

Process Development for Dry Etching Polydimethylsiloxane for Neural Electrodes

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Abstract—In order to create high density electrode arrays, a reactive ion (dry) etching process was developed using sulphur hexafluoride (SF₆) and oxygen (O₂) plasma to pattern microstructures in medical grade polydimethylsiloxane (PDMS). The surface topography and etch performance were analyzed by employing surface profilometry, scanning electron micrographs (SEM) and atomic force microscopy (AFM). The maximum etch rate was approximately 0.22 μm/min. The chemical modification of the PDMS structure in SF₆ and O₂ plasma was investigated through x-ray photoelectron spectroscopy (XPS). Micro-scale openings in PDMS were achieved using a dry etching method to allow charge injection at the electrode-tissue interface.

I. INTRODUCTION

High density platinum (Pt) electrode arrays are successfully used in neuroprosthetic devices to evoke or record neural activity. Successful stimulation relies on the electrode-tissue interface that supplies current to depolarize neurons. Patient outcomes may be improved by increasing the number of individual stimulating sites on the array, thus enabling the stimulation of discrete neuronal populations.

Electrode arrays used by the Australian Vision Prosthesis group (AVPG) are created using a multi-layer approach whereby polydimethylsiloxane (PDMS) is used as the substrate and for encapsulating the current carrying tracks and stimulating pads [1]. The underlying Pt must be exposed to permit charge injection to the target neurons [2]. Feasible methods employed to open the contacts from the overlying PDMS layer include wet etching, dry etching and laser ablation [3], the latter being the method that is currently used [1]. Laser ablation has been shown to create irregular roughening of the Pt surface attributed to the heat generated by the laser beam [3-5]. Non-uniform surface roughness may result in inconsistent charge injection, causing irreversible chemical reactions of the electrode in the electrolyte [6-7]. An alternative to laser ablation is dry etching, which has been reported to produce smaller features in PDMS. It was also found favorable in terms of aspect ratio and selectivity,

thereby preventing the roughening of the underlying metal surface [1, 8].

This study explored the process of dry etching using fluorine based plasma as a method to create micro-scale openings in the silicone substrate and offers one alternative to permit the up-scaling of electrode quantities without damaging the underlying Pt surface and surrounding PDMS.

The plasma of fluorine based gases such as sulfur hexafluoride (SF₆), carbon tetrafluoride (CF₄) as well as oxygen (O₂) have been used by numerous groups to etch PDMS [3, 8-11]. Garra et al. pioneered this work with their investigation of CF₄ and O₂ plasma, achieving a maximum etch rate of approximately 0.33 μm/min at 270 W and 47 mTorr in a reactive ion etcher (RIE) [8]. Szmigiel and his team furthered the investigation with the use of SF₆ and O₂ plasmas for increased etch rates [10-12]. They achieved a maximum etch rate of 1.9 μm/min, using an inductively coupled plasma (ICP) reactor at an RF source power of 800 W, RF bias power of 100 W and 5 mTorr pressure at 50 °C.

The radio frequency (RF) power, chamber pressure, gas flow rate, processing time and temperature are factors that affect the etch rate and the surface morphology of PDMS [8, 12]. The aims of this study were to tailor a dry etching process to create micro-scale openings in PDMS for specific applications in stimulating neural electrodes, extending on a micro-patterning method devised by Suaning et al. [1] and to characterize the surface morphology post reactive ion etching.

II. MATERIALS AND METHODS

A. Substrate Preparation

Hexagonal test electrodes were made using medical grade silicone adhesive MED-1000 (NuSil Technology, Carpinteria, CA, USA) and micromachined using a method previously described by Suaning et al. [1]. After micro-machining, a patterned aluminium foil mask was placed on the surface of the cured silicon. The electrode openings consisted of diameters ranging from 200 μm to 1.5 mm. The mask pattern was kept constant due to reported loading effects [13]. The underlying Pt contact pad was exposed by etching through a PDMS thickness of 25-50 μm. Following the etching process, the mask was removed manually. The power, pressure and time were varied to determine the maximum etch rate. The openings were the only exposed area on the slide, with the remaining area protected by the aluminium foil mask.

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B. Reactive Ion Etching

A custom built hollow cathode reactive ion etcher (HCRIE) was used for the dry etching processes. In the HCRIE system, the top and bottom aluminium electrodes were driven by an RF generator at a frequency of 13.56 MHz. The electrodes acted as the cathode and the body as the anode (connected to ground). The RF matching network consisted of a coil (inductor) and capacitors (C_{load} and C_{tune}). These cathodes were protected by a silicon wafer to reduce damage and aluminium sputtering, and were water cooled throughout the process. The pumping system consisted of a turbo and rotary pump, the latter used for low vacuum pumping. The flow rates of the gases were controlled by mass flow controllers and the pressures were regulated by capacitive manometers, driven by a feedback control system.

The chamber was pre-cleaned with oxygen plasma at 300 W, 15 Pa and 20 sccm for 10 min. When running the etching process, the RIE chamber was allowed to pump down for 40 min to allow the pressure to stabilize below 0.01 Pa. The gas flow and pressure were allowed to stabilize prior to igniting the plasma.

To ensure an optimum etching process the chamber pressure and RF power were varied within the limits of the plasma tool, from 5-30 Pa and 5-280 W respectively, at a constant processing time. The etch process was assessed qualitatively through cross-sectional SEM images and quantitatively through surface profilometry. The forward bias voltage (V_{dc}) and peak to peak voltage (kV_{p-p}) were recorded for all combinations of pressure and power. Irreversible temperature labels were used to give an indication of the in-process temperature of the chamber. The gas mixture used was based on published results, at a 4:1 ratio of $SF_6:O_2$ [10-12].

After the optimal pressure and power had been established, the processing time was increased until there was complete removal of material. For this, the design of the substrate was modified to incorporate a 25 μm /layer thickness of PDMS required to be etched for test electrodes. The processing time was then controlled to ensure the complete etching of PDMS until the Pt etch stop layer.

C. Surface Profilometry

Surface profiles were measured using a surface profilometer (Dektak Sloan II). The samples were cleaned with 80% EtOH and left to air dry. The stylus was run through the center of the etched surface step, recording the maximum height.

D. Scanning Electron Microscopy

The post-etched surface morphology was analyzed using an SEM. The silicone only samples were cleaned and sputter coated with a layer of gold using a gold sputter coater (EmiTech K550, USA) to prevent charge accumulation on the surface of the silicone. SEM images were taken using a Hitachi S3400 at a 15 kV accelerating voltage, under high vacuum. The images were captured at 1100x magnification.

For the test electrodes containing the Pt contact pad, SEM images were taken on a JEOL Neoscope JCM-5000 (USA). Preparatory gold coating steps were not required as the underlying Pt alleviated charge build up. The SEM was set to high vacuum at 10 kV acceleration voltage.

E. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed to determine the elemental composition before, during and after the plasma etching process. This was carried out using an ESCALAB250Xi (ThermoScientific, USA), with a monochromatic Al K alpha (energy 1486.68 eV) irradiation source. The pressure in the chamber was 2×10^{-9} mbar. Measurements were recorded at 55 W, 4 mA and 13.57 kV. The photo-electron take off angle was 90° and the pass energy was 100 eV.

The elements contained in the top atomic layers of the material were determined and the atomic concentration was calculated from the areas under the peaks. Controls of pure Pt and PDMS were also analyzed for comparison.

F. Atomic Force Microscopy

The roughness of the post-etched platinum surface was measured using AFM (Digital Instruments NanoScope, Veeco, USA) and compared to unaltered platinum foil. The scan size and rate were 100 μm and 1.001 Hz, respectively. The number of samples taken per sample was 256.

G. Cleaning

Post etched remnants were removed using ultrasonic cleaning in 80% ethanol and wiped with cotton swabs. An evaluation of the cleaning efficacy was achieved through XPS analysis.

III. RESULTS

A. Etch Rates

Previous work completed in this area suggests that the maximum etch rate using an RIE system would be measured at 270 W and 240 mTorr (Table I) using a gas mixture of 4:1 ($SF_6:O_2$). Because the performance of the etch depends on the individual plasma tool used, various settings were trialled and measured to compare with results obtained in the literature. The etch rate was calculated by dividing the etch depth by the etch time. In the power range of 5-150 W and power 5-30 Pa, the measured etch depths were too low and a significant etch depth could only be measured after 2 h. At a power of 150 W and 10 Pa, an etch rate of 0.1 - 0.16 μm /min was recorded. The etch rate remained in this lower range for power settings up to 250 W.

Therefore the parameters recommended in [10] were used. The pressure was then varied at 270 W. At a pressure of 6.6 Pa, the etch rate was approximately 0.1 μm /min. A higher pressure of 30 Pa resulted in an etch rate of ~ 0.22 μm /min. Increasing beyond this point resulted in high temperatures ($>143^\circ C$) that burnt the PDMS structure (Fig. 1). Therefore

the maximum etch rate achieved was approximately 0.22 $\mu\text{m}/\text{min}$. Deep trenches (25-50 μm) were successfully etched to the Pt surface but this process was time consuming.

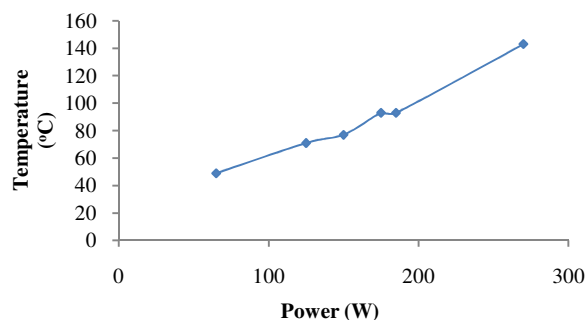


Fig. 1. Power versus temperature of RIE processing chamber showing the increase of temperature with power.

B. Surface Analysis

The dry etching process produced a translucent white roughening on the PDMS surface (Fig. 2A-D). Complete etching was indicated by a dark brown residue on the Pt surface that was easily removed by cleaning in an ultrasonic bath (Fig. 3). SEM images of the underlying Pt showed no roughening of the surface (Fig. 3).

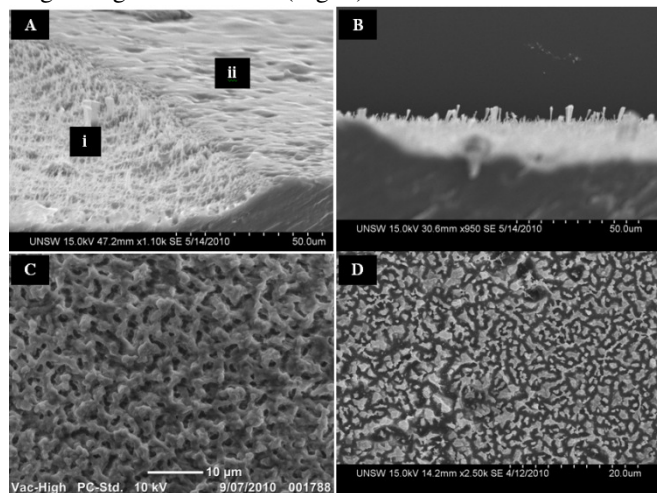


Fig. 2. SEM of etched surface showing surface roughening of PDMS; A) Comparison between etched surface (i) and non-etched PDMS surface (ii); B) Cross section showing PDMS pillars; C) Top view of white PDMS pillars; D) Top view of brown PDMS pillars showing progressive etching, with increased inter-pillar space.

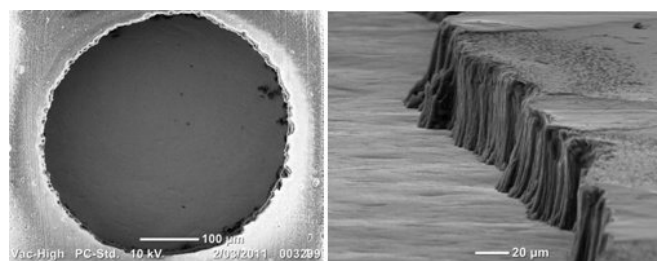


Fig. 3. SEM of 380 μm diameter electrode opening and sidewall after RIE etching process using SF_6 and O_2 gas (4:1 ratio) at 270 W, 30 Pa.

SEM images taken of the etched sidewall at 270 W, 30 Pa showed slightly sloped sidewalls, at an angle of

approximately 75.5° from the bottom of the etched edge to the top of the etched edge.

XPS analysis showed the elemental change of the PDMS and Pt following reactive ion etching, compared with untreated PDMS and Pt. The elemental constitution and binding energies (BE) are contained in Table I. The etch residues contained F, Al and S that were introduced by the process gases and backscattering of the Al mask. The F and Al content were removed with the surface residues.

TABLE I
ATOMIC PERCENTAGES AND BINDING ENERGIES (eV) OF ELEMENTS BY XPS

1. Unaltered PDMS, 2. In-process etching, 3. Completely dry etched surface, 4. Pt and 5. Over-etched Pt surface.

Elemental									
Constitution (At%)	C1s	O1s	F1s	Pt4d5	Pt4f	Al2s	S2p	Si2p	N1s
1	48.1	24.0						27.9	
2	12.9	52.2	2.6		0.3			32.0	
3	14.8	7.8	45.7	4.8		19.1	7.8		
4	56.19	19.30			10.6			11.9	1.13
5	39.29	20.18			10.83		13.6	13.6	

Elemental									
Binding Energies									
(eV)	C1s	O1s	F1s	Pt4d5	Pt4f	Al2s	S2p	Si2p	N1s
Peak centre	285	531.8	685.7	314.5	72.6	117.9	164	100.1	398.4
1	285.2	533.0						103.1	
2	280.6	528.8	683.0		71.7			99.3	
3	285.0	532.9	686.9	315.4		121.8	163.3		
4	285.06	532.03			72.29			102.34	
5	282.06	529.22			70.31		160.37	99.59	

The results from the AFM surface analysis are shown in Fig. 4. The surface roughness (R_a) decreased by approximately 26 nm after reactive ion etching.

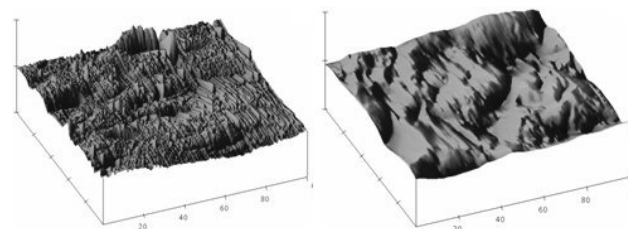


Fig. 4. AFM images of Pt surface before RIE (left) and after RIE (right), where $x = 20 \mu\text{m}/\text{div}$ and $z = 2000 \text{ nm}/\text{div}$

IV. DISCUSSION AND CONCLUSION

Dry-etching may be a possible method to create micro-scale openings in PDMS. Using SF_6 and O_2 (4:1 mixture) in a custom built reactive ion etching tool at 270 W, 30 Pa, a 0.22 $\mu\text{m}/\text{min}$ etch rate was achieved. The RF power and DC bias voltage showed a direct correlation, owing to the dependence between the DC bias and ion flux hitting the surface [9]. Our experiments showed that increasing the power produced a higher etch rate. This is not unexpected as higher RF power causes an increase in ion bombardment and atomic fluorine concentration resulting in higher etches rates [13]. An increase in chamber pressure caused a decrease in bias voltage, showing that the ion bombardment and energy are reduced as the pressure is increased. Etch residues were

formed during the etching process on the surface were easily removed once the PDMS had been etched through to the Pt layer, indicated here by an over-etch step. One possible explanation for this effect was provided by Garra et al. who reported that roughening of the surface may be caused by random deposition of the aluminium mask on the polymer surface due to its sputtering and backscattering by the plasma [8]. The etch rates achieved were however lower than those reported in literature. The reasons for this discrepancy include limitations using a HCRIE and current masking methods. The latter possibly induces a mask shadow onto the smaller feature sizes. One possible way to reduce this effect might be to increase the energy, by increasing the power or reducing the pressure. However, the increase in temperature associated with high power damaged the PDMS surface and lowering the pressure resulted in lateral sidewall etch.

The XPS spectra showed the compositional changes that occurred after etching with SF₆ and O₂ gases. The unaltered PDMS surface contained 48.1 % C 1s, 27.9 % Si 2p and 24 % O 1s. The results showed that the etching process introduced S, F and Al on the surface. The presence of Al may be due to sputtering of the aluminium mask foil during etching. S and F are most likely attributed to the dissociation of SF₆ gas [13]. These contaminants were removed after an over etching process step and subsequent cleaning.

The chemical changes occurring on the surfaces can be described by the binding energy (BE) of the elements. The BE of silicon (Si 2p) when bonded to the polymer chain (C-Si-O) was 103.1 eV, which reduced to a lower chemical state of 99.3 eV after plasma exposure and increased to 32 %. There were two chemical states of C 1s at 285.2 eV and 280.6 eV for unaltered and plasma exposed PDMS, respectively. The carbon content lowered significantly from 48.1 % in unaltered PDMS to 12.9 % after plasma exposure, indicating that the oxygen radicals were reacting with the methyl group. After the etching process, the exposure of the Pt contact was confirmed by the presence of Pt4f with the same atomic % as pure Pt. The composition of the cleaned (etched) Pt surface did not show any contamination, indicated by the stable BE for carbon.

AFM provided a 3D image of Pt surface in the nanoscale resolution to visualise the transformation of the surface during the etching process. The surface roughness (Ra) of the Pt surface decreased by approximately 26 nm after reactive ion etching. As Pt is inert, the flattening of the surface was most likely due to high energy ion bombardment at high power and pressure, breaking the binding energy of the platinum surface. Further testing would be required to measure the thickness of the platinum to verify that the sputtering had not removed layers of material.

Micro-scale features were successfully etched through PDMS, without irregular roughening of the underlying Pt. There was no carbon contamination on the surface of exposed area. Feature sizes below 500 µm in diameter were easily etched in PDMS and showed good sidewalls. The anisotropy may be improved with better masking methods and etching tools such as an ICP reactor, which has been

shown to produce significantly higher etch rates and vertical etch walls than those achieved in conventional RIE tools [11].

The experimental results recorded are in agreement with theoretical etching mechanisms. In comparison with the exposure method currently used, RIE shows promising results [3].

Future work to determine the suitability of this process for neural applications will focus on investigating the *in vitro* cytotoxicity of the exposed area and electrochemical characterization of the modified Pt surface.

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