Poly(dimethylsiloxane) Based Micro- and Nanofluidic Device Fabrication for Electrophoresis Applications

DISSERTATION

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By

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Abstract

Poly(dimethylsiloxane) (PDMS) is one of the most widely used polymers in microfluidic device applications due to its low cost of fabrication and its physical and chemical properties. With soft lithography being the standard technique used in fabrication of PDMS microfluidic devices, this study proposed an alternative plasma etching process to fabricate microfluidic devices in PDMS. PDMS, which is a silicon-based polymer, requires a fluorocarbon plasma to etch the Si-O backbones and an O₂ plasma to etch the organic part. Plasma etching was performed in a Lam AutoEtch 590 plasma etcher and SPR 220-7 photoresist was used as a protective mask. The O₂/CF₄ compositions were varied to obtain an optimized etch rate and etch profile. It was found that 20 sccm of O₂ and 40 sccm of CF₄, at 2.8 Torr, 450 W and 0.38 gap spacing results in the fastest etch rate and anisotropic etching of microfluidic patterns into PDMS on a Si wafer. The etched surface was found to be smooth with a surface roughness, R_{RMS} less than 1 nm. For a PDMS microfluidic device on a Pyrex 7740 borosilicate glass wafer, the plasma etch rate was much slower and the R_{RMS} of the etched PDMS surface was 18.433 nm.

The fabrication of a PDMS nanofluidic device was also studied. The nanochannel structure in PDMS was fabricated on both Si and Pyrex wafers using the sacrificial layer lithography (SLL) technique. The microfeatures on the PDMS surface were created by
microtransfer molding from a master SU-8 2005 wafer. A Ti sacrificial layer was
deposited via e-beam evaporation on one side of the PDMS microfeatures using a self-
shadowing technique. The second PDMS layer was spin coated on top and patterned with
SPR 220-7 to function as a protective mask when etching in O$_2$/CF$_4$ plasma to create
reservoirs and expose the Ti layer. The Ti metal was subsequently removed in HCl
solution, leaving a nano space in the PDMS structure.

An integrated micro- and nanofluidic device in PDMS was fabricated on a Pyrex
wafer with the fabrication process adapted from the PDMS nanofluidic fabrication on
Pyrex wafer. Cracks were found on the etched surface, although the $R_{\text{RMS}}$ was 9.510 nm,
smaller than that of the PDMS microfluidic device fabricated on a Pyrex wafer.
Dedicated to my mother
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Chapter 1

Introduction

1.1 Background

Electrophoresis is a technique involving separation of charged particles and molecules by the influence of an electric field. Tiselius was the first person to perform electrophoretic separation of serum in free solution [Oda and Landers, 1997; Tiselius, 1937]. With his separation column cross section of millimeter scale, Tiselius acknowledged the need to reduce the size of the separation column in order to improve the separation resolution. With electrophoresis performed in borosilicate capillaries of micron-scale dimensions, higher separation resolution could be achieved [Jorgenson and Lukacs, 1983]. Capillary electrophoresis (CE) offers advantages over traditional electrophoretic separation. The increase of surface-to-volume ratio helps dissipate Joule heating more effectively. CE also has the advantage of reduced reagent volume, faster run time, portability, low cost and low power consumption [Sia and Whitesides, 2003].

With the well-developed field of microelectromechanical systems (MEMS) that uses techniques from semiconductor industry, microfluidic devices have been fabricated for biological and chemical applications, including electrophoretic separations [Harrison et al., 1993; Jacobson et al., 1994]. Traditionally, microfluidic devices are made of silicon (Si) and glass since the fabrication processes are well-developed but the techniques used are expensive and time consuming [McDonald and
Whitesides, 2002]. Polymers have also used to fabricate microfluidic devices. They include, but are not limited to, Polyethylene terephthalate glycol (PETG) [Henry et al., 2002], polymethyl methacrylate (PMMA) [Brister and Weston, 2006], and poly(dimethylsiloxane) (PDMS) [Gawron et al., 2001]. PDMS, in particular, has been increasingly used as an alternative for microfluidic device fabrication because of the quick and cost-effective fabrication procedure using the soft lithography technique [Xia and Whitesides, 1998]. PDMS was first used by the Effenhauser group for microfluidic device fabrication in DNA fragments separation [Effenhauser et al., 1995].

1.2 PDMS properties

The chemical formula of PDMS is CH$_3$(SiOCH$_3$)$_n$CH$_3$. Some of the chemical and physical properties of PDMS that make it well-suited for microfluidic capillary electrophoresis applications are listed in McDonald (2002). Basically, it is optically transparent in the UV-visible light range, making it compatible with many optical detection methods. It is also biocompatible, inert and impermeable to liquid water. There are, however, some disadvantages of PDMS. It is hydrophobic, which makes it difficult to fill a small channel with liquid water, and it tends to adsorb hydrophobic molecules [McDonald, 2000]. Another issue with PDMS is its low thermal conductivity [Erickson, 2003]. The heat generated during electrophoretic separation could build up inside the channel, causing band broadening and lower resolution [Weinberger, 2000].
Xia and Whitesides (1998) described three possible structural deformations of PDMS replica molding (Figure 1.1). First, if the aspect ratio of structures is too high, the adjacent structures could collapse and merge (a). Second, if the aspect ratio is too low, the roof structure could collapse or sag (b). Lastly, the swelling and shrinking property of PDMS may result in size different from the original master (c).

![Figure 1.1 PDMS molding structural deformations](image)

1.3 PDMS microfluidic device fabrication

1.3.1 Soft lithography technique

The most commonly used soft lithography technique for fabricating PDMS microfluidic devices is replica molding. The process is illustrated in Figure 1.2. The master can be made using photolithography with negative or positive tone photoresists, or a micromilling process. A mixture of 10:1 base and curing agent is poured on top of a master microfluidic structure and cured either by baking in an oven
or leaving at room temperature. Once the PDMS is cured, the negative replica structure is peeled off the master and placed on substrates such as a glass slide or a Si substrate by way of either reversible or irreversible bonding to create the microfluidic structure embedded in PDMS. The reservoirs can be created either by placing posts on the master before casting PDMS or punching holes in the cured PDMS structure.

![UV exposure of SU-8 photoresist coated Si substrate](image1.png)

![Patterned SU-8 photoresist on Si substrate](image2.png)

![Casting of base/curing agent mixture and cure](image3.png)

![PDMS with reservoirs and channel patterns](image4.png)

Figure 1.2 Soft lithography PDMS microfluidic fabrication process.

1.3.2 Other techniques

Besides the soft lithography technique, alternatives to creating microfluidic patterns in PDMS structures wet and dry etching. The Takayama group (2001) used a multiphase laminar flow technique to carry tetrabutylammonium fluoride (TBAF) etchant in N-Methylpyrrolidinone (NMP) solvent (3:1 (v/v) NMP:TBAF) in and out of a PDMS flat slab using molded PDMS as guided capillaries. The experimental setting and etched profile is shown in Figure 1.3. Both the molded capillary and slab PDMSs were etched and showed the same etched profiles.
Garra et al. (2002) also used 3:1 (v/v) NMP:TBAF solution for PDMS etching. The etching was done by immersing PDMS in the etchant solution and a thin aluminum (Al) layer was used as a protecting mask on PDMS. The authors cited the isotropic etching results and failure of Al as a protecting mask.

Vlachopoulou et al. (2005) demonstrated using a plasma etching technique in an inductively coupled plasma (ICP) tool for fabricating PDMS microfluidic devices. The authors used sulfur hexafluoride (SF$_6$) as the etch gas and Al as the protecting mask. They reported a 2 µm etch depth in 3 min but did not mention the topology of the etched surface. The follow-up publication by the authors at the same conditions
showed a rough etched PDMS surface with surface roughness of 133 nm after 2 min of etching [Tserepi et al., 2006].

1.4 PDMS surface modification

The hydrophobic property of PDMS could cause serious problems for CE applications. Hydrophobic molecules could be adsorbed on to the surface of PDMS and consequently hinder separation detection. There will also be a problem filling a microfluidic device with aqueous solutions. There are several methods to modify PDMS hydrophobicity that can be grouped into two main strategies: physical and chemical approaches [Wong and Ho, 2009].

1.4.1 PDMS surface activation

Prior to surface modification, the PDMS surface needs to be activated to create silanol (Si-OH) functional groups as depicted in Figure 1.4.

Figure 1.4 Plasma surface oxidation on PDMS surface [Slentz et al., 2002]
Various techniques have been reported for PDMS surface activation, including exposure to oxygen (O$_2$) plasma [Hillborg et al., 2000], air plasma [Hong et al., 2006], corona plasma [Makamba et al., 2003] and UV and/or ozone plasma [Holgerson et al., 2005]. Studies have reported up to tens of nanometer thickness of SiO$_x$ forming at the surface of PDMS [Holgerson et al., 2005; Vickers et al., 2006]. Although surface modification by these methods offers an easy and quick route to rendering PDMS hydrophilic, the hydrophobicity recovers within an hour after surface treatment [McDonald et al., 2000; Ren et al., 2001]. It is hypothesized that hydrophobic recovery is due to the migration of uncrosslinked low molecular weight (LMW) chains from the bulk material to the surface [Kim et al., 2000]. Figure 1.5 illustrates the migration of uncrossed low molecular weight chains to the plasma treated PDMS surface.

![Diagram showing different layers of PDMS after O2 plasma treatment. LMW chains migrate to top surface through cracks in silica-like layer [Kim et al., 2000].](image)

Submerging treated PDMS in water can prolong the hydrophilic property [Sia and Whitesides, 2003]. Eddington et al. (2006) reported longer lasting hydrophilicity
of PDMS upon exposing to an O₂ plasma by thermal aging of the material prior to O₂ plasma exposure and found that PDMS could retain the hydrophilic property for 14 days when kept in an ambient environment. Vickers et al. (2006) reported a two-step extraction/oxidation process to produce a long-term stabilized hydrophilic PDMS surface. The PDMS substrate was submerged in a series of organic solvents to cause PDMS to swell and remove LMW chains, resulting in weight reduction of about 5% in PDMS. The treated PDMS was later oxidized with an air plasma and the PDMS surface hydrophilicity was found to be stable in an air environment for 7 days.

1.4.2 Physical approach

PDMS physical surface modification techniques use hydrophobic or electrostatic interactions between the PDMS surface and adsorbed molecules. Surface modification of PDMS by physical means is accomplished by incubating PDMS in surfactant solutions. Lenz et al. (2004) patterned PDMS surfaces with lipid bilayers and observed the dependence of phospholipid adsorption on the degree of PDMS surface plasma oxidation as illustrated in Figure 1.6. Lee and Vörös (2005) demonstrated grafting poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG) copolymer on O₂ plasma oxidized PDMS via the electrostatic interaction between the negatively charged PDMS surface and the positive charges on polycationic PLL. The modified surface was shown to be resistant to protein adsorption on the surface.
1.4.3 Chemical approach

Although physical approaches to PDMS surface modifications are simple, the modified PDMS surfaces tend to be less stable due to weak interactions. A chemical approach offers a stronger interaction via covalent bonding. Hu et al. (2002) used a graft polymerization technique to covalently bond acrylic acid (AA), acrylamide (AM), dimethylacrylamide (DMA), 2-hydroxylethyl acrylate (HEA), and poly(ethylene glycol)-monomethoxylacrylate (PEG). While immersed in monomer solution, the PDMS surface was activated by UV radiation, generating radicals on the PDMS surface. Miyaki et al. (2007) immobilized Poly (L-glutamic acid) (PGA) on a PDMS surface via amide bonding with aminopropylmethylethoxysilane (APDMES) which was silanized to the oxidized surface. Bhushan et al. (2006) used a vapor phase
deposition technique to modify PDMS surfaces. The PDMS surface was first activated under O_2 plasma. The surface was later silanized with vaporized fluorosilanes under vacuum conditions.

1.5 Nanofluidics as electrophoresis application

Nanofluidics is defined as the transport process that occurs within systems having at least one dimension of 1-100 nm [Prakash et al., 2008]. Enabled by recent developments in nanofabrication techniques, there have been experiments studying molecular transport and biomolecular separation using nanofluidic devices. The noted benefits are small sample volume, low driving voltage, and the short time and distance needed for separation performance [Yuan et al., 2007]. The interaction between molecules of interest and the nanofluidic channel walls is significantly stronger than that of a microfluidic system since the surface to volume ratio is increased drastically.

There have been a number of recent studies about electrophoresis phenomena in nanochannels. Garcia et al. (2005) fabricated arrays of nanochannels with widths varying from 35 to 200 nm on Si wafers using standard semiconductor manufacturing techniques and integrated them with microfluidic channels to separate neutral dyes from negatively charged dyes. The group reported that the velocity of negatively charged dyes is faster than neutral dyes due to a repulsive interaction between negatively charged dyes and negatively charged walls that forces dyes to the center of the channels while the neutral dyes are adsorbed on the channel walls. Han and Craighead (2000) fabricated entropic traps consisting of micro- and nanochannels on
a Si substrate, as illustrated in Figure 1.7, to separate DNA strands of two different length via an applied electric field. The authors found that the longer DNA strands are mobilized faster than the shorter ones through the traps. They hypothesized that the longer DNA molecules have a larger surface area in contact with the boundary and therefore have a higher probability of escaping the traps.

Figure 1.7 Schematic setting of DNA separation device [Han and Craigshead, 2000].

1.6 PDMS nanofluidic fabrication reviews

Although the pattern transfer molding technique is widely used for creating microfluidic devices in PDMS, the nanochannels fabricated from the soft lithography technique pose some challenges to channel structural integrity. Moa (2005) found that horizontal PDMS nanochannels molded from masters of height smaller than 100 nm with a 3 µm width suffers from structural collapse due to the softness of PDMS. The
features are also subject to rounding of sharp corners via deformation by surface tension [Odom et al., 2002]. Schmid and Michel (2000) developed a different siloxane polymer that has higher stiffness and could transfer patterns up to 80 nm.

There are also alterations to microtransfer molding in fabricating PDMS nanochannels. Chung et al. (2008) created wrinkle nanochannels (WNCs) on a PDMS surface by exposing the stretched PDMS surface to O$_2$ plasma. Upon releasing the prestretched surface, nano scale wrinkles are formed. The wrinkled surface is bonded with another PDMS surface, forming nanochannels in the PDMS structure. The schematic drawing of the wrinkles fabrication process is shown in Figure 1.8.

![Figure 1.8 Wrinkles formation process on PDMS surface [Chung et al., 2008].](image)

With this technique, the authors could produce WNCs with smallest dimensions of 50 nm. Park et al. (2009) used controlled collapsing technique to create nanochannels as small as 60 nm in PDMS structures. The PDMS was molded from thin photoresists or a metal layer and later bonded with another substrate. The nanochannel was created
from the collapsing of a PDMS layer to the other flat substrate, as illustrated in Figure 1.9.

![Diagram of PDMS nanochannel fabrication](image)

Figure 1.9 Roof collapse technique in PDMS nanochannel fabrication [Park et al., 2009].

1.7 Thesis objectives

The purpose of this thesis is to use novel techniques to fabricate micro- and nanofluidic devices in PDMS for electrophoresis applications. In microfluidic device fabrication, this thesis explores plasma etching as an approach to fabricating smooth and anisotropic etched PDMS. For the fabrication of nanochannels, sacrificial layer lithography (SLL) is used to create controllable vertical arrays of nanochannels in PDMS structures. The integrated micro- and nanofluidic device fabrication adapts the nanofluidic fabrication process for creating an integrated device in PDMS. The fabricated devices are characterized and tested for applicability to electrophoresis.
1.8 Thesis outline

This thesis focuses on the fabrication and characterization of PDMS micro- and nanofluidic devices. Chapter 2 discusses the basic physics of electrokinetics in micro- and nanochannels. Chapters 3, 4 and 5 focus on fabrication and characterization of microfluidic, nanofluidic and an integrated micro- and nanofluidic PDMS devices, respectively. The final chapter concludes with remarks and suggestions on future work on the device fabrication as well as applications.
Chapter 2

Electrokinetic Phenomena in Electrophoresis

2.1 Electric double layer

Substrates normally acquire surface charge when in contact with an aqueous solution [Everett, 1988]. Some charge acquiring mechanisms include ionization of surface functional groups, ion adsorption, and ion dissolution of surfaces [Everett, 1988; Masliyah and Bhattacharjee, 2006]. Counterions are attracted to the charged surface while coions are repelled from the surface. Far away from the surface,
electrical neutrality is reached. The Electric Double Layer (EDL) consists of a layer of charge at the surface and a region of counterions near the surface. Suppose the capillary wall is positively charged, then negative ions in electrolyte solution are attracted to the surface while positive ions are repelled. The first layer of negative ions next to the positively charged surface form a rigid layer called Stern layer. A potential at this plane, which is the shear surface between immobile charged surface and moving electrolyte, is called zeta ($\zeta$) potential. Further away from Stern layer, there is a diffuse layer where ions obey the Boltzmann distribution [Probstein, 1989] until they feel no effect of the charged surface. The EDL hence consist of two layers, the Stern layer and the diffuse layer. The approximate thickness of the EDL is the distance at which the potential drops to 1/e of the initial wall potential, and is called the Debye length, $\lambda_D$, which is defined as [Baldessari and Santiago, 2006]

$$\lambda_D = \left( \frac{\varepsilon k_B T}{e^2 \sum_i z_i^2 n_i} \right)^{1/2}$$ (2.1)

where $\varepsilon$ is the permittivity of the medium, $k_B$ is Boltzmann’s constant, $T$ is temperature, $e$ is the elementary charge, $z_i$ and $n_i$ refer to valency and number density of charge component in electrolyte, respectively. Debye length varies from order of 1 nm for moderately dilute electrolyte to several hundred nanometers for an extremely dilute electrolyte [Conlisk, 2005]. Far away from the wall, ($y \gg \lambda_D$, $y$ being distance away from the wall), the electrical neutrality of the solution is valid. In the case where EDL thickness is large or the channel dimension is comparable with the EDL thickness the electrical neutrality need not be preserved [Conlisk, 2005]. Figure 2.2 shows the cases where (a) the EDL is thin compared to channel dimension and (b) EDL is of the same order as channel dimension.
Figure 2.2 Schematic drawing of case where (a) channel dimension is larger than EDL thickness and (b) the channel dimension is in the same order as EDL thickness [Conlisk, 2005].

2.2 Electroosmosis

Potential distribution in EDL can be obtained by Poisson-Boltzmann equation,

\[
\nabla^2 \psi = -\frac{1}{\varepsilon} \sum_i e z_i n_i \exp \left( \frac{-e z_i \psi}{k_B T} \right) \tag{2.2}
\]

For the case where \( e \psi \ll k_B T \) or Debye-Huckel approximation, equation (2.2) reduces to

\[
\nabla^2 \psi = \frac{\psi}{\lambda_D^2} \tag{2.3}
\]

If an electric field is applied parallel to a charged surface in contact with liquid, the field exerts force on mobile ions in the diffusion layer. The migration of charged mobile ions will drag along solvent with them, causing movement of
solution. Under the applied electrical field strength $E$ and assuming no pressure gradient, the fluid is moving with electroosmotic velocity $u_{eo}$,

$$u_{eo} = -\frac{\varepsilon \zeta E}{\eta} \left(1 - \frac{\psi}{\zeta}\right)$$  \hspace{1cm} (2.4)$$

where $\eta$ is the viscosity of the fluid. For channel with dimension much larger than $\lambda_D$, the velocity of the fluid far away from the channel wall ($\psi \to 0$) is reduced to

$$u_{eo} = -\frac{\varepsilon \zeta E}{\eta}$$  \hspace{1cm} (2.5)$$

Figure 2.3 electroosmotic velocity profile when (a) $h = 10\lambda_D$ and (b) $h = \lambda_D$ [Yuan et al., 2007]

In the case of a microchannel where EDL is small compared to channel dimension, the fluid moves in a plug flow fashion. As for the case of nanochannel where channel dimension is in the same order as EDL, the velocity profile no longer flows as a plug but follows the profile of potential distribution in the channel. Figure 2.3 shows the electroosmotic velocity distribution in the cases that (a) channel dimension ($h$) is ten times larger than $\lambda_D$ and (b) where channel dimension equals $\lambda_D$. 

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2.3 Electrophoresis

Electrophoresis is the induced motion of charged molecules in aqueous solution that results from the application of an electrical field [Devasenathipathy and Santiago, 2005]. Charged molecules are screened by electrolytes in aqueous solution hence forming an EDL to cover the molecules. When the electric field is applied, the molecules and counterions in the EDL are moving in the opposite directions. So the electrophoretic velocity, $u_{ep}$, of a molecule depends on the thickness of the EDL which could be categorized as a thick or thin EDL compared with the size of a charged molecule [Schoch et al., 2008].

First, the case where EDL is thin compared with molecular size. The $u_{ep}$ is given by

$$u_{ep} = \frac{\varepsilon \zeta E}{\eta}$$  \hspace{1cm} (2.6)

In the case where EDL is thick compared with molecular dimension, the electric force acting on molecule is balanced by drag force, leading to

$$u_{ep} = \frac{qE}{6\pi \eta r}$$  \hspace{1cm} (2.7)

where $q$ is the effective net charge and $r$ is hydrodynamic radius of the molecule [Prichett and Robey, 1997].

The apparent mobility $\mu$, velocity per applied electrical field strength, results from the addition of electroosmotic and electrophoretic mobility on the charged molecule,

$$\mu = \mu_{eo} + \mu_{ep}$$  \hspace{1cm} (2.8)
Both anionic and cationic electrolytes will migrate in the same direction when electroosmotic flow outweighs electrophoretic velocity of the electrolytes [Kirby and Hasselbrink, 2004].

2.4 Reviews of flow characterization on surface modified PDMS microfluidics

There are numbers of publications regarding fluid flow characterization for PDMS with different surface treatment conditions. Spehar et al. (2003) reported native PDMS EOF mobility of $2.3 \times 10^{-4}$ cm$^2$/Vs when performed in 100 mM $N$-(2-acetamido)-2 aminoethanesulfonic acid (ACES) at pH 9. Ren et al. (2001) reported an electroosmotic flow (EOF) mobility of $1.1 \times 10^{-4}$ cm$^2$/Vs of native a PDMS microfluidic device while an oxidized PDMS device had almost four times greater mobility. The experiment was performed with 10 and 20 mM phosphate buffers at pH 7. Lee et al. (2005) found the EOF mobility of atmospheric plasma treated PDMS, when kept in deionized (DI) water, were decreased from $2.5 \times 10^{-4}$ cm$^2$/Vs 30 min after plasma treatment to $3.5 \times 10^{-5}$ cm$^2$/Vs 48 hr after the plasma treatment. As for the plasma treated PDMS that was kept in air environment, the EOF mobility decreased ten folds from $2.5 \times 10^{-4}$ cm$^2$/Vs after 48 hr. Liu et al. (2000) found that PDMS dynamic coated with cationic polymer polybrene (PB) had a reverse mobility of -4.29 to -1.95 $\times 10^{-4}$ cm$^2$/Vs when performed in pH 3-10 phosphate buffer. Luo et al. (2006 a) doped PDMS prepolymer with 0.5 wt % undecylenic acid (UDA) prior to curing process and found the EOF to be $7.6 \times 10^{-4}$ cm$^2$/Vs, two folds increased from native PDMS when performing in 19 and 20 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer, pH 8.5. Roman et al. (2005) put PDMS microfluidic device in heated solution containing ethylamine, resulting in
Silicon dioxide (SiO$_2$) particles formation on sidewall. The modified device showed EOF mobility of $8.3 \times 10^{-4}$ cm$^2$/Vs, two times higher than that of native PDMS device. The experiment was performed in 1mM sodium phosphate (Na$_2$HPO$_4$)/ 9 mM potassium chloride (KCl) buffer at pH 8.5.

2.5 Effect of surface roughness on EOF performance

In a microfluidic channel, the surface roughness becomes more important when the channel size is getting smaller. There are some recent studies regarding the effect of surface roughness to microfluidic device EOF performance. Most of the studies investigated the roughness effect using computer simulation. Hu et al. (2003) used rectangular prism as a representation of a surface roughness and found that the rough surface increases the flow inside a microchannel. Kleinstreuer and Koo (2004) used a porous medium layer (PML) model for a rough surface and found the roughness affect the friction factor hence reducing the EOF. Schrott et al. (2009) studied the surface properties of albumin coated PDMS and implied that the albumin coating of the PDMS surface increases resistant to EOF and the coated albumin shielded the charged surface.
3.1 Introduction

There have been a handful of studies using plasma to etch the PDMS layers either to create structures in PDMS or just to remove the residual PDMS layer from a molding process. Several gases have been used in etching PDMS. Garra et al. (2002) proposed using a combination of tetrafluoromethane (CF$_4$) and O$_2$ to etch PDMS since it contains both siloxane bonds (Si-O) and methyl groups (-CH$_3$). The etching experiment was performed in an Oxford Plasma Technology µP 80 parallel plate reactor and the authors found that a 1:3 ratio of O$_2$ to CF$_4$ gives an anisotropic etch with the highest etch rate of 20 µm per hour. The etching was performed at 47 mTorr and power of 270 W. The etched surface, however, is very rough. To remove residual PDMS, Oh (2008) found that a 1:1 ratio of O$_2$ to CF$_4$ gives the highest PDMS etch rate of 1 µm/min when performed in a Trion Sirius RIE tool. The etching parameters were 100 W and 300 mTorr. The author also found that the higher the concentration of O$_2$, the rougher the etched PDMS surface. The Tserepi group argued that the O$_2$ plasma causes formation of a silica-like layer on the PDMS surface, which decreases the etch rate of the fluorine-containing plasma [Tserepi et al., 2003a, b]. Using a pure SF$_6$ plasma for PDMS etching in an inductively-coupled plasma (ICP) Micromachining Etch Tool, the Tserepi group reached almost 0.8 µm/min etch rate when operating at 10 mTorr, and 1900 W [Vlachopoulou et al., 2005].
Although none of the aforementioned experiments used the same plasma etching tools to perform the experiment, they all agreed on one observation. The etched PDMS surfaces were rough.

A Lam AutoEtch 590 plasma etcher has been used in the semiconductor industry to etch SiO\textsubscript{2} layers. The etcher is designed to reduce structural damage on the etched surface by reducing ion bombardment. Because PDMS has a similar structure to SiO\textsubscript{2}, this study explored the Lam 590 etcher as a tool for etching PDMS. In oxide etching, the fluorocarbon polymers generated from etch gases deposit and form a sidewall passervation film that protects sidewalls from being attacked by reactive neutral species.

3.2 Plasma etching mechanisms

Plasma etching has many advantages over traditional chemical etching including simplicity, more anisotropic etching and minimal hazardous waste products. The three plasma etching mechanisms: physical, chemical and ion enhanced.

3.2.1 Physical etching

In physical etching, energetic ionic species are accelerated by an electric field to bombard the substrate. The etched material is removed by means of sputtering, which is not selective between mask and substrate since the impacting energy is large compared to the surface bonding energies of mask and substrate [Madou, 2002]. Physical etching needs to be carried out at low pressure to ensure a long ion mean free path. The etch profile is anisotropic, but the etch rate is low. The surface damage and roughening due to
high energy ion bombardment can be problematic. The schematic drawing of physical etching is shown in Figure 3.1.

![Figure 3.1 Physical etching mechanism.](image)

3.2.2 Chemical etching

![Figure 3.2 Plasma chemical etching mechanism [Madou, 2002].](image)
The principle of chemical etching can be broken down into six steps as illustrated in Figure 3.2. The neutral reactive species are generated in plasma, so the role of plasma is just to supply the reactive species for etching. The reactive species diffuse, adsorb onto and react with the substrate surface. The reaction products desorb, and either diffuse back into the gas or plasma, or are evacuated. Since the etching process is purely chemical, the etched result is highly selective. However, reactive neutral species are adsorbed onto the surface at random angles, causing an isotropic etched profile.

3.2.3 Ion enhanced etching

Figure 3.3 depicts the Si etch rate when Xenon difluoride (XeF₂) gas and Argon ions (Ar⁺) were used as etchants. Only when the two are combined, does a significant etch rate prevail. The bombardment of inert ions damages and dangles surface bonding, enhancing the etch rate by chemical etching. By combining both mechanisms, the etch profile can be anisotropic and highly selective.

Figure 3.3 Ion enhanced etching mechanism [Coburn and Winters, 1979].
3.3 Materials and fabrication process

3.3.1 Microfluidic device design

A schematic drawing of a PDMS microfluidic device is shown in Figure 3.4. The microfluidic device consists of 100 µm wide channels, featuring double T junction for a plug formation when performing electrophoresis. Reservoirs 1, 2 and 3 have 5 mm diameter while reservoir 4 has 7 mm diameter. A separation section, connecting the T junction and reservoir 4, is 10 mm long. The distances from reservoir 1, 2, and 3 from double T junction are all 1.5 mm.

![Schematic drawing of a PDMS microfluidic device](a)

![Image of double T junction in the device](b)

Figure 3.4 Schematic illustration of microfluidic device (a) and image of double T junction in the device (b).

3.3.2 Materials

Si and Pyrex 7740 wafers (100 mm) were from University Wafer (South Boston, MA, USA). PDMS elastomer kit (Sylgard 184) was from Dow Corning (Midland, MI, USA). Toluene was purchased from Mallinckrodt Baker (Phillipsburg, NJ, USA). Syringe filters, 0.45 µm PTFE membranes were from Sigma-Aldrich (St. Louis, MO, USA). SPR 220-7 photoresist and MF-319 developer were both from MicroChem
3.3.3 PDMS microfluidic device fabrication

The process flow for the fabrication of a microfluidic device is shown in Figure 3.5. The process breaks down into several steps as follows:

Spin coating PDMS on substrate

SPR 220-7 coating, UV exposure, and developing

Plasma etching of PDMS using SPR 220-7 as mask

Removal of protective mask

Microfluidic device assembling

Figure 3.5 PDMS microfluidic device fabrication process flow.
PDMS substrate preparation

The PDMS base was mixed with the curing agent at a 10:1 weight ratio. The mixture was further diluted with toluene at 50% by weight. The solution was stirred using a vortex mixer (Fisher Scientific, Pittsburgh, PA, USA) to make sure the PDMS was fully dissolved. The PDMS solution was placed in a desiccator to remove air bubbles and this was followed by filtering with a PTFE 0.45-μm membrane filter to remove undissolved particles. The PDMS solution was then spin coated on a Si wafer using a Cost Effective Equipment (CEE) 100 CB spin coater (Brewer Science, Rolla, MO, USA). The spin coating was performed with the final spin speed of 1000 revolutions per minute (rpm) for 60 s with an acceleration of 500 rpm/s. The substrate was then cured in a Blue M 146 series convection oven with PRO-550 controller (Blue M Electric, Watertown, WI, USA) at 65º C for 2 hrs. After being cured, the substrate was cross-sectioned and investigated using a Hitachi S-3000H scanning electron microscope (SEM) (Hitachi, Tokyo, Japan).

Photolithography processing

Prior to casting with photoresist, the PDMS surface was activated with an O₂ plasma to promote surface adhesion using a Micro-RIE 800-II Reactive Ion Etcher (Technics, Concord, CA, USA). The operating recipe was 10 standard cubic centimeters per minute (sccm) of O₂, 100 W for 5 s. Positive photoresist SPR 220-7 was spin coated on the substrate with a final spin speed of 3000 rpm using the CEE spin coater. The substrate was then softbaked on an HS40 digital programmable stirring hotplate (Torrey Pines Scientific, San Marcos, CA, USA) at 90º C for 1 hr and ramped down to room temperature at 20º C/hr. The UV exposure of the photoresist was done on an Electronic
Visions (EV) Group 620 contact aligner (EV Group, Schärding, Austria) for two cycles of 8 s at 15 W/cm² with a 60 s time interval to render the microfluidic pattern on the SPR 220 layer. The substrate was held for 35 min and was processed with a post-exposure bake (PEB) using the same process as soft baking. The substrate was then developed in an MF-319 developer until the exposed areas were completely dissolved.

Plasma etching

The substrate was plasma etched to create the microfluidic structure in the PDMS using an AutoEtch 590 plasma etcher (Lam Research, Fremont, CA, USA). The Etch gases were a combination of O₂, CF₄ and/or He. After the etching was finished, the etched depth was measured with a Dektak3 surface profilometer (Sloan Technology, Santa Barbara, CA, USA). The SPR 220-7 photoresist mask was removed by dissolving it in acetone and rinsing with 2-propanol. The depth of the etched PDMS microfluidic structure was measured again with the profilometer. The etched structures were also investigated by SEM. The roughness of PDMS surfaces were measured with an MFP-3D-BIO Atomic Force Microscope (AFM) (Asylum Research, Santa Barbara, CA, USA). The root mean square (rms) surface roughness calculation was done using software provided with the AFM. The contact angle measurements were done by taking pictures of 2µm droplets of DI water on PDMS surfaces with a Nikon D90 camera. The contact angle measurement was carried out with GNU Image Manipulation Program (GIMP) version 2.6.6.
Microfluidic device assembling

A 5 mm thick slab of PDMS was made by mixing a 10:1 ratio of PDMS base and curing agent and pouring into a flat bottomed container. The mixture was put into a vacuum desiccator to remove trapped air and subsequently baked in the Blue M oven at 65° C for 2 hrs. Once the PDMS was cured, a piece of PDMS slightly bigger than the size of the microfluidic structure was cut from the slab. Holes were punched in the piece aligned with microfluidic reservoirs. Both the PDMS slab and the microfluidic PDMS structure surfaces were treated with an O₂ plasma using a reactive ion etcher with 40 sccm O₂ and 20 W for 30 s, and the two surfaces were consequently brought into contact, with the reservoirs and the punched holes aligned, for an irreversible seal. The device was kept in 1:1 (volume) 2- propanol and DI water until it was ready for the device testing.

3.4 Results and discussion

3.4.1 Spin coating

In designing this microfluidic device, the idea was to create a structure in a thin PDMS layer, so that any heat generated during electrophoresis would be dissipated quickly. With the final spin speed of 1000 rpm, the measured PDMS thickness using SEM was about 17 µm as shown in Figure 3.6.
3.4.2 Photoresist processing

The SPR 220-7 manufacturer recommends a softbaking process at 115° C on a hotplate. However, for a PDMS substrate, significant number of cracks was observed right after the substrate was removed from the hotplate. They were believed to have been created from a mismatch in coefficients of thermal between solidified SPR 220-7 photoresist and PDMS. The softbaking temperature was lowered to 90° C to avoid photoresist cracking, but cracking persisted. Finally, the programmable hotplate was used to slowly ramp the hotplate temperature down and the number of cracks was drastically reduced. The substrate was, however, still sensitive to any direct contact to its surface. Figure 3.7 shows cracks formed on the SPR 200-7 layer.
The ideal profile for photoresist to be used as a mask is to have a vertical sidewall. The UV exposure time was varied to optimize the sidewall profile of SPR 220-7 on PDMS. The optimum UV exposure time was found to be 16 s. The photoresist sidewall profile at 16 s UV exposure time is illustrated in Figure 3.8.
The operation mode had to be in proximity to prevent new cracks from forming. Another observed phenomenon was that after exposure to UV radiation, bubbles were created in the photoresist in the exposed area if the exposure was done continuously. The exposure had to be divided into cycles and alternated with a relaxation interval time to allow the photoresist to cool down before the next exposure. The image of the bubble area after being developed is shown in Figure 3.9.

![Bubble formed in UV exposure area of SPR 220-7.](image)

**Figure 3.9** Bubble formed in UV exposure area of SPR 220-7.

3.4.3. Plasma etching

The Lam AutoEcth 590 plasma etcher is a capacitively coupled plasma (CCP) etcher designed to operate at high pressure and narrow gap spacing between two electrodes to create high intensity plasma with low bias energy. There are several parameters involved in the Lam 590 plasma etching: operating pressure, radio frequency (RF) power, gap spacing, and gases flow rates. It is recommended for the Lam 590 etcher
to have an operating pressure of 2.8 Torr and a gap spacing of 0.38 cm in semiconductor processing [Williams and Muller, 1996] so this study kept the operating pressure and gap spacing fixed while varying RF power, O\textsubscript{2}:CF\textsubscript{4} ratio, and He on or off.

The etching experiment was first carried out by varying the O\textsubscript{2} and CF\textsubscript{4} ratio to find the conditions that give the highest PDMS etch rate and, at the same time, etch SPR 220-7 at an equal or lower rate. The experiments were done at 2.8 Torr, 700 W, 0.38 cm gap spacing and 5 cycles of a 1 min etch with 3 min interval time. Interval etching was chosen due to avoid exposing the substrate to plasma for a long time which result in high heat accumulation on a substrate that would cause the formation of stress and cracks. The 3 min interval was sufficient for the electrode to cool down to a base temperature before starting the next cycle. The etch results measured with a Dektak profilometer are given in Table 3.1.

At higher O\textsubscript{2} gas ratios, the photoresist etches faster than PDMS. The 30:120 ratio of O\textsubscript{2} to CF\textsubscript{4} gave to highest PDMS etch rate and etched PDMS faster than photoresist. The etcher has maximum flow rates of 50 sccm for O\textsubscript{2} and 200 sccm for CF\textsubscript{4}.

Upon further investigation with the SEM, the sidewall profiles of 1:4 O\textsubscript{2} to CF\textsubscript{4} showed the closest to being vertical as compared with other conditions. The SEM images of sidewall profiles of varied O\textsubscript{2}:CF\textsubscript{4} conditions after photoresist removal are shown in Figure 3.10.
Table 3.1 Etch rate of PDMS and SPR 220-7 with varying O₂ and CF₄ flow rate ratio.

<table>
<thead>
<tr>
<th>O₂:CF₄ and actual flow rates (sccm)</th>
<th>PDMS etch rate (µm/min)</th>
<th>SPR 220-7 etch rate (µm/min)</th>
<th>PDMS:SPR 220-7 etch rate ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30:60</td>
<td>0.712</td>
<td>1.212</td>
<td>0.587</td>
</tr>
<tr>
<td>50:100</td>
<td>0.938</td>
<td>2.090</td>
<td>0.449</td>
</tr>
<tr>
<td>1:3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30:90</td>
<td>0.728</td>
<td>0.808</td>
<td>0.901</td>
</tr>
<tr>
<td>50:150</td>
<td>0.734</td>
<td>0.974</td>
<td>0.753</td>
</tr>
<tr>
<td>1:4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30:120</td>
<td>0.772</td>
<td>0.692</td>
<td>1.116</td>
</tr>
<tr>
<td>50:200</td>
<td>0.678</td>
<td>0.818</td>
<td>0.829</td>
</tr>
<tr>
<td>1:5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30:150</td>
<td>0.658</td>
<td>0.498</td>
<td>1.321</td>
</tr>
</tbody>
</table>
Figure 3.10 Sidewall profile of etched PDMS at (a) 30:60, (b) 30:90, (c) 30:120, and (d) 30:150 sccm of gas mixture O$_2$:CF$_4$ condition.

The etched surfaces of all etch conditions except for 1 O$_2$: 5 CF$_4$ ratio investigated by the SEM also showed smooth etched surface area. Figure 3.11 shows the etched surface of conditions shown in Figure 3.10.
The cracks formed during the photolithography process and some during UV exposure pose a challenge in using SPR 220-7 photoresist as a mask. Figure 3.12 shows etched PDMS in the cracked area. It was observed that there were more cracks created during plasma etching even though cycle etching was used to prevent new cracks from being created.
Figure 3.12 Etched PDMS structure created by cracks formed during the photoresist process (a) with SPR 220-7 mask and (b) after mask removal.

Figure 3.13 Etch rate of PDMS and SPR 220-7 as function of added He gas.

The next experimental step was to determine the effect of adding He to the gas mixture. He is a nonreactive gas that is added to stabilize, dilute etchants, and improve heat transfer in a plasma [Madou, 2002]. Variable flow rate of He gas was added to a
fixed mixture of 30 sccm O₂ and 120 sccm CF₄ and the etch rate results of PDMS and SPR 220-7 are shown in Figure 3.13. The other etch conditions were kept the same as previous experimental set up. It was observed that even though the added He gas slowed the etch rates of both PDMS and SPR 220-7, it helped improve the etching selectivity of PDMS.

When the 30 sccm O₂ and 120 sccm CF₄ mixture was used to etch the substrate for a longer period, the sidewall profile of PDMS showed a two-slope feature, as shown in Figure 3.14.

![Figure 3.14 Side-wall profile of PDMS when etched for 6 cycles of 1:30 min.](image)

Further investigation showed that the double slope sidewall arose from the fact that the profile of SPR 220-7 itself was not perfectly straight and vertical. The corner of SPR 220-7 mask was etched faster than the rest of the mask and was eventually worn off. The profile of both PDMS and SPR 220-7 after being etched at 700 W for 10 cycles of 45 s is shown in Figure 3.15.
Figure 3.15 Cross section of PDMS-SPR 220-7 structure after etched for 10 cycle of 45 s at 700 W.

To solve the double-slope sidewall problem, a lower RF power was chosen so the photoresist would be etched at slower rate [Williams and Muller, 1996]. The plasma RF generating power was set at 450 W and the resulting sidewall profiles are shown in Figure 3.16. The etching was performed in 10 cycles of 45 s each. The etch rate of PDMS was 0.661 µm/min while that of SPR 220-7 was 0.952 µm/min.

Although lowering the plasma RF generating power resulted in a faster etch rate of SPR 220-7, the erosion of the photoresist was reduced hence improving the sidewall profile of the etched PDMS.
Next, at 450 W, the \( \text{O}_2 : 4 \text{ CF}_4 \) ratio, was further explored to find the optimal actual flow rate ratio. As observed in previous section, the more \( \text{O}_2 \) present in the plasma, the lower the PDMS etching selectivity. The gas mixtures used were 10:40 and 20:80 sccm of \( \text{O}_2 : \text{CF}_4 \). The etch recipes were 10 cycles of 1 min each. Figure 3.17 shows the resulting profiles of etched PDMS. The etch rates were measured with a Dektak3 profilometer and the results are shown in Table 3.2.
Figure 3.17 Etched PDMS profile at gas mixture of (a) 10 sccm $O_2$: 40 sccm $CF_4$ and (b) 20 sccm $O_2$: 80 sccm $CF_4$.

Table 3.2 Etch rate of PDMS and SPR 220-7 of 1 $O_2$: 4 $CF_4$ ratio at 450 W.

<table>
<thead>
<tr>
<th>1 $O_2$:4 $CF_4$ (sccm)</th>
<th>PDMS etch rate ($\mu$m/min)</th>
<th>SPR 220-7 etch rate ($\mu$m/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:40</td>
<td>0.586</td>
<td>0.416</td>
</tr>
<tr>
<td>20:80</td>
<td>0.775</td>
<td>0.945</td>
</tr>
</tbody>
</table>

The 20 sccm $O_2$: 80 sccm $CF_4$ gives the highest PDMS etch rate, although it etches SPR 220-7 at faster rate. Since the thickness of SPR 220-7 is around 11 µm, and the targeted etched PDMS is around 7-8 µm, there will be sufficient photoresist left after etching the PDMS to the desired depth.
The effect of etch time on PDMS etch rate was also studied. At 20 sccm O₂: 80 sccm CF₄ gas mixture and 450 W RF power, 6 cycles of different etch times were used and the resulting PDMS etch rates are shown in Table 3.3.

Table 3.3 PDMS etch rate at different etch time.

<table>
<thead>
<tr>
<th>Etch time</th>
<th>PDMS etch rate (µm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 cycles of 1:00 min</td>
<td>0.683</td>
</tr>
<tr>
<td>6 cycles of 1:10 min</td>
<td>0.644</td>
</tr>
<tr>
<td>6 cycles of 1:20 min</td>
<td>0.750</td>
</tr>
<tr>
<td>6 cycles of 1:30 min</td>
<td>0.738</td>
</tr>
</tbody>
</table>

The study also conducted one continuous etching of 8 min with the other parameters set the same as in the earlier experiment. The PDMS etch rate was 0.752 µm/min. Surprisingly, it was found that cracks appeared to be formed in much smaller numbers after etching and further SEM investigation found that etching through crack areas did not appear as extensively etched as for cycle etching. Figure 3.18 shows etched PDMS in a cracked SPR 220-7 area next to microfluidic structure.

The proposed explanation is that doing cycle etching promotes further crack formation in SPR 220-7 due to repeated swelling and contracting of the PDMS structure underneath causing stress in the SPR 220-7 layer. In doing single cycle etching, the
existing cracks were sealed as the PDMS expanded due to heat generated during the etch process.

![Image](image.png)

Figure 3.18 Etched PDMS in crack area formed in SPR 220-7 layer.

3.4.4 PDMS etched surface characterizations

The etched surfaces were characterized for surface roughness using an AFM over a 5x5\(\mu\text{m}^2\) area. The surface roughness was compared with a reference PDMS surface. The Image of the reference PDMS surface topology is shown in Figure 3.19. The AFM imaging was done in a tapping mode with a NSC15/AIBS probe (MikroMasch, San Jose, CA, USA). The surface of etched PDMS at 20 sccm O\(_2\), 80 sccm CF\(_4\), 450 W, 0.38 cm gap spacing and 8 min etching is shown in Figure 3.20.

After etching the PDMS, the area protected by the photoresist mask during plasma etching was exposed to O\(_2\) plasma in the bench top RIE to activate the surface prior to bonding with another PDMS surface to assemble the device. The O\(_2\) plasma surface activation recipe was 40 sccm O\(_2\), 20 W for 30 s.
Figure 3.19 AFM surface topology of untreated PDMS.

Figure 3.20 AFM surface topology of etched PDMS.
This recipe was based on the Bhattacharya et al. (2005) studies on effects of plasma treatment on a PDMS. The image of an etched PDMS surface after O$_2$ plasma treatment is shown in Figure 3.21. The surface roughness (root mean squared, R$_{RMS}$) measurements calculated by the AFM software are illustrated in Table 3.4.

![AFM surface topology of etched PDMS and O$_2$ plasma treatment.](image)

**Table 3.4 Surface roughness measurements of PDMS surfaces.**

<table>
<thead>
<tr>
<th>Condition</th>
<th>Surface roughness, R$_{RMS}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>0.273</td>
</tr>
<tr>
<td>O$_2$:CF$_4$ etching</td>
<td>0.914</td>
</tr>
<tr>
<td>O$_2$:CF$_4$ etching and O$_2$ treatment</td>
<td>1.093</td>
</tr>
</tbody>
</table>
Figure 3.22 A DI water droplet on PDMS of (a) native surface, (b) O$_2$/CF$_4$ plasma etched surface, and (c) the etched surface after O$_2$ plasma treatment.
Images of the PDMS surfaces of different treatment conditions were also taken for contact angle measurement. Figure 3.22 shows images of a 2µm DI water droplet on (a) a native PDMS surface, (b) an O₂/CF₄ plasma etched PDMS microfluidic device and (c) the etched device with further O₂ plasma treatment. As for (b) and (c), the images were taken within 15 min after conditioning the PDMS surfaces.

For the PDMS microfluidic device testing, the fluorescence microscopy was chosen as a detection tool for the device performance testing. Si wafer substrate was not compatible with the experimental set-up, in which an inverted microscope (transmitted light, requiring a transparent substrate) is preferred over an upright microscope (reflected light, works for opaque substrate). The device had to be fabricated on a transparent substrate. The study chose a Pyrex 7740 borosilicate wafer as a substrate because its thickness is compatible to a Si wafer. The process for fabricating microfluidic device on Pyrex wafer remained to same as with a Si wafer, except for the photolithography and plasma etching steps.

The profiles of microfluidic device on a Pyrex wafer after being etched with plasma with the same conditions as a Si wafer is shown in Figure 3.23. With 8 min etch, the PDMS was etched for 2.98 µm compared with 6.02 µm of PDMS being etched on Si wafer. The sidewall shows a double-slope feature, the same result for the corroded photoresist mask on Si wafer in previous section. Further investigation on the SPR 220-7 mask exposed with UV at 2 cycles of 8 s each, found that the profile of the mask itself did not share the same profile as with a Si wafer. The SEM image of SPR 220-7 masked PDMS on a Pyrex wafer is shown in Figure 3.24.
Figure 3.23 Sidewall profile at double T junction of etched PDMS microfluidic device on Pyrex wafer.

Figure 3.24 Profile of developed SPR 220-7 photoresist on PDMS on Pyrex wafer.
Figure 3.25 Etched PDMS via crack formed in SPR 220-7 mask on Pyrex wafer.

Figure 3.26 SPR 220-7 mask on PDMS on Pyrex wafer when exposed to UV at 2 cycles of 5 s each.

The PDMS plasma etch on a Pyrex wafer had a much lower etch rate than that for the Si wafer substrate when using the same etching recipe. It is believed that this is due to the difference in thermal conductivity between Si and Pyrex wafers, with the conductivity being 149 and 1.1 W/m-K for Si and Pyrex wafers, respectively. The etching of PDMS
through cracks formed in the SPR 220-7 mask seems to be more severe for Pyrex wafers than for Si wafers. Figure 3.25 shows the etching of PDMS through a crack in SPR 220-7 photoresist.

The transparency of a Pyrex wafer may have played a role in causing a sloped SPR 220-7 mask. The UV exposure time for a Pyrex wafer was varied and found that at 2 cycles of 5 s each, the profile of SPR 220-7 mask was almost vertical, as shown in Figure 3.26.

To alleviate the problem with cracking in SPR 220-7 layer, the post-exposure bake step was bypassed to avoid putting new stress in the SPR 220-7 layer and lower the plasma RF power to 350 W. The etched result for both PEB and non-PEB samples showed no difference in terms of etch rate. Since the PDMS etching had a slower rate, the etch time for Pyrex substrate was increased to 20 min. When the etch time exceeded 22 min, the protected SPR 220-7 mask was completely etched out. Figure 3.27 shows the profile of etched PDMS at 350 W for 20 min on a Pyrex wafer.

The Dektak profilometer measurement showed a 4.52 µm in etch depth. It was also noticeable that the PDMS etched surface was rougher than the etched results on a Si wafer. The surface roughness of the etched PDMS on a Pyrex wafer was measured over 5 x 5 µm² surface area with an Asylum AFM and the resulting surface topography is shown in Figure 3.28. The calculated $R_{RMS}$ was 18.433 nm.
Figure 3.27 Sidewall profile of etched PDMS on pyrex wafer when etched at 350 W for 20 min.

Figure 3.28 AFM surface topology of etched PDMS on Pyrex wafer.
3.5 Device testing

Figure 3.29 shows finished PDMS microfluidic device on a Pyrex wafer. Upon the PDMS microfluidic device on Pyrex 7740 testing, the device was flushed with 6.7 mM phosphate buffered silane (PBS) solution (Hyclone, Logan, UT, USA) 3 times, before filling the device again with PBS solution. Bovine serum albumin (BSA) with Alexa Flour 484 conjugate (Molecular Probes, Eugene, OR, USA) was use to render visualization the flow in microfluidic device. The albumin solution was injected to reservoir 2. The voltages were applied via electrodes to all 4 reservoirs as a two step operation to inject and to plug flow formation. Table 3.5 shows voltage setting for a two step operation.

![Figure 3.29](image)

Figure 3.29. PDMS microfluidic device on Pyrex wafer (a) compared with the design (b).
Table 3.5 Potential applied to microfluidic reservoirs in a two step device operation.

<table>
<thead>
<tr>
<th>Step</th>
<th>Reservoir/ Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Injection</td>
<td>-2</td>
</tr>
<tr>
<td>Separation</td>
<td>ground</td>
</tr>
</tbody>
</table>

The power supply used was an Agilent E 3620 A dual output DC power supply (Agilent, Santa Clara, CA, USA). The three voltage outputs from the power supply were connected to a switch for a fast switching between injection and separation steps. The slightly negative voltage was used in the injection step to make sure that albumin would not diffuse to reservoirs 1 and 4. The Nikon Eclipse TE2000-S inverted microscope (Nikon, Tokyo, Japan) was used to monitor the albumin flow. Figure 3.30 shows the albumin flow at the double T junction during injection and separation steps. A plug flow of albumin was moving along separation column as shown in Figure 3.31.
Figure 3.30 Flow of albumin in PDMS microfluidic device during (a) injection and (b) separation steps.

Figure 3.31 An albumin plug flows along separation column to reservoir 4.
3.6 Conclusion

The goal of the study was to develop process for fabricating microfluidic structure in PDMS using plasma etching technique. Lam AutoEtch 590 was used to optimize the etching condition of PDMS since it has been used extensively in semiconductor industry to etch SiO2 substrates. It was found that 20 sccm O2 and 80 sccm CF4 in 2.8 Torr process pressure, 450 W RF power and 0.38 cm gap spacing gave the best etched results in anisotropic etching of PDMS on a Si wafer substrate. The etch surface was found to be smooth with the surface roughness less than 1 nm. The etched surface also shows hydrophilic property. As for a Pyrex wafer substrate, the PDMS plasma etch rate was much slower than for a Si wafer. The etched PDMS also shows a rougher surface with the R_{RMS} of 18.433 nm. The PDMS microfluidic device on Pyrex wafer was successfully tested for albumin injection and plug flow demonstration.
Chapter 4

PDMS Nanofluidic Device Fabrication

4.1 Introduction

One of the techniques used in fabricating nano structures in the semiconductor field is sacrificial layer lithography (SLL) [Bhushan, 2008]. In this technique, the patterned nano scale sacrificial layer is selectively removed to create a space of the same dimensions as the sacrificial layer. The surrounding materials act as channel walls to create nanochannels. Stern et al. (1997) fabricated horizontal silicon nitride (Si₃N₄) using low pressure chemical vapor deposited (LPCVD) amorphous Si as the sacrificial layer. Amorphous Si sacrificial layer as thin as 20 nm were removed by wet etching in tetramethylammonium hydroxide (TMAH) solution. The amorphous Si etch rate is more than 10,000 times faster than that of Si₃N₄, providing the high etching selectivity necessary for removing the 10 mm long amorphous Si layer without removing the Si₃N₄ substrate. The horizontal Si₃N₄ nanochannel is shown in Figure 4.1.
Figure 4.1 The SEM images of 100 nm high Si$_3$N$_4$ channels with channel width of (a) 0.5 µm and (b) 1 µm [Stern et al., 1997].

Figure 4.2 Silicon nanochannels fabrication process flow [Bhushan, 2008].
Hansford et al. (2001) fabricated vertical silicon nanochannels using thermal silicon oxide as the sacrificial layer. The nanochannel fabrication process is illustrated in Figure 4.2. The process starts with depositing low stress Si$_3$N$_4$ using LPCVD to act as the etch stop layer. The polysilicon is then deposited on top of the Si$_3$N$_4$ (a). Holes are created in the polysilicon layer with standard photolithography masking and plasma etching (b). The sacrificial oxide layer is deposited and selectively plasma etched to leave anchor points at one side of the holes (c). Next, the second polysilicon layer is deposited to fill the holes (d). The vertical nanochannels are exposed by chemical mechanical polishing (CMP) down to the top of the first polysilicon layer (e). The sacrificial layer of silicon oxide is removed by hydrofluoric acid wet etching (f).

Bellan et al. (2008) used a non cleanroom process with electrospun polyethylene oxide (PEO) nanofibers as the sacrificial material in creating nanochannels connecting with reservoirs. The traditional PDMS microtransfer molding technique was used and the PEO was removed by soaking the PDMS substrate in water.

This chapter describes the fabrication of high density PDMS nanochannels based on the SLL technique. A nanometer scale sacrificial layer of metal was deposited on a micrometer scale PDMS structure using self-shadowing deposition technique. Once the second PDMS layer was coated on top and allowed to cure, plasma etching of the PDMS exposed the sacrificial layer that was later removed in an acid bath, leaving nanochannels in the PDMS structure.
4.2 Materials and method

4.2.1 Nanofluidic device design

A schematic drawing of the PDMS nanofluidic device is shown in Figure 4.3. The nanochannels are 10 mm long, 6 µm apart from each other over a 4 mm wide. The two ends of the nanochannels are connected with large rectangular reservoirs.

![Figure 4.3 Schematic drawing of PDMS nanofluidic device.](image)

4.2.2 Materials

Si and Pyrex 7740 wafers (100 mm) were from University Wafer (South Boston, MA, USA). SU-8 2005 and SPR 220-7 photoresists, SU-8 and MF-319 developers, and EBR PG edge bead remover were purchased from MicroChem (Newton, MA, USA). PDMS elastomer kit (Sylgard 184) was from Dow Corning (Midland, MI, USA). Hexamethyldisilazane (HMDS) was from Shin-Etsu MicroSi (Phoenix, AZ, USA). Toluene was purchased from Mallinckrodt Baker (Phillipsburg, NJ, USA). Syringe filters, 0.45 µm PTFE membrane were from Sigma-Aldrich (St. Louis, MO, USA). 3 µm lines, 3µm spacing chrome mask was from Sine Patterns (Pittsford, NY, USA). Aluminum (Al) pellets, 99.999% purity and titanium (Ti) pellets, 99.995% purity were
from Kurt J. Lesker (Clairton, PA, USA). Hydrochloric acid, Acetone, 2-propanol, and hydrochloric acid (HCl) were purchased from J.T. Baker (Phillipsburg, NJ, USA).

4.2.3 PDMS nanofluidic device fabrication

The PDMS nanofluidic device fabrication process flow is shown in Figure 4.4. The process can be broken into steps as follows:

Master wafer preparation

SU-8 2005 negative tone photoresist was chosen to create master features on the Si wafer. SU-8 2005 was spin-coated using a CEE 100 CB spin coater at a final spin speed of 3000 rpm to obtain final resist layer of 5 µm. The substrate was then soft baked for 2 min at 95° C on a contact hotplate (Barnstead International, Dubuque, IA, USA). The substrate was UV exposed with a chrome mask with 3µm lines and spaces, 10 mm long on an EV Group 620 contact aligner for 2.4 s using vacuum hard contact mode. The substrate was then put in a PEB process at 95° C for 3 min on the contact hotplate. The substrate was developed in SU-8 developer for 1 min to obtain lines 3 µm wide and 5µm tall. The rendered SU-8 master wafer was annealed on the hotplate for 5 min at 150° C.
Figure 4.4 PDMS nanofluidic device fabrication process flow.

- Micro pattern transfer molding of PDMS
- Self-shadowed metal deposition via e-beam evaporator
- Spin coating 2\textsuperscript{nd} layer of PDMS
- SPR 220-7 coating and UV exposure
- Develop to remove UV exposed area of SPR 220-7
- Plasma etching to create reservoir structures
- Removal of metal layer in acid bath
- Nanofluidic device assembling
PDMS microtransfer molding

The SU-8 master wafer was primed with HMDS in a YES-3 vacuum bake/ vapor prime processing system (Yield Engineering Systems, San Jose, USA) to prevent surface adhesion between master wafer and PDMS. The master wafer was later spin-coated with a PDMS mixture with accelerating at 85 rpm/s to a final spin speed of 3000 rpm for 90 s and the wafer edge was cleaned with edge bead remover and allowed to set for 10 min. A Si substrate, the base substrate, was surface treated with O₂ plasma at 10 sccm, 100 W and 5 s in a Technics Micro-RIE reactive ion etcher before being placed on top of the PDMS coated master wafer. The joined wafers were cured at 65°C for 2 hr in Blue M oven. Once the PDMS was cured, the top wafer with transfer molded PDMS was carefully peeled off from the master wafer.

Sacrificial layer patterning

The metal sacrificial layer was deposited over features on the PDMS layer using a 502A electron gun evaporator from Denton Vacuum (Mooresstown, NJ, USA). The self-shadowing deposition technique was employed to ensure that metal was deposited on only one side of microfeatures. A special sample holder with adjustable angle was used in the metal deposition step. Figure 4.5 shows a special sample holder designed to be used in angled metal deposition.
Figure 4.5 Sample holder for angled metal deposition in e-beam evaporator.

The featureless areas of PDMS were covered by ultra high vacuum aluminum foil (All Foils, Cleveland, OH, USA) to prevent metal from being deposited on the surface that causes the formation of wrinkles and cracks [Patel et al., 2009].

Formation of nanochannels

The metal-deposited sample was treated with O\textsubscript{2} plasma to promote surface adhesion. The recipe used was 10 sccm O\textsubscript{2}, 100 W and 5 s in a Technics Micro-RIE reactive ion etcher. A 50% PDMS mixture in toluene solution was spin-coated on the substrate using and acceleration of 500 rpm/s to a final spin speed of 1000 rpm for 60 s on a CEE 100 CB spin coater. The substrate was allowed to set for at least 1 hr to make sure that the second PDMS layer was evenly coated before being placed in a Blue M oven at 65°C for 2 hrs for curing. After the PDMS was cured, the substrate was once again surface activated with O\textsubscript{2} plasma. The substrate was subsequently spin-coated with SPR 220-7 photoresist at a final spin speed of 3000 rpm using a CEE spin coater. The
substrate was soft baked at 90 °C for 1 hr and cooled down to room temperature at 20° C/hr on an HS40 hotplate. The substrate was then exposed to UV radiation on an EV Group contact aligner using proximity mode at 15 W/cm² for 2 cycles of 8 s and 60 s interval to render rectangular reservoirs at the ends of the PDMS microfeatures. The substrate was held for 35 min before doing PEB by the same process as the soft baking. The substrate was developed in MF-319 developer until the UV exposed area was completely clear of photoresist.

The substrate was plasma etched to create reservoirs connected by microfeatures using Lam AutoEtch 590 plasma etcher. The Etching recipe used was the recipe optimized from PDMS microfluidic device etching, which is 20 sccm O₂, 80 sccm CF₄, 450 W RF power, and 0.38 cm gap spacing. After the etching was finished, the metal was removed by chemical etching in 1:1 (volume) 37% HCl and DI water at 50° C on a hotplate. Once the metal was completely removed, the sample was rinsed thoroughly and dried.

Device packaging

A piece of PDMS slightly bigger than the size of the nanofluidic device structure was cut out from the slab. Holes were punched in the piece in alignment with the two reservoirs. Both the PDMS slab and microfluidic PDMS structure surfaces were treated with O₂ plasma using a reactive ion etcher with 40 sccm O₂, 20 W for 30 s, and the two surfaces were consequently brought into contact, reservoirs and punched holes were aligned, for irreversible sealing. The device was kept in 1:1 (volume) 2-propanol and DI water until it was ready for the device testing.
4.3 Results and discussion

4.3.1 SU-8 2005 master fabrication

The SU-8 2005 was chosen based on the 3µm lines, 3µm spacing chrome mask. The SU-8 2005 target thickness is 5 µm. and the preferred aspect ratio is between 1 and 2. The structure’s aspect ratio could not be too large, or the molded PDMS structure would suffer deformation. An SEM image of SU-8 2005 master structures on a Si wafer is shown in Figure 4.6. Dektak profilometer measurements revealed the actual feature height of 4.86 µm.

![SEM image of cross sectioned SU-8 2005 on Si wafer.](image)

4.3.2 PDMS microtransfer molding

The pattern-transfer-molded PDMS on Si wafer is supposed to have a thin layer for the same reason as PDMS microfluidic device fabrication. In this experiment, the 50% PDMS mixture in toluene solution was the first choice in spin coating on the master
wafer. The spin coating recipe was the same as that for the PDMS microfluidic device. The process of peeling a thin PDMS layer supported by a Si wafer is challenging since the applied peeling force could break the SU-8 master wafer [Luo et al., 2006 b]. Also, there appear to be voids that form in the PDMS layer caused by air trapped as a result of placing the wafer on top of a pre-cured, coated PDMS substrate. The PDMS layer preparation was switched to PDMS with a final coating spin speed of 3000 rpm, 85 rpm/s for 95 s [Mata et al. 2005] to create a PDMS layer of about 20 µm thick. In the peeling process with thicker PDMS, the master was saved from breaking from the peeling force. Fig 4.7 shows the transferred features on PDMS layer prepared by (a) 50% PDMS in toluene solution and (b) 100% PDMS.

Although there were still voids formed in the cured PDMS layer, the number of voids was much lower than that in the PDMS layer prepared from a 50% PDMS mixture in toluene solution. Figure 4.8 shows void spaces in PDMS layer.
Figure 4.7 Transfer molded features on PDMS prepared with (a) 50% PDMS in toluene and (b) PMDS.
4.3.3 Sacrificial layer patterning

With rectangular microfeatures 3 µm wide, 3 µm spacing and 4.86 deep, the sample must be held at an angle of 32°, as illustrated in Figure 4.9, with respect to incident metal atoms in order to not have metal deposited on the bottom surface of the feature. In experiments, it was found that at a 36° the metal was deposited right on the foot of the feature sidewall but not on the bottom layer. Figure 4.10 shows 50 nm of Ti metal deposited at 32° and 36° on PDMS microfeatures.
Figure 4.10 A 50 nm Ti layer deposited at (a) 32° and (b) 36° angle on PDMS microfeature structures.

The wave-like character of deposited metal on PDMS sidewalls was observed when the deposition rate was higher than 1 Å/s. Figure 4.11 shows the wave formation on a 100 nm Ti film on sidewalls of PDMS microfeatures. It is believed that the wave formation is due to bulking of PDMS during high power metal deposition. The problem
was corrected by depositing metal at rate of 1 Å/s or lower. As previously mentioned, metal layers deposited on unmasked areas of PDMS surface tend to crack. Figure 4.12 demonstrates the cracks appearing on unmasked areas of PDMS when deposited with a 100 nm Ti film.

Figure 4.11 Wavy formation of 100 nm Ti film on microfeatures sidewalls.

Figure 4.12 Cracks in 100 nm Ti film on a PDMS surface.
Figure 4.13 shows the profile of a 200 nm Ti layer deposited on PDMS microfeatures. The relatively thick Ti layer seems to have acted as a PDMS swelling and shrinking restriction on metal deposited side during and after metal layer deposition, causing PDMS microfeatures to deform after the deposition was complete.

4.3.4 Nanochannels realization

The original nanochannel design was to just have a vertical component. So attempts were made to remove the metal layer deposited on top of microfeatures. Al was the first metal used for nanochannel definition. Al requires Borontrichloride –Chlorine (BCl₃-Cl₂) plasma etching to remove the top Al layer [Purdes, 1983; Williams and Muller, 1996], which was not available for the experiment. The next step was to cover the Al-deposited microfeatures by spin coating a second layer of PDMS, and then optimized plasma blanket etching this PDMS layer to the top of the microfeatures to expose the Al
layer. Finally, the Al layer was removed in an HCl acid bath solution. Figure 4.14 shows the top surface of first PDMS layer after blanket plasma etching and Al removal.

![Nanochannel](image)

Figure 4.14 Top view of PDMS 200 nm nanochannels after blanket plasma etch and Al removal.

It is evident that Al etching is not compatible with PDMS etching. The sputtered nonvolatile Al was deposited back on the PDMS layer and caused a rough etched surface on the non Al deposited area. Also, the PDMS etch rate for the blanket etching is much slower than the microfluidic device etching. The choice of deposition metal was changed to Ti since it was suggested that its plasma etching recipe is compatible with PDMS [Williams and Muller, 1996]. Figure 4.15 shows the top view of PDMS nanochannels after plasma blanket etch of second PDMS layer and Ti removal in HCl solution.
As can be seen in Figure 4.15, the etched surfaces of non metal deposited areas on Ti devices are smoother than those on Al devices. It should also be noticed that the blanket etch did not result in a uniform etch of the unprotected area. The area on the right of Figure 4.15 was etched down shallower than the area on the left. Uniform etching is critical for obtaining the planar etched surface necessary for surface bonding with another PDMS substrate.

The next strategy was an attempt to remove the top Ti layer with plasma etching prior to casting the second PDMS layer. The Lam 590 etcher Ti etching recipe suggested by Williams and Muller was used to etch the 100 nm Ti on top of PDMS microfeatures. The etching recipe was 90 sccm CF$_4$, 30 sccm CHF$_3$, and 120 sccm He at 2.8 Torr, 0.38 cm gap spacing, 750 W for 40 s. Once the etching was complete, the sample was treated with O$_2$ plasma and spin-coated a second layer of PDMS and cured in a Blue M oven at
65° C for 2 hrs. The sample was cleaved and soaked in an HCl acid bath to remove the Ti layer. The SEM images of Ti etched and non etched samples are shown in Figure 4.16.

Figure 4.16 Cross section SEM images of (a) Ti etched and (b) Ti not etched, 100 nm Ti deposited on microfeatures.
It can be seen that Ti etch removes the top Ti layers as well as the side wall layers when compared with the non etched sample. More importantly, viewing the Ti etched sample under an Olympus BX51TRF Optical Microscope (Olympus, Tokyo, Japan) shows that the microfeatures were deformed during the Ti etch, as shown in Figure 4.17. Since trying to remove the Ti top layer has unintended consequences, the top metal layer was left untouched in pursuing nanochannel fabrication.

Figure 4.17 Optical microscope image of PDMS microfeatures after Ti plasma etching.

The SPR 220-7 photoresist mask to create reservoirs at the ends of microfeatures was aligned in such a way that the reservoirs overlap with microfeatures. Figure 4.18 shows an etched reservoir area, exposing the PDMS and Ti layers in the overlapping area. The deposited Ti layer was selected to be 200 nm thick for ease of investigation.
Figure 4.18 Etched reservoir structures in PDMS and Ti layer on a Si substrate.
The PDMS etch recipe evidently etched through the Ti layer and into the underlying PDMS layer. Removal of the Ti layer in HCl solution reveals PDMS parts that were once protected by the Ti layer at the entrance of the nanochannels. Figure 4.19 shows nanochannel structures after removal of the 200 nm Ti layer. Note that for the 200 nm Ti layer devices, once the Ti metal was removed, the top nanochannel parts were not evident, possibly due to the weight causing collapse of the second layer.

Figure 4.19 PDMS nanochannels connecting to reservoirs after Ti removal.

As the fluorescence microscopy was also chosen as a tool to investigate the nanofluidic device performance, the nanofluidic device on a Pyrex 7740 wafer was also fabricated using the same fabrication process as for microfluidic device fabrication on a Pyrex wafer as described in chapter 3. In brief, a SPR 220-7 photoresist was exposed to UV for 2 cycles of 5 s and 60 s interval time to improve a mask profile. The PEB step
was omitted to prevent new cracks form be created on a mask layer. The plasma etch time was increased to 20 min to compensate the low PDMS etch rate on a Pyrex supporting wafer.

Figure 4.20 Exposed 200 nm Ti layer in PDMS after Plasma etch on Pyrex wafer.

Figure 4.20 shows the side wall profile of a nanofluidic reservoir, exposing a 200 nm Ti layer while etching through the PDMS. Figure 4.21 shows etching of PDMS through a crack in photoresist, creating unwanted exposure of nanochannels. Notice also that the sidewall of the reservoir is not as vertical as that of microfludic device on a Pyrex wafer.
Figure 4.21 Etched PDMS via crack from in SPR 220-7 photoresist on Pyrex wafer.

Figures 4.22 and 4.23 show 200 nm nanochannels in PDMS structure once a Ti layer was removed in HCl acid bath.

Figure 4.22 Array of 200 nm channels in PDMS structure on a Pyrex wafer.
Figure 4.23 Magnified 200 nm channels in PDMS structure on Pyrex wafer.

Figure 4.24 Profile of etched microfeatures in first layer of PDMS.
It was expected that PDMS etching from the second to the first layer in areas where no Ti layer was deposited would be seamlessly transitioned. However, figure 4.24 shows that microfeatures on the right side, where there were no Ti deposited on, have different etch profile than the adjacent second PDMS layer. More investigation is needed to see whether this is due to different in prepolymer PDMS concentrations of the first and second layers, or the shape of microfeatures itself that contributes to different etched profiles between the two layers.

Another observed phenomenon was that if substrate was not allowed to set long enough after being spin coated with second PDMS prepolymer before putting it in an oven, the PDMS layer was not evenly coated. This led to PDMS etching that exposed to microfeatures at different depths. Figure 4.25 shows nanochannels in PDMS structure at various heights of microfeatures being exposed.
Figure 4.25 200 nm channels in PDMS structure with various heights of microfeatures being etched.
4.4 Device testing

Figure 4.26 PDMS nanofluidic device on Pyrex wafer (a) compared with the design (b).

Figure 4.26 shows the fabricated PDMS nanofluidic device on a Pyrex wafer. Prior to a device testing, the device was rinsed with 6.7 mM PBS solution 3 times before refilling it with PBS solution. The power supply used in the test was Tenma 72-6695 laboratory DC power supply (Tenma, Springboro, OH, USA). The voltage was applied via electrode across the two reservoirs to drive 10^{-5} M neutral fluorescence dye Rhodamine B (Sigma-Aldrich, St. Louis, MO, USA) in Tris-HCl buffer through 200 nm PDMS nanochannels filled with PBS solution. The voltage used was 17 V, one reservoir at 17 V the other at ground. The Rhodamine B solution was loaded in grounded reservoir. An Olympus IX81 inverted microscope (Olympus, Tokyo, Japan) was used as a tool to investigate the propagation of the fluorescence.

Figure 4.27 shows the moving of Rhodamine B in nanochannels as time progressed. It can be seen that Rhodamine B molecules moved along the 200 nm
channels when the electric field was applied. Once the electric field was turned off after 75 min, the propagation front was stalled.

Figure 4.27 Propagation of Rhodamine B through 200 nm channels in PDMS structure when 18 V was applied across reservoirs.
4.5 Conclusion

PDMS nanochannels have been fabricated using sacrificial layer lithography (SLL) technique. Ti metal was deposited on PDMS microfeatures using the self-shadowing technique to ensure the deposition on one side of the microfeatures. O$_2$/CF$_4$ plasma etching technique was used to create reservoir structures and to expose the deposited sacrificial Ti layer, which later was removed in HCl solution. The nanofluidic device on a Pyrex wafer was successfully tested by driving Rhodamine B across nanochannels via the application of an electric field.
Chapter 5
PDMS Integrated Micro- and Nanofluidic Device Fabrication

5.1 Introduction

Capillary electrophoresis application in microfluidic device offers advantages over small reagents used, fast analytical process. Inability to collect molecules on interest after the electrophoretic separation poses a restriction to the application on microfluidic device. Adding a nanofluidic component to microfluidic device gives a more variety applications for a device performance. Kuo et al. (2003) connected a nuclear track-etched polycarbonate (PCTE) containing nanometer scale holes to 2 PDMS microfluidic channels, allowing selected separated components from one microfluidic channel to be further examined in the other. Figure 5.1 shows schematic drawing of their device at microfluidic channels intersection.

Figure 5.1 Schematic drawing of 2 microfluidic channels connected with PCTE [Kuo et al., 2003].
Flachsbart et al. (2005) also used the same device design concept to fabricate a multilayered PMMA with PCTE for electrophoretic application. In PCTE membrane, the pore radius is the average number and the pores is randomly distributed over the membrane. The PDMS nanofluidic device fabrication process offers precise, controllable size, and uniformly distributed nanochannels in integrating with a microfluidic channel.

5.2 Materials and method

5.2.1 Integrated device design

A schematic drawing of the PDMS integrated micro- and nanofluidic device is shown in Figure 5.2. It is essentially a combination of the microfluidic and nanofluidic devices design. The microfluidic design part was kept the same as previously described in chapter 3. For the nanofluidic part, since it took long time to drive florescent molecule across 10 mm long nanofluidic device in chapter 4 experiments, the length of the nanochannels for the integrated device were shortened to 1.5 mm from the microchannel intersection to the nanochannel reservoirs. The nanofluidic channels were place across the microfluidic separation column, toward reservoir 4.

![Figure 5.2 Schematic drawing of PDMS integrated micro- and nanofluidic device.](image)

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5.2.2 Materials

Si and Pyrex 7740 borosilicate wafers (100 mm) were from University Wafer (South Boston, MA, USA). SU-8 2005 and SPR 220-7 photoresists, SU-8 and MF-319 developers, and EBR PG edge bead remover were from MicroChem (Newton, MA, USA). PDMS elastomer kit (Sylgard 184) was purchased from Dow Corning (Midland, MI, USA). HMDS was from Shin-Etsu MicroSi (Phoenix, AZ, USA). Toluene was purchased from Mallinckrodt Baker (Phillipsburg, NJ, USA). Syringe filters, 0.45 µm PTFE membrane were from Sigma-Aldrich (St. Louis, MO, USA). 3 µm lines, 3µm spacing chrome mask was from Sine Patterns (Pittsford, NY, USA). The integrated micro- and nanofluidic device chrome mask was from Infinite Graphics Incorporated (IGI) (Minneapolis, MN, USA). Ti pellets, 99.995% purity were from Kurt J. Lesker (Clairton, PA, USA). Hydrochloric acid, Acetone and 2-propanol were purchased from J.T. Baker (Phillipsburg, NJ, USA).

5.2.3 PDMS integrated micro- and nanofluidic device fabrication

In this chapter, the PDMS integrated micro- and nanofluidic device was fabricated on a Pyrex wafer only. The device fabrication process flow is shown in Figure 5.3. The process was similar to that for PDMS nanofluidic device fabrication on a Pyrex wafer described in chapter 4.
Micro pattern transfer molding of PDMS on Pyrex 7740 wafer

Self-shadowed Ti deposition via e-beam evaporator

Spin coating 2\textsuperscript{nd} layer of PDMS

SPR 220-7 coating and UV exposure, no PEB step

Developing to render SPR 220-7 etch mask

Plasma etching to create microfluidic structure and nanofluidic reservoirs

Removal mask and wet etching to remove Ti layer

Integrated device assembling

Figure 5.3 PDMS integrated micro- and nanofluidic device fabrication process flow.
Master wafer preparation

The SU-8 2005 negative tone photoresist was used for creating master features on the Si wafer. The SU-8 2005 was spin-coated using the CEE 100 CB spin coater at a final spin speed of 3000 rpm to obtain final resist layer of 4.86 µm. The substrate was then soft baked for 2 min at 95 °C on a contact hotplate. The substrate was UV exposed with 3µm lines, 10 mm long and 3µm spacing chrome mask on an EV Group 620 contact aligner for 2.4 s using vacuum hard contact mode. The substrate was then put in PEB process at 95 °C for 3 min on the contact hotplate. The substrate was developed in SU-8 developer for 1 min and the rendered SU-8 2005 master wafer was annealed on the hot plate for 5 min at 150 °C.

PDMS microtransfer molding

Upon the molding process, the SU-8 master wafer was primed with HMDS in a YES-3 vacuum bake/ vapor prime processing to prevent surface adhesion between master wafer and PDMS. The master wafer was later spin-coated with a PDMS mixture with a final spin speed of 3000 rpm with 85 rpm/s acceleration for 90 s and the wafer edge was cleaned with edge bead remover and allowed to set for 10 min. A Pyrex wafer surface was treated with O₂ plasma at 10 sccm, 100 W and 5 s in Micro-RIE reactive ion etcher before being placed on top of the PDMS coated master wafer. The wafers were cured at 65 °C for 2 hr in Blue M oven. Once PDMS was cured, the Pyrex wafer with transfer molded PDMS layer was carefully peeled off from the master wafer.
Sacrificial layer patterning

A 200 nm Ti layer was deposited over features on the PDMS layer using a 502A electron gun. The special sample holder with adjustable angle was used to hold the pattern transferred PDMS on the Pyrex wafer at 36° relative to metal incident angle in a self-shadowing Ti deposition. The non-feature area of PDMS was covered with an ultra high vacuum aluminum foil.

The microfluidic structure and nanochannels realization

The Ti-deposited substrate surface was treated with an O₂ plasma at 10 sccm O₂, 100 W for 5 s in a Micro-RIE reactive ion etcher. A 50% PDMS mixture in toluene solution was spin-coated on the substrate at final spin speed of 1000 rpm with 500 rpm/s acceleration for 60 s on a 100 CEE spin coater. The substrate was allowed to set for at least 1 hr before being placed in a Big M oven at 65 °C for 2 hr for curing. After PDMS was cured, the substrate was once again surface activated with an O₂ plasma. The substrate was subsequently spin-coated with SPR 220-7 photoresist at a final spin speed of 3000 rpm using a CEE spin coater. The substrate was soft baked at 90 °C for 1 hr and cooled down to room temperature at 20 °C/hr on a HS40 digital programmable stirring hot plate. The substrate was then exposed to UV radiation on an EV Group contact aligner using proximity mode at 15 W/cm² for 2 cycles of 5 s and 60 s interval. The fluidic structure chrome mask was aligned on top of the substrate in such a way that the microfluidic separation column crosses at a 90° angle with the nanochannels and the nanochannels were placed closer to reservoir 4 rather than a center of the separation column so the flow of fluorescence molecules to be tested has enough distance for a fully
developed plug flow formation before arriving the nanochannels intersection. The substrate was held for 35 min before being developed in MF-319 developer until the exposed area was clear of photoresist.

The substrate was plasma etched to create microfluidic structure and reservoirs using an AutoEtch 590 plasma etcher. The Etching recipe used was the recipe optimized from PDMS nanofluidic device etching on a Pyrex wafer, which is 20 sccm O₂, 80 sccm CF₄, 350 W RF power, 0.38 cm gap spacing and etching for 20 min. After the etching was finished, the metal was removed by chemical etching in 50% HCl in DI water solution at 50 °C on a hotplate. Once the metal was completely removed, the sample was rinsed thoroughly and dried.

Device packaging

A 5 mm thick piece of PDMS slightly bigger than the size of the integrated micro- and nanofluidic device structure was cut. Six holes were punched in the piece aligned with 6 reservoirs of the integrated device. Both the PDMS slab and etched PDMS structure surfaces were treated with O₂ plasma using a reactive ion etcher with 40 sccm O₂, 20 W for 30 s, and the two surfaces were consequently brought into contact, , with the reservoirs and the punched holes aligned, for an irreversible seal. The device was kept in a 50% 2- propanol in DI water until it was ready for the device testing.
5.3 Results and discussion

The profile of etched PDMS integrated device structure is shown in Figure 5.3. The Dektak profilometer measurement shows a depth of 12.6 µm in the etched structure. The faster PDMS etch rate of the integrated micro- and nanofluidic device than that of the microfluidic device on Pyrex wafer needs to be further investigated of whether or not the different in composition of PDMS prepolymer, or even the thickness of PDMS plays any role in increasing the etch rate. The interface between PDMS first and second layer could easily be seen from Figure 5.4. It is noticeable also that the etched surface shows some roughness but looks rather different from the etched surface of microfluidic device on Pyrex wafer shown in chapter 3. The surface roughness was measured with the AFM over 5x5 µm² area. The resulting AFM scanning image is shown in Figure 5.5.

Figure 5.4 Etched profile of PDMS integrated device structure on a Pyrex wafer.
Figure 5.5 AFM surface topology of etched PDMS integrated structure on Pyrex wafer.

Figure 5.6 PDMS microfluidic channel created by etching through microfeature layer.
The calculated $R_{RMS}$ was 9.510 nm. From the AFM image, one could notice cracks on the etched surface, which was not observed on the etched surface of PDMS microfluidic device. The intersection between a microchannel and nanochannels is shown in Figure 5.6. Figure 5.7 shows the exposed 200 nm Ti layer on microfeatures (a) and nanochannels after Ti being removed (b).

![Figure 5.7 Microchannel and nanochannels intersection before (a) and after (b) Ti metal was removed.](image)
One problem in integrated micro- and nanofluidic device was the void structures created during micro-pattern transfer molding. In the mask aligning step, the void structures were avoided to be place in or intersecting the microfluidic structure and nanofluidic reservoirs because it caused unleveled etch surface that led to seal leaking and sometime collapsing of fluidic structure. Excluding void structures was not always possible due to the aligning limitation. Figure 5.8 shows void structures in different locations on fluidic structure.

Figure 5.8 Void structures in various locations of PDMS integrated device.
Figures 5.9 and 5.10 show optical microscopic images of void structures in microchannel. The spin coating of a second layer PDMS prepolymer on top of the first layer did not fill void spaces since it was not thick enough. When etched PDMS to create integrate device structures, the second PDMS layer could be completely removed, exposing the Pyrex wafer surface to the device.
Another problem which was also observed in nanofluidic device fabrication was the non even coating of second PDMS layer. Although in some device a second PDMS layer was set to cure at room temperature for 2 days, the unlevel problem still persisted. Figure 5.11 shows different thickness of second PDMS layer coating on Ti deposited microfeatures at the etched microchannel interface.

Figure 5.11 Non uniformity coating of a second PDMS layer on Ti deposited microfeatures.
5.4 Device testing

Figure 5.12 PDMS integrated micro- and nanofluidic device on Pyrex wafer (a) compared with the design (b).

The PDMS integrated micro- and nanofluidic device is shown in Figure 5.12. Before the device testing, it was repeatedly rinsed with PBS solution 3 times before refilling with the PBS solution. Goat anti-mouse IgG-RPE (SouthernBiotech, Birmingham, AL, USA) was used in monitoring the flow in the integrated device. The voltages were applied via electrodes to reservoirs 5 (ground) and 6 (+15 V) to drive IgG compound from reservoir 5 across nanochannels pass microchannel to the other nanochannels site to reservoir 6. The Nikon TE2000-S inverted microscope was used in investigating to flow. Figure 5.13 shows the nanochannels entrance from reservoir 5. Figure 5.14 shows the images of intersection between microchannel and nanochannels.
Figure 5.13 IgG-RPE fluorescence image at the nanochannels entrance from reservoir 5.

Figure 5.14 IgG-RPE fluorescence image at microchannel and nanochannels intersection.
Figure 5.15 IgG-RPE fluorescence image at the nanochannels exit to reservoir 6.

Figure 5.15 shows nanochannels exit to reservoir 6. For the microchannel and nanochannels intersection images in Figure 5.14, it could be implied that the plasma etching exposed Ti metal deposited microfeatures at different depths, as previously discussed in chapter 4.

5.5 Conclusion

Integrated micro- and nanofluidic device have been fabricated in PDMS structure on a Pyrex wafer. The nanofluidic part was fabricated using the SLL technique, while the microfluidic part was created by O₂/CF₄ plasma etching using LAM 590 etcher. The plasma etch was found to be faster for integrated device than that of a microfluidic device on Pyrex wafer. Although the etched surface of the integrated device was smoother than the microfluidic one, the etched surface showed crack formation which was not observed
in the microfluidic device. The integrated device was tested by driving IgG-RPE across
nanochannels, crossing microfluidic channel to the other side and exit to other reservoir.
Chapter 6

Conclusions and Future Outlook

PDMS is one of the most frequently used materials in the microfluidic fabrication due to the low cost and the ease of fabrication. The work presented in this dissertation focused on fabricating PDMS devices using technology available in the semiconductor industry to offer an alternative fabrication route that potentially lead to a new way of fabricating PDMS devices in mass production.

In PDMS microfluidic device fabrication, a LAM AutoEtch 590 was used to etch down microfluidic structure in PDMS on both Si and Pyrex 7740 wafers. The etch recipe was 20 sccm O₂, 80 sccm CF₄, at 2.8 Torr and 0.38 cm gap spacing. For a Si base wafer, the etched surface was found to be smooth with R<sub>RMS</sub> less than 1 nm. For a Pyrex base wafer, the PDMS etch rate was lower than that for the Si wafer substrate and the etched surface shows a rougher topography with R<sub>RMS</sub> of 18.433 nm.

PDMS nanofluidic devices were fabricated using a sacrificial layer lithography (SLL) technique. A Ti metal sacrificial layer was deposited on one side of PDMS micro transferred feature using a self-shadowing technique. PDMS nanofluidic devices were fabricated on both Si and Pyrex wafers. The resulted device in PDMS structure offers dense, controllable size, and uniformly distributed nanochannels.
The integrated PDMS micro- and nanofluidic device was also fabricated on a Pyrex wafer using nanochannel fabrication principle. The plasma etched surface has the $R_{\text{RMS}}$ of 9.510 nm.

The ultimate goal of the PDMS micro- and nanofluidic device fabrication is to use the nanofluidic part for affinity separation applications to further investigate bands of samples separated in traditional CE in microfluidic part. In order to do so, the PDMS surface chemistry in nanochannels has to be modified so the nanochannel surface selectively interacts with just certain type of molecules. A vapor phase deposition system, as shown in Figure 6.1 will be use to modify the PDMS surface in nanochannels, by placing a reactive species in a vapor phase and bring it to contact with the PDMS surface.

![Figure 6.1 Schematic diagram of Vapor phase deposition system for PDMS surface modification [Bhusan et al., 2006].](image)

Figure 6.1 Schematic diagram of Vapor phase deposition system for PDMS surface modification [Bhusan et al., 2006].
From the PDMS nanofluidic fabrication process, the second PDMS layer will be etched down to expose the Ti sacrificial layer and, subsequently soaked in HCl acid bath to remove the Ti metal. The PDMS with opened nanochannel spaces will be put in the vapor phase deposition for a surface modification with desired chemistry. Figure 6.2 shows the exposed 200 nm Ti layer after the second PDMS layer was plasma etched (a) and nanochannel space after the Ti layer was removed (b).

![Figure 6.2 Exposed Ti layer after second PDMS layer etch (a) and nanochannel spaces after Ti removal (b).](image)
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