array can be easily realized by the proposed process, without the problems of etching saturation and loss of piezoelectricity. It is possible to fabricate much fine and denser of arrayed microstructures by means of appropriate photomask pattern design. The etching characteristics are reported in detail with respect to experimental results.**

***Index Terms*—β-PVDF, etch rate, microstructure, RIE, skin sensor.**

I. INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is an important fluoropolymer because of its piezoelectric, pyroelectric and ferroelectric properties. PVDF is also known to have biological compatibility, and same time to have an extremely high chemical stability and mechanical strength combined with excellent mechanical flexibility [1]. The material is pliant, tough, lightweight, and commercially available in sheets of various thicknesses (down to 6 μm). It could also be used to cover large areas and was potentially inexpensive, and could generate voltages 10-25 times higher than that of piezoceramics at the same input pressure [2]. Because of these favorable material properties, PVDF has attracted considerable attention and become a popular candidate for tactile images. Much basic and applied research aimed at robotic skin sensors has been reported [3], [4], however, to the best of our knowledge, no tactile sensors with the sensation of skin that are pliant and have high resolution have been reported until now. The motivation of our work is to develop an optimized micro fabrication process technology for the fine patterns and densely arrayed microstructures directly on a β-phase PVDF film without losing much of its piezoelectricity and with a high of etch-rate as well. Such a technology will be useful for many applications especially for high sensitivity and high resolution robotic skin sensors, and for minimally invasive surgery (MIS) palpation sensors [5].

In the existing research on PVDF-based skin sensors, the common feature for high spatial resolution has been to use a single sheet of β-PVDF film as the sensing element, with electrodes arranged in patterns on the same film surface. However, one major problem with this type of sensor is the high degree of crosstalk between adjacent tactile elements (an undesirable response from the nearest neighbor sensing elements that leads to error in measurement) due to the lateral stiffness of the PVDF substrate. This limits the spatial resolution to a few millimeters [6]-[14], which is far from that required (100-200 μm in certain parts like at the fingertip). These problems are often reported where a PVDF film is used to design a matrix of high spatial resolution tactile sensors [15]. To avoid or mitigate crosstalk problems in PVDF based skin sensors, it is advisable to arrange the sensing elements in a discrete manner by microfabrication technology to achieve high spatial resolution.

One of the most convenient methods for PVDF micro patterning is soft lithography with the use of elastomeric polydimethylsiloxane (PDMS) molds, which has been extensively reported [16]-[21]. PVDF is synthesized by polymerizing CH_2=CF_2 monomers, and is a semi-crystalline polymer with at least four crystalline phases, α, β, γ, and δ [22]-[25], of which only the β-phase exhibits piezoelectricity [26]-[29]. The crystallographic phase of PVDF obtained by soft lithography (melt at 170-200 °C and cool) will be the α- or γ- phase; therefore, no piezoelectricity is possible [26], [30]-[33], so that this method is not suitable for application to tactile sensors. β-phase is not typically produced from a melt, due to the requirement of high-pressure or epitaxial techniques. β-PVDF can be generally obtained by mechanical deformation or electrical poling. For mechanical deformation, it is necessary to stretch the sheets to 3-5 times their original size under high temperature and pressure, and when only electrical poling is used, as much as 500 MV m^{-1} of high voltage must be applied [23],[26]. Park et al. [34] has reported a method for PVDF micro-patterning from PVDF solutions using various organic solvents; however, the PVDF produced by this method was mainly the α- or γ- phase. There is no other well-defined method to obtain β-phase PVDF apart from mechanical stretching, which is quite difficult to apply to thin films during microfabrication processes [34].

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Hirofumi Miki, Department of Systems Engineering, Wakayama University, Wakayama, Japan, +81(73) 457-8210,

K. Morimoto, Department of Systems Engineering, Wakayama University, Wakayama, Japan, +81(73) 457-8182,

T. Tamaki, Department of Systems Engineering, Wakayama University, Wakayama, Japan, +81(73) 457-8182,

S. Tsuchitani, Department of Systems Engineering, Wakayama University, Wakayama, Japan, +81(73) 457-8146,

It is nontrivial to pattern PVDF using conventional methods because of its chemical stability. Manohara et al. [1] reported a direct photo-etching microfabrication method to pattern oriented PVDF films using synchrotron X-rays. They realized maximum etch depths of 7.6±0.3 μm and 8.9±0.3 μm using synchrotron X-rays at 1.3 GeV/60000 mA min and 1.5 GeV/50000 mA min, respectively. However, this method has a problem of high energy consumption with a low etching rate, in addition to an etching limit because the etching process approaches saturation over exposure time, and finally the process stops. Similar behavior has also been reported by other groups [35]-[39].—The etching limit with X-ray photo-etching is due to its etching mechanism. Manohara et al. determined the evolution of H_2, F, and HF species during X-ray photo-etching of PVDF by mass spectroscopy measurements, but no carbon-containing species were detected. The carbon fraction in PVDF increases gradually as the etching progresses, which results in gradual darkening of the etched regions and a pure carbon layer is formed that blocks further etching (etching depth limit: 7-9 μm) and has high electrical conductivity [1].

The formation of the carbon layer inhibits design flexibility of the device structure, and the high electrical conductivity also results in serious signal problems with sensor applications. A. Bratnik et al [40] realized a through hole of 60×60 μm^2 on a 50-μm thick PVDF without etching saturation behavior by using a laser-plasma EUV (extreme ultraviolet) source. Because EUV cannot penetrate lens and absorbed by any material include atmosphere, the whole optical system need to be composed of reflective mirror and stored in a vacuum case which make the whole system became huge and high cost. Furthermore, there remains some question about the behavior of decay in PVDF piezoelectricity under EUV irradiation due to the high of energy and temperature. Jiang YongGang et al [41] reported a microfabrication process for poly (vinylidene fluoride - trifluoroethylene) (P(VDF-TrFE) using spin coating and reactive ion etching (RIE) techniques. However, micro structuring of the P(VDF-TrFE) film is a critical process for fabrication of flexible piezoelectric devices [41]. Furthermore, based on the basic principle of piezoelectric effect, the thicker of sensing element is of great advantage to the sensor sensitivity than thin structure [42], but, P(VDF-TrFE) is good with thin film below 2 μm and have problems of adhesion, crystallization and decrease of piezoelectricity in thicker of film [43].

The goal of this research is to develop a new method to fabricate an arrayed fine pitch and higher of microstructure on β-PVDF film which method has no problem like the etching saturation or significant loss of piezoelectricity. Previously [42] we reported the results associated with PVDF dry etching characteristics in O_2 RIE. This time we present a new process, based on mixture gas of CF_4+O_2, CHF_3+O_2 and SF_6+O_2 plasma etching. The process technology presented here will include an optimized etchant and the mixing ratio for the higher of etch rate and low loss of piezoelectricity. The etching characteristics are reported in detail with respect to experimental results.

II. MATERIALS AND EXPERIMENTS

A. Materials

A 52 μm thick β-PVDF film (purchased from Tokyo Sensor Co. Ltd., Japan) was used as the sensing material. The manufacturer-supplied physical and electrical properties of β-PVDF film as well as the comparison of some well-known piezoelectric material characteristics are given in Table 1 and Table 2. A photosensitive (at 405nm, 355nm of UV) dry film Photec RD-1125 and HM-6050 (from Hitachi Chemical Co. Ltd., Japan) were used as the PVDF dry etching mask during PVDF etching process. Mixed etching gases such as CF_4/O_2, CHF_3/O_2 and SF_6/O_2 are applied in this work for the PVDF plasma etching.

B. Experimental details

Dry film micro patterns for the PVDF etching mask was fabricated with conventional photolithography process. A photomask having arrayed micro patterns (Line & space (L/S): 70 μm/130 μm) was used in this work. The process details of dry film etching mask pattering and the removal of etching mask after PVDF plasma etching are presented in our previous work [42], [44], [45]. PVDF film micro patterning was performed with a commercial RIE instrument (RIE-10NR-WS, Samco Co., Ltd, Japan). After the pattern fabrication under each process condition, the etched depth on the PVDF film was measured with a stylus-type surface profilometer (Dektak 150, Ulvac) and the average etch rate was calculated by dividing the etch depth with the duration of etch time. The effects on the PVDF piezoelectric constant d_{33} after RIE etching was measured with PiezoMeter Systems PM300 (purchased from Piezo Test Co. Ltd, UK). The images of fabricated micro patterns on PVDF film were evaluated by scanning electron microscopy (SEM; JSM-6390, Jeol).

The variables for the PVDF RIE etching experiments are the etching duration (etch time), applied plasma power, process pressure and gas type as well as the gas flow. The electrode separation in our RIE instrument was set as 55 mm, and the temperature-controlled cooling system was set as 20 °C respectively. The etching process was performed at a process pressure of 20 Pa to achieve stable plasma. Plasma etching was performed during period of 30 minutes with the applied RF power at 100 W/13.56 MHz by keeping the total gas flow rate constant at 48 sccm (sccm denotes cubic centimeter per minute at STP). In order to characterize the gas composition dependence of the etch rate, the RIE system was fed with CF_4+O_2, CHF_3+O_2 and SF_6+O_2 gas mixtures, respectively. The oxygen concentration was varied from 0 to 100 vol % to investigate an optimized etching gas type and the mixing ratio for the higher of etch rate and low loss of piezoelectricity.

C. Experimental results and discussion

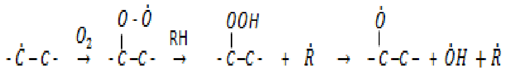
The samples were exposed to feed gas of CF_4+O_2, CHF_3+O_2 and SF_6+O_2. The etch rate variations of PVDF film as a function of the gas composition are plotted in Fig. 1 and displayed in Table 3 as well. Several observations can be made from Fig. 1. First, the etch rates of PVDF in fluorine-containing gases only are lowest, and by increasing the O_2 concentration in CF_4+O_2, CHF_3+O_2 and SF_6+O_2 mixture, the etch rates increase monotonously. As a result, it can be concluded that the oxygen is one of the most effective species in the plasma responsible for the PVDF dry etching process. The etch rate in O_2 gas only was 285 nm/min. It is 8 times higher than that of single CF_4 or CHF_3, and 3.8 times higher than that of single SF_6 at the same process condition. However, there is an optimized composition of the CF_4+O_2, CHF_3+O_2 and SF_6+O_2 gas mixture to achieve the highest etching rate. From Fig. 1, it can be known that the highest etch rates in CF_4+O_2, CHF_3+O_2 and SF_6+O_2 are respectively about 770, 600 and 300 nm/min at around 75~80 % of O_2 concentration. In the mixture of CF_4+O_2, the highest etch rate is about 3 times higher than that of pure oxygen, and even 22 times higher than that of X-ray photo-etching as in [1], respectively. Unlike X-ray photo-etching, neither visible darkening of the surface nor etching saturation phenomenon was observed in our process. This is considered to be due to the differences in the etching mechanisms.

Manohara et al. reported that the products from X-ray photo-etching were H_2, F_2, and HF, and no carbon containing species were detected [1], [35]-[39]. The remaining carbon in PVDF under X-ray photo-etching results in a gradually increasing carbon fraction along the depth of exposed region (C-fraction: maximum at exposed surface). The carbon-rich layer that is formed acts as a barrier to prevent further etching, which results in saturation of the etching process [1]. In contrast, in RIE process, PVDF is removed by ion-bombardment-induced sputtering and by chemical etching at the presence of reactive species, which results in the breaking of carbon bonds in PVDF and produces volatile products such as CO or CO_2. This assumption is also supported by other reports [46], [47]. Egitto [46] reported that besides the role of ions and photons in oxygen plasmas, atomic oxygen free radicals initiate the etching process shown in equations (1) and (2) :

$$-C-C- + O: \rightarrow -\dot{C}-C- + \dot{O}H \qquad (1)$$

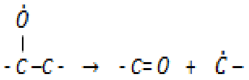
$$RH + \dot{O}H \rightarrow \dot{R} + H_2O \qquad (2)$$

Hansen et al. [47] outlined a possible autoxidation process:



$$-\dot{C}-C- \xrightarrow{O_2} -\overset{O-\dot{O}}{\overset{|}{C}}-C- \xrightarrow{RH} -\overset{OOH}{\overset{|}{C}}-C- + \dot{R} \rightarrow -\overset{\dot{O}}{\overset{|}{C}}-C- + \dot{O}H + \dot{R} \qquad (3)$$

From these structures, scission processes can occur that lead to the production of volatile etching products such as CO and CO_2 [46]:



$$-\overset{\dot{O}}{\overset{|}{C}}-C- \rightarrow -C=O + \dot{C}- \qquad (4)$$

Consulting with in [41], the following mechanism is suggested for the PVDF RIE process when the feed gas is the mixture of fluorine-containing gas and oxygen (X+O_2; X denotes the fluorine-containing gas CF_4, CHF_3 and SF_6):

$$[CH_2CF_2]_n + F \rightarrow +CF_2^{+} + HF \qquad (5)$$

$$[CH_2CF_2]_n + O \rightarrow CF_2O + CO + CO_2 + HF \qquad (6)$$

$$CF_2O \rightarrow CO + 2F \qquad (7)$$

From above equations, it can be seen that the concentration of fluorine atoms can be improved by the addition of oxygen. The relative concentration of oxygen and fluorine atoms is responsible for the etch rete of PVDF when X+O_2 feed gas mixture is utilized.

Further details of characterization could be considered. As is well known, plasma-polymer interaction results in both the formation and removal of organic etch masks [46], [48], [49]. For high concentration of oxygen in X+O_2 mixture, the reactions taking place in the heterogeneous plasma polymer boundary layer give rise to volatile species such as CF_2O, while for high concentrations of X in X+O_2 mixture, polymer-forming stable species can deposit on the substrate to form very thin (several nm) barrier (i.e., CF_i, i=1, 2, 3) [50], [51]. This protective layer acts as a diffusion barrier for both F radicals to reach the surface of the material to be etched and also for volatile compounds to diffuse out. Hence, the etch rates of PVDF are inversely proportional to the thickness of this polymer layer [52]. The addition of O_2 in plasma provides additional reaction paths that decrease the thickness of the polymer barrier layer. The relative concentration of the O and F species responsible for the etching phenomena increases in the plasma. This leads to an increases of the etch rate by producing chemically stable HF and CO compounds by interaction with the polymeric surfaces.

Table 4 and Fig. 2 show PVDF piezoelectric constant change at different gas composition and mixture ratio. The characteristics of PVDF piezoelectricity did not deteriorate remarkably after RIE etching, and could maintain as high as 64 % of its original level even at the process condition of the highest etching rate. We also measured PVDF piezoelectric constant change as a function of annealing temperature rise in the constant-temperature oven as shown in Fig. 3. From Fig. 3 it is known that PVDF piezoelectricity deteriorates monotonously and almost linearly with the annealing temperature rise, and at the condition of the highest etch rate in feed mixture CF_4+O_2, the process temperature is supposed to be around 105 °C. At the condition of other composition mixture, the RIE process temperature will be keeping below 90 °C. Fig. 4 shows the scanning electron microscopy images of the patterned PVDF at the condition of pure feed gas and 50 vol % of X+O_2 mixture. From Fig. 4 it is easy to understand that PVDF etch rate at pure fluorine-containing gases (i.e., CF_4, CHF_3 and SF_6) is very low comparing to pure O_2 feed, but by mixing these fluorine-containing gases with oxygen, the etch rate can be greatly increased. Besides, it is also known that high density micro structure array having 70 μm/130 μm of line & space could be easily realized by our process and it is possible to fabricate smaller and denser of arrayed microstructures by means of appropriate photomask pattern design.

III. SUMMARY AND CONCLUSIONS

In summary, a detailed examination on the conventional fabrication process technology to realize small pitch microstructure array on the PVDF film was performed, and a new fabrication process was proposed using reactive ion etching technology. Feed gases of CF_4, CHF_3, SF_6 and O_2 were investigated to optimize the etching conditions at 100 W/13.56 MHz of RF power and 20 Pa of process pressure by keeping the total feed gas constant at 48 sccm.

The experimental results indicate that the PVDF etch rate in the feed of pure CF_4, CHF_3 and SF_6 is very low compared to that of pure O_2. The etch rate in the feed of O_2 only was 285 nm/min, and it is 8 times higher than that of pure CF_4 or CHF_3, and about 4 times higher than that of pure SF_6. In addition, by mixing small amount of fluorine-containing gas to the feed of O_2, the etch rate could be increased further. The optimized feed composition was around 75~80 vol % of O_2 concentration to achieve the highest etch rate. In the feed of CF_4+O_2, as high as 770 nm/min of etch rate could achieved, and it is about 3 times higher than that of pure oxygen, and even 22 times higher than that of X-ray photo-etching. The experimental results also indicate that a microstructure array having 70/130 μm of line & space can be easily realized without the problems of etching saturation and loss of piezoelectricity. It is possible to fabricate much fine and denser of arrayed microstructures by means of appropriate photomask pattern design. The proposed method and the results of this work will be useful for many applications besides that of tactile sensing.

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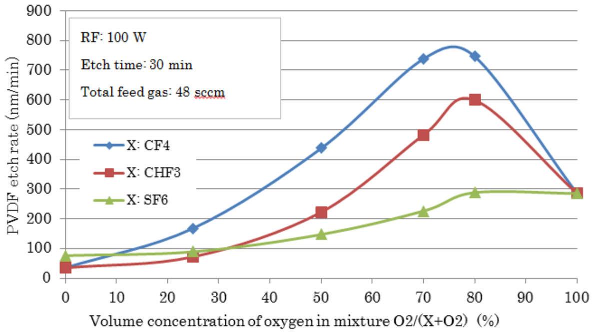

Fig. 1 PVDF etch rate as a function of the feed gas composition

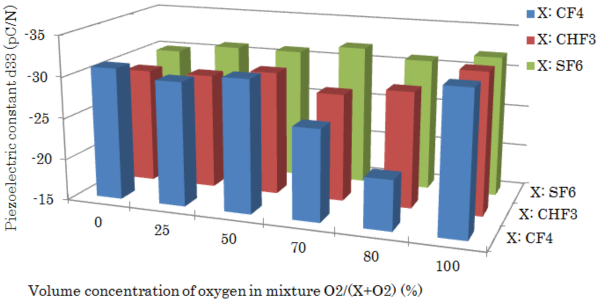

Fig. 2 PVDF piezoelectric constant d_{33} as a function of the feed gas composition

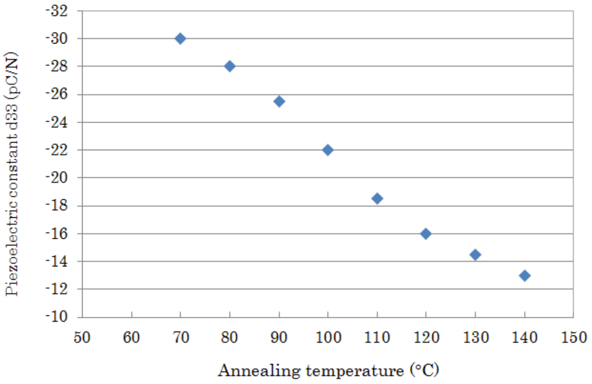

Fig. 3 PVDF piezoelectric constant as a function of annealing temperature rise

Table 1 Physical and electrical properties of PVDF film (Tokyo Sensor Co. Ltd., Japan)

Symbol	Parameter	PVDF	Units
t	Thickness	9, 28, 52, 110	µm (micron, 10^{-6})
d_{31}	Piezo Strain Constant	23	10^{-12} $\frac{m/m}{V/m}$ or $\frac{C/m^2}{N/m^2}$
d_{33}		-33	
g_{31}	Piezo Stress Constant	216	10^{-3} $\frac{V/m}{N/m^2}$ or $\frac{m/m}{C/m^2}$
g_{33}		-330	
k_{31}	Electromechanical Coupling Factor	12%	
k_c		14%	
C	Capacitance	380 for 28 µm	pF/cm², @1kHz
Y	Young's Modulus	2-4	10^9 N/m²
V_0	Speed of Sound stretch:	1.5	10^3 m/s
	Thickness:	2.2	
P	Pyroelectric Coefficient	30	10^{-6} C/m² °K
ε	Permittivity	106-113	10^{-12}F/m
$\varepsilon/\varepsilon_0$	Relative Permittivity	12-13	
ρ_m	Mass Density	1.78	10^3kg/m
ρ_e	Volume resistivity	$>10^{13}$	Ohm meters
$R_\square$	Surface Metallization Resistivity	<3.0	Ohms/square for NiAl
$R_\square$		0.1	Ohms/square for Ag Ink
tan δ_e	Loss Tangent	0.02	@1kHz
	Yield Strength	45-55	10^6 N/m² (stretch axis)
	Temperature Range	-40 to 80…100	°C
	Water Absorption	<0.02	% H_2O
	Maximum Operating Voltage	750 (30)	V/mil (V /µm), DC, @ 25°C
	Breakdown Voltage	2000 (80)	V/mil (V /µm), DC, @ 25°C

Table 2 Comparison of some well-known piezoelectric materials (Tokyo Sensor Co. Ltd., Japan)

Property	Units	PVDF Film	PZT	$BaTiO_3$
Density	10^3kg/m³	1.78	7.5	5.7
Relative Permittivity	$\varepsilon/\varepsilon_0$	12	1200	1700
d_{31} Constant	(10^{-12})C/N	23	110	78
g_{31} Constant	(10^{-3})Vm/N	216	10	5
k_{31} Constant	% at 1 kHz	12	30	21
Acoustic Impedance	(10^6) kg/m²-sec	2.7	30	30

Table 3 PVDF etch rate as a function of the feed gas composition $O_2/(X+O_2)$ (X denote pure CF_4, CHF_3 and SF_6)

	PVDF etch rate (nm/min)					
$O_2/(X+O_2)$ [vol %]	0	25	50	70	80	100
X: CF_4	35	168	437	738	746	285
X: CHF_3	35	72	222	482	599	285
X : SF_6	76	89	147	226	288	285

Table 4 PVDF piezoelectric constant as a function of feed gas composition $O_2/(X+O_2)$ (X denote pure CF_4, CHF_3 and SF_6)

	PVDF piezoelectric constant d33 (pC/N)					
$O_2/(X+O_2)$ [vol %]	0	25	50	70	80	100
X: CF_4	-31	-30	-31	-26	-21	-32
X: CHF_3	-29	-29	-30	-28	-29	-32
X : SF_6	-30	-31	-31	-32	-31	-32

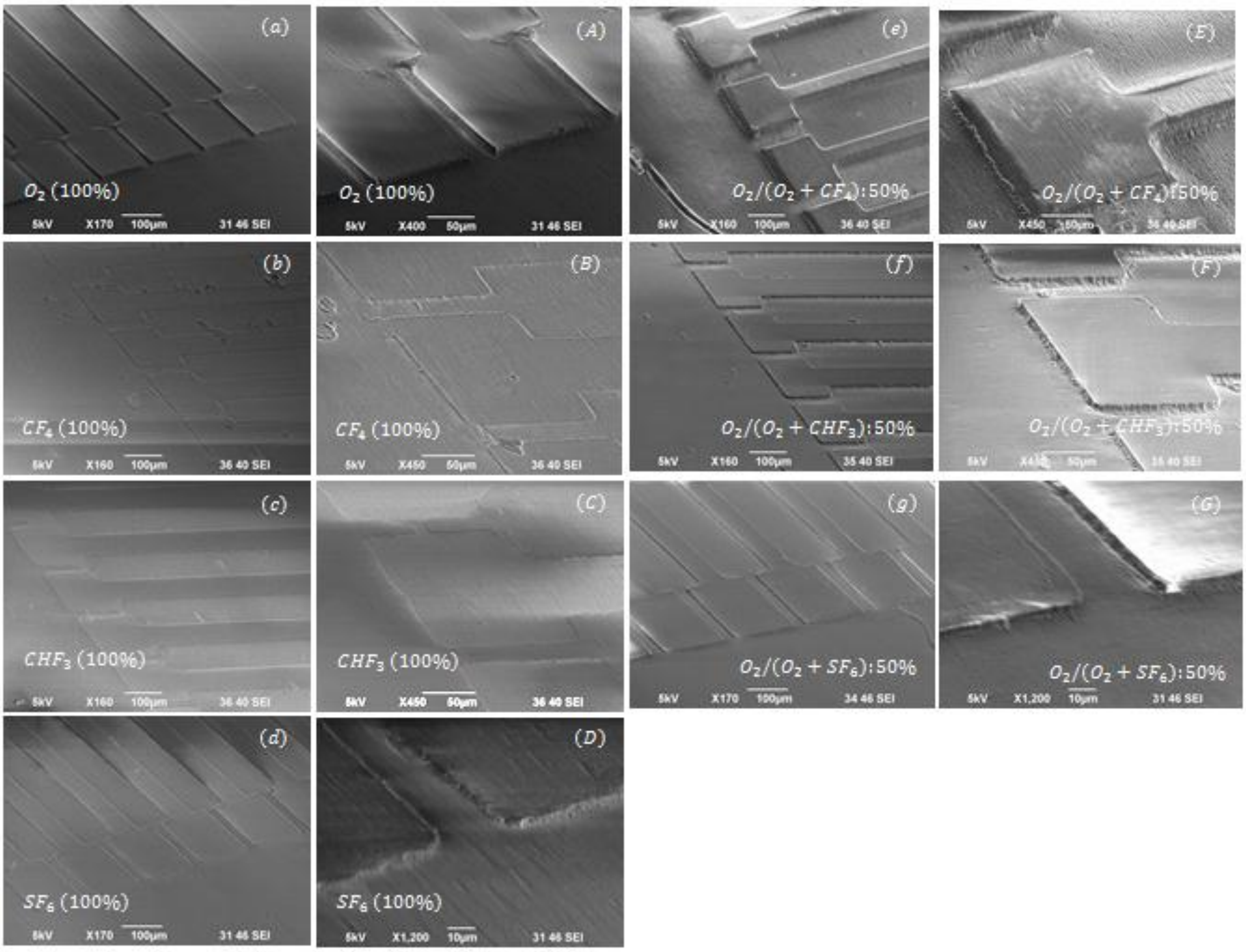

Fig. 4 SEM images of PVDF micro fabrication by reactive ion etching utilizing same photomask patterns and same process conditions except the composition of feed gas: (a)-(d) show the results at different pure feed gas and (e)-(g) show the results at mixed feed gas; Pictures having a capital letter of serial number (SN) show the enlarged view that related to that of small letter SN.