Lithographic Techniques for Nanofabrication

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I. Introduction

Because most biochemical analytes of interest are naturally found in complex matrices, separations are necessarily an important part of their analysis. Advances in microfabricated devices have demonstrated their enormous potential for use in separations and subsequent analysis. Their advantages stem from the fact that separation efficiency improves with decreased size. For capillary electrophoresis and related separations, smaller structures dissipate heat more effectively. For chromatographic separations, decreased channel size results in better mass transfer. Each of these effects results in increased efficiency for smaller devices. Assuming that the separation is injection-limited (as in high speed cases) and that the channel width is equal to the injection length, the separation time, separation length, and applied voltage (for CE or similar separations) all decrease linearly with channel width. Figure 1 demonstrates this relationship between size and efficiency and indicates that micro- and nano-separations systems may offer the possibility of better, faster and cheaper analyses. 1

In addition to offering higher efficiencies, miniaturized devices present the possibility of single molecule

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detection. Scaled-down separation systems could be used both to quantify and to characterize individual analyte molecules based on their behavior in a specific environment. Scaling down of separation devices reaches a logical limit at the size of the molecules being separated. For channel widths on the order of a single molecule, the analysis begins to resemble resistive pulse sensing, in which individual particles are sized and counted.

Resistive pulse sensing refers to measurement of a change in current or voltage which occurs when a particle enters a comparably-sized aperture between two conducting solutions. This method has the advantages of being simple and readily miniaturizable for incorporation into micro- and nanofluidic systems. Additionally, it does not require tagging of analyte molecules, yields nanometer resolution and provides a variety of information, such as particle size, interaction with pore walls, and concentration.2,3

Realization of an on-chip resistive pulse device requires interfacing microfluidic channels, reservoirs and connections to the nanofluidic analysis channel(s) for delivery of analyte and buffer solutions. Well-established photolithographic techniques can be used to produce features down to approximately 200 nm. Several possibilities exist for fabrication of even smaller nanometer-scale features, and advances in fabrication techniques are offering an ever-widening range of possibilities. Both polycarbonate track-etch membranes4,5 and polydimethylsiloxane molding6,7 present attractive options for producing robust, reproducible nanopores.

The primary objective of this research was to develop lithographic techniques to fabricate nanometer-scale channels and pores. These techniques will be useful in developing a variety of chemical analysis systems. We are currently pursuing electron beam lithography (EBL) techniques for writing structures in positive and negative tone resists to remove or create structures, respectively. EBL of positive tone resists is used to create two-dimensional patterns in thin chromium films for subsequent production of three-dimensional structures from two-dimensional patterns. EBL of negative tone resists has been used to create features that can be used directly as sensing elements or as sacrificial layers for further device processing. Success in refining these fabrication techniques will enable us to produce chemical sensors with features from 500 nm down to 50 nm.

II. Materials and Methods

A. Substrate Preparation

Substrates for PMMA lithography were first cleaned using a modified RCA method. One inch square microscope slides were heated in aqua regia for 20 minutes, rinsed in water and acetone, sonicated 15 minutes in 3:1 acetone:methanol, rinsed in acetone and dried in nitrogen. The surface was then hydrolyzed by soaking 20 minutes in sodium hydroxide solution. Finally, substrates were rinsed in ultrapure water and dried with nitrogen prior to metal deposition.

After cleaning, 130 nm of thermally evaporated Cr were deposited on the substrates. For other experiments, chromium mask substrates were purchased from Telic; these films are produced by vacuum deposition/DC sputtering in Class 100 conditions.
After metal deposition, approximately 200 nm of 950 kDa PMMA in anisole was spin-coated onto the substrates, using a 5 s spread cycle at 500 rpm and a 30 s spin cycle at 4000 rpm with a ramp of 1000 rpm/s. The PMMA was then softbaked by placing the substrates on a 180 °C hot plate for 15 minutes.

For SU-8 lithography, one inch square substrates were prepared by rinsing with acetone and methanol and then drying with nitrogen. For gold coated substrates, the glass slides were then sputter-coated to produce an 80 nm thick gold layer. For Omnicoat treated substrates, 0.5 mL of Omnicoat was dispensed onto the substrates. After a 5 s spread cycle, the Omnicoat was spin-coated for 30 s at a speed of 3000 rpm and then softbaked for one minute on a 200 °C hot plate.

SU-8 2010 was diluted to 25% by volume in cyclopentanone. The diluted resist was then spun to a thickness of approximately 750 nm at a speed of 3000 rpm for 30 s after a 5 s spread cycle. SU-8 substrates were then softbaked for one minute at 65 °C and for two minutes at 95 °C. The temperature ramp was 100 °C/h for both steps.

B. Electron Beam Lithography (EBL)

Patterns for lithography were designed using DesignCAD software. The Nanometer Pattern Generation System (NPGS) was then used to define run files designating the dose each pattern feature would receive. For PMMA, typical doses were 200-800 μC/cm² for areas, 5-25 nC/cm for lines and 1-10 fC for points. For SU-8, typical doses were 0.5-2 μC/cm² for areas, 0.01-0.05 nC/cm for lines and 2-10 fC for points. Lithography was performed using a Leo 1430 scanning electron microscope (SEM) with the scan speed set to 10. Before writing, the electron beam was allowed to warm up and stabilize for at least half an hour. Typically, accelerating voltages (EHT) of 29 kV and 25
kV were used for PMMA and SU-8, respectively. The beam current was set to 80 μA, and the probe current was set to about 10 pA, resulting in a spot size of approximately 145. After beam optimization, probe current was adjusted to yield a specimen current of 10 pA, as measured in a Faraday cup.

C. Post-processing

After e-beam writing, samples were removed from the SEM for further processing. PMMA samples were immediately developed in either 1:1 or 3:1 isopropyl alcohol: methylisobutylketone (IPA:MIBK) for 1-2 minutes and then rinsed in IPA. SU-8 samples were post-exposure baked (PEB) on a hot plate for one minute at 65 °C and then for three minutes at 95 °C to complete cross-linking. Temperature ramps were 300 °C/h for both steps. SU-8 samples were then developed for 1-2 minutes in Nano PG Developer and rinsed with IPA.

After development, patterns were imaged using optical or scanning electron microscopy. Some samples were processed further. Developed PMMA samples were etched in 50% Cr etchant in water for 30-60 s. Gold etchant was used to remove the sputtered gold used for SEM imaging before the chromium etch was performed. After etching, the remaining PMMA was removed from the samples by rinsing with acetone.

Etched patterns could then be used as masks for UV exposure on a different substrate or as a mask for SU-8 spin-coated onto the sample itself. For the former experiment, the etched sample was placed metal film side down onto a substrate coated with the positive UV resist Shipley S1813. The substrate was then exposed with collimated UV light using an OAI mask aligner/exposure system. For the latter experiment, neat SU-8 2010 was spun onto the sample and softbaked as described in the
sample preparation section. The sample was then placed on the exposure system with the SU-8 coating facing away from the light source and exposed for 1-10 minutes. Post-exposure bake and development were completed as described above.

To determine the transmission behavior of the pillars, SU-8 EBL samples were coated with thermally evaporated metal. Approximately 10 nm of chromium was evaporated first as an adhesion layer, followed by 200 nm of aluminum. The thermal evaporation procedure is directional and leaves the vertical sidewalls of the SU-8 uncoated. Transmission through the sides of the SU-8 features was determined using an optical microscope, CCD camera, and WinView/32 software (Roper Scientific). Samples were then etched in Cr etchant in an attempt to remove the layer of metal atop the features. Future processing steps will include attempts to remove the SU-8 features with Remover PG solution to leave apertures in the metal film.

Some SU-8 features were used as molds for polydimethylsiloxane (PDMS) features. In these cases, a 10:1 mixture of PDMS prepolymer:curing agent was poured over the SU-8 features and cured for several hours at 70 °C. After curing, the PDMS slab could be peeled up for imaging of the molded features.
Figure 2 summarizes the steps for PMMA and SU-8 lithography and the various post-processing steps.

III. Results and Discussion

A. Electron Beam Lithography with Polymethylmethacrylate

Accelerating voltage (EHT) refers to the voltage used to accelerate electrons from the filament into the SEM sample chamber. Electrons strike the sample, exposing the resist and also producing secondary electrons from the resist and from the substrate. Secondary electrons provide the bulk of the exposure dose and increase the effective
beam diameter by about ten nanometers. Additionally, primary electrons experience small-angle scattering, which also increases the effective beam diameter. Forward angle scattering can be reduced by using a higher EHT, since the higher energy electrons are deflected less as they pass through the sample. For PMMA EBL, it is therefore desirable to use the highest possible EHT for sharp, well-defined features. Figure 3 shows images of the same pattern written at EHT values of 25 kV and 29 kV, the maximum allowable voltage for the instrument used. The higher accelerating voltage produced noticeably sharper and narrower features as compared to the lower EHT.

Exposed PMMA is developed in a mixture of isopropyl alcohol (IPA) and methylisobutylketone (MIBK). MIBK acts as the developing agent, and the relative concentration of IPA determines the speed and sensitivity of resist development. A 1:1 ratio produces harsher development conditions, resulting in faster development but lower contrast. Higher contrast can be obtained by using a 3:1 IPA:MIBK solution. Figure 4

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shows the results of developing exposed PMMA samples in varying developer conditions. For the conditions investigated, developing for two minutes in 3:1 IPA:MIBK developer yielded the best results, as determined by the sharpness of the resulting features.

![Image](image1.png)

Figure 4. Effect of developer concentration and duration on PMMA patterns. Images shown are optical micrographs. For each sample, the same pattern of funnels was written four times with the dose received increasing from top to bottom. Development conditions were as follows: (a) 1 min in 1:1 IPA:MIBK, (b) 1 min in 3:1 IPA:MIBK, (c) 2 min in 3:1 IPA:MIBK. Scale bars are each 5 µm.

Different deposition methods for the chromium layer on the substrate were found to affect the etching step during processing. Figure 5 shows etched patterns in thermally evaporated chromium versus patterns etched in a mask-grade chromium layer, which is produced by vacuum deposition/DC sputtering in a class 100 clean room environment.

![Image](image2.png)

Figure 5. Effect of Cr film deposition on etching results. As in Fig. 4, the same pattern was written four times on each sample with applied doses of 200 to 500 µC/cm², increasing from top to bottom. The underlying substrate was (a) 130 nm thermally evaporated chromium and (b) mask grade chromium. Images are optical micrographs; white scale bars are 5 µm.
Patterns in the mask-grade chromium etched more cleanly and appeared to have sharper points and edges, probably because of the higher-quality, more uniform film.

Figure 6 shows images of a single pattern through the various processing stages from developed PMMA to etched chromium film to developed SU-8 structures. The sample shown was written on a layer of thermally evaporated chromium. It is hoped that using a mask-grade chromium film will allow for cleaner etched patterns, and consequently better SU-8 exposure. Previous research has shown that the height of the polymerized SU-8 features is proportional to the size of the aperture through which the exposing radiation is transmitted. In Figure 6, it is evident that the narrow line resulted in a much shorter feature than the wider funnel patterns. Future plans therefore include

Figure 6. Complete processing of a single PMMA sample. (a) Developed patterns in PMMA. (b) Etched patterns in chromium film after PMMA removal. (c) Polymerized SU-8 structure produced by exposing the photoresist through the etched pattern. (d) The same SU-8 structure imaged at an 81° tilt.

optimizing the SU-8 exposure dose to produce topography proportional to the light transmitted through the etched patterns.

**B. Electron Beam Lithography with SU-8**

SU-8 is a much more sensitive EBL resist than PMMA and requires exposure doses approximately two orders of magnitude less than those used for PMMA. Figure 7 shows a pattern composed of several adjacent squares of varying doses which increase from 0.5 to 1.0 \( \mu \text{C/cm}^2 \). Structure height increases with increasing dose. This effect has been seen by other groups and can be used to produce gray scale structures.\(^\text{11}\) Features with up to 16 distinct levels and vertical resolution of about twenty nanometers have been produced using this technique.\(^\text{12}\) Future work will focus on writing similar gray scale features which scale to nanometer dimensions. The features could then be used to mold PDMS channels.

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Figure 7. Effect of exposure dose on SU-8 structures. Images are scanning electron micrographs of a series of steps produced by varying the exposure dose received by each block. (a) Four blocks, receiving doses of 0.5, 0.7, 0.8 and 1.0 \( \mu \text{C/cm}^2 \) from left to right (b) The same structure imaged at an \( 81^\circ \) with doses decreasing from foreground to background.

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SU-8 EBL was investigated on a variety of substrates. Figure 8 shows the same pattern written in SU-8 on a variety of substrates, including those with a conducting metal layer below the SU-8 (a and b) and those without (c and d). Substrate composition seemed to have little effect on the resulting structures, except in the case of substrates coated with Omnicoat (d). Omnicoat is a proprietary substrate coating meant for increasing adhesion of SU-8 to surfaces and for aiding in resist lift-off (removal).

![Figure 8](image_url)

Figure 8. Effect of substrate on SU-8 EBL. Images are scanning electron micrographs of pillars produced by writing an array of 1 μm points in SU-8 on various substrates: (a) 80 nm sputtered Au, (b) 130 nm thermally evaporated Cr, (c) glass, (d) Omnicoat on glass.

Samples coated with Omnicoat had structures that were wider, less resolved and sometimes distorted. This result is consistent with those of similar experiments in the literature. Distortion was likely caused by swelling during the development step. This problem can be minimized by increasing the exposure dosage and consequently
increasing the amount of cross-linking. SU-8 requires a higher dose when exposed on a substrate coated with Norland Optical Adhesive 61, a UV-curing polymer used for bonding optical elements; the same may be true for samples coated with Omnicoat.

The pillars seen in Figure 8 will be used for additional fabrication steps. Coating the features with metal and subsequently removing the SU-8 with Remover PG will leave regular arrays of nanometer scale apertures. This technique will provide an alternative to nanosphere lithography, which produces randomly distributed holes and is limited in the aspect ratio of the holes produced.

C. Isolating Single Pores in Polycarbonate Track Etched (PCTE) Membranes

Preparation of PCTE membranes, such as the one in Figure 9, for stochastic sensing makes use of a commercial product that can be used to create numerous pores of variable diameter fairly easily. One drawback, however, is the requirement that an individual pore be isolated before use.

Special order membranes, with a pore density of about 50 pores per cm², have been used to aid in this process. In such a case, individual pores were identified by coating the membrane with a layer of sputtered gold and allowing a fluorescein solution to wick through to the other side. Dye droplets were identified using fluorescence microscopy, and an individual pore was isolated by using tape to cover adjacent pores. The many advantages of using PCTE membranes make finding a more efficient and effective way of isolating single pores desirable.
Preliminary investigations to this end have included sealing PCTE membranes between PDMS so that they could be addressed by a system of micro- or nanochannels. Researchers at the University of Illinois have shown that a PCTE membrane sealed between crossed channels in PDMS can transport analyte molecules between the two channels.\(^\text{13}\) This method does not isolate a single pore, but it does limit the number of pores available for transport to those in the region where the two channels cross. EBL could be used to write an array of appropriately sized apertures in photoresist on top of a PCTE membrane. For a membrane with a pore density of \(4 \times 10^8\) pores per cm\(^2\), a hole 560 nm in diameter would be expected to isolate a single pore. If spacing between the rows of the array were the same as the width of the microfluidic channel, then a single pore should be isolated when the patterned membrane is sealed between two crossed PDMS channels; Figure 10 depicts how such a device would look. It was determined that SU-8 could not be used for the purpose of writing the array, as polycarbonate is soluble in the SU-8 developer solution. However, work with PMMA is ongoing.

**D. Producing Molds in Polydimethylsiloxane**

Artificial pores produced using PDMS soft lithography are advantageous because individual pores can be produced quickly, reproducibly and inexpensively from a single master. PDMS pores also offer the additional benefit of being easily integrated with other access.
microfluidic structures. Using the standard formulation of PDMS Sylgard 184 it is possible to obtain a resolution of approximately 150 nm, but other formulations can be used to produce structures as small as 80 nm. Resistive pulse sensors have been made using SU-8 and polystyrene masters to mold PDMS. These earlier studies have used EBL to pattern nanoscale structures in polystyrene, and then used standard photolithography to add micron-scale connections with SU-8. The SU-8 EBL work discussed in this paper makes it likely that an entire master could be fabricated in one EBL step using SU-8 resist.

SU-8 structures produced as discussed in Section B have been used to mold PDMS. Figure 11 shows an optical micrograph of PDMS molded from the SU-8 features shown in Figure 6. PDMS structures will also be examined using scanning electron microscopy and possibly atomic force microscopy to determine their depth more accurately. Future work will include fabrication of reproducible channels with nanoscale dimensions and integration of these channels into devices with microfluidic interconnects for use in separations and resistive pulse sensing.

**IV. Conclusions and Future Work**

Effective process conditions, including exposure dose, development time and developer strength, and etch time have been determined for EBL in PMMA. SU-8 features have been successfully polymerized through etched patterns produced from
lithography in PMMA. Future work will include optimizing the SU-8 UV exposure dose in order to produce gray scale features. Direct writing of SU-8 by EBL has been achieved, and appropriate doses for the desired patterns have been determined.

Possibilities for continuing work include fabrication of gray scale structures based on exposure dose, investigation of the transmission properties of SU-8 features, and further processing of pillar features as an alternative to nanosphere lithography. Additionally, SU-8 structures produced by UV-exposure through chromium masks have been used to mold PDMS. The next step is to determine optimum conditions for molding nanochannels in PDMS and subsequently to add microfluidic connections to the nanochannels. Isolation of a single PCTE membrane pore using EBL of SU-8 to define an array of holes on the membrane was unsuccessful, but work using PMMA is in progress.

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