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Full Length Article

# Selective etching of PDMS: Etching technique for application as a positive tone resist

S.Z. Szilasi[a,*], C. Cserháti[b]

[a] Institute for Nuclear Research, Hungarian Academy of Sciences, H-4001 Debrecen, P.O. Box 51, Hungary
[b] University of Debrecen, Dept. of Solid State Physics, H-4010 Debrecen, P.O. Box 2, Hungary

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ABSTRACT

Although, poly(dimethylsiloxane) (PDMS) is a widely used material in numerous applications, such as micro- or nanofabrication, the method of its selective etching has not been known up to now. In this work authors present two methods of etching the pure, additive-free and cured PDMS as a positive resist material.

To achieve the chemical modification of the polymer necessary for selective etching, energetic ions were used. We created 7 μm and 45 μm thick PDMS layers and patterned them by a focused proton microbeam with various, relatively large fluences. In this paper authors demonstrate that 30 wt% Potassium Hydroxide (KOH) or 30 wt% sodium hydroxide (NaOH) at 70 °C temperature etch proton irradiated PDMS selectively, and remove the chemically sufficiently modified areas. In case of KOH development, the maximum etching rate was approximately 3.5 μm/min and it occurs at about $7.5 \times 10^{15}$ ion × $cm^{-2}$. In case of NaOH etching the maximum etching rate is slightly lower, 1.75 μm/min and can be found at the slightly higher fluence of $8.75 \times 10^{15}$ ion × $cm^{-2}$.

These results are of high importance since up to this time it has not been known how to develop the additive-free, cross-linked poly(dimethylsiloxane) in lithography as a positive tone resist material.

## 1. Introduction

The continuous development of lithographic techniques demand the improvement of both the development methods and resist materials. By emerging new methods or materials, new possibilities become attainable making the existing methods simpler, more reliable, better quality or faster.

Poly(dimethylsiloxane) (PDMS) is the most widely used silicon-based, organic, cross-linkable polymer. The cross-linked PDMS is a rubbery solid, it does not permanently deform under stress or strain. Since it is chemically inert and by a chemical or physical treatment it can be turned into biocompatible, PDMS is widely used in medical fields also. Its high oxygen permeability, good mechanical properties, chemical stability and easy processing make it an ideal raw material for ophthalmological products (e.g. contact lenses [1]) or implants that are in direct, and sometimes prolonged contact with human tissues [2]. The high optical clarity, low attenuation [3] and the excellent stability against weathering makes this polymer applicable for creating optical waveguides or microlenses [4,5]. Poly(dimethylsiloxane) is undoubtedly the most commonly used microfluidic material in research laboratories. It is also hydrophobic, chemically resistive, cost effective and easy to use. With plasma treatment, it can easily be bonded to another PDMS layer, to a glass or Si substrate [6]. All these features together are highly desirable at fabrication and prototyping of microfluidic chips and lab-on-a-chip devices. These devices, and thus Poly (dimethylsiloxane), have demonstrated significant potential in countless applications, such as chemical separation [7], separation and processing of biological cells [8], fuel cells [9], chemical microreactors [10] or even spacecraft thrusters [11].

Despite its versatility and the numerous advantageous properties mentioned above, PDMS is mainly used as a mold, a casting or replicating material [12]. However, recent researches pointed out that PDMS can be applied as a resist material also. In 2002, Constantoudis et al. applied electron beam lithography to pattern a thin layer of liquid, uncured PDMS and then used the structures as a hard mask [13]. In 2009, Szilasi et al. observed that significant compaction occurs at the irradiated areas [14] and applied it to create parallel lines with curved surfaces [15] and microlenses [4] in one step, without the need of any further development. Microlenses were created later also by Kato et al. by varying the distribution of the proton dose [16]. In 2011, Tsuchiya et al. reported that the uncured, liquid phase PDMS polymer crosslinks, thus acts as a negative resist if it is exposed to proton irradiation and created microstructures in it [17]. Bowen et al. created structures by electron beam lithography and studied the change of Young's modulus

* Corresponding author at: Institute of Nuclear Research of the Hungarian Academy of Sciences, H-4026 Debrecen Bem tér 18/c, H-4001 Debrecen, POB. 51, Hungary.
*E-mail address:* szilasi.szabi@gmail.com (S.Z. Szilasi).

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as a function of the delivered dose in 2012 [18]. In 2016, Gorissen et al. patterned PDMS through SU8 mask by reactive ion etching (RIE) [19]. Others use various additives to make the pre-polymer photosensitive [20] and apply photolithography. In one of our recent work, we have introduced the additive-free, cured PDMS as a negative tone resist material [21]. This paper is the continuation of that work introducing how to selectively etch PDMS as positive resist. That paper provides data on the solvent compatibility of poly(dimethylsiloxane) microstructures but further detailed works such as [22–24] contain even more detailed information on this topic.

Since protons are light ions, they do not sputter PDMS, which can be verified by SRIM simulations [25]. This means that a proton beam can not be used to directly sputter material from a target as in case of focused ion beam (FIB) technique that utilizes heavier ions to create microstructures.

The key to the application of PDMS as a resist material is the change of its chemical properties where it is exposed to various types of radiation. Due to irradiation, chain scissioning happens in the polymer, the main Si-O-Si chain brakes, functional groups split and the volatile products (e.g. $H_2$, $CH_4$ and $C_2H_6$ gases) leave the irradiated volume [26,27]. As a result of these processes, PDMS shrinks at the place of irradiation and the initially elastic polymer becomes a rigid, brittle and glass-like material [15]. Since the cured PDMS is chemically very resistant, it has been unknown how to selectively etch the modified areas to create micro/nanostructures directly in the polymer.

Some studies show that cured and unirradiated PDMS resists potassium hydroxide (KOH) solution relatively well. Brugger et al. used PDMS seal rings during etching of silicon wafers with KOH solution at 60 °C [28]. In these experiments, the PDMS rings were reused many times after more than 30 h of etching. Mata et al. found that shallow PDMS microstructures damage after immersing them into KOH solution for 27 h [29].

The above result show that cured poly(dimethylsiloxane) withstands KOH solution for an extended period of time, but it is also known that amorphous silicon, crystalline silicon and $SiO_2$ can be selectively etched by the same solution [30,31]. Since the irradiation degrades the polymer significantly which becomes glass-like, and $SiO_x$ forms [21], we expected that the reaction rate of KOH with the degraded PDMS would increase. In many applications potassium hydroxide is almost interchangeable with sodium hydroxide (NaOH). The two substances have very similar chemical properties, so we tested and compared the performance of both in etching irradiated PDMS. The result of this study is the subject of this paper.

Since the method of selective etching of PDMS as a positive tone resist has not been known up to know, these results may be of high importance in various micro- and nanolithography techniques. Our findings make possible the direct/maskless creation of micro- and nanostructures, microfluidic systems or even lithography masks in fewer steps, without the need of molds, directly in cured PDMS.

## 2. Material and methods

To create the samples, Sylgard 184 kit (Dow-Corning) was used. The base polymer and the curing agent were mixed with the volume ratio of 10:1, respectively, spin coated on glass substrates in 7 μm and 45 μm thicknesses and baked at 125 °C for 30 min.

The samples were irradiated by a 2 MeV focused proton beam at the nuclear microprobe facility at HAS-ATOMKI, Debrecen, Hungary [32]. The size of the beam spot was 2.5 μm × 2.5 μm, the scanning resolution of the irradiated patterns (i.e. the distance between neighbouring pixels) was ~1 μm. Since the beam spot was larger than the scanning resolution, the beam spot overlaps with itself multiple times when scanning neighbouring pixels. SRIM calculations showed that the penetration depth for 2 MeV protons is ~85 μm in PDMS. Since the polymer layer is much thinner than the maximal penetration depth, the particles easily penetrate through the resist layer without considerable lateral scattering making the creation of vertical sidewalls possible. To test if the etching method works and to find the ideal irradiation and etching parameters, 7 μm thick samples were irradiated with 15 parallel lines. Each line received a different fluence in increasing order between $1.33 \times 10^{15}$ ion × $cm^{-2}$ (2130 nC × $mm^{-2}$) and $2 \times 10^{16}$ ion × $cm^{-2}$ (32,050 nC × $mm^{-2}$) in approximately $1.25 \times 10^{15}$ ion × $cm^{-2}$ (2000 nC × $mm^{-2}$) increments. These samples were called fluence test samples. Other test structures, such as circles with different diameters, squares in different sizes and lines with various widths were also irradiated in 7 μm and 45 μm thick cured PDMS. These structures received $1.19 \times 10^{16}$ ion × $cm^{-2}$ (19,000 nC × $mm^{-2}$) fluence. The beam current was 1.4 nA in every case.

To remove the irradiated areas of the cured PDMS, 30 wt% Potassium Hydroxide (KOH) and 30 wt% sodium hydroxide (NaOH) were used. The samples were placed in one of these solutions for various times to find the best etching parameters. Since the temperature of the solutions was 70 °C in every case, the beaker needed to be covered to avoid evaporation and thus the change of the concentration of the etchant. The solutions were continuously stirred magnetically during etching. The volume of the etchant was 30 $cm^3$ in every case and after etching 3–4 samples in one experiment, the saturation of the etchant was not experienced.

The samples were inspected visually to determine when the structures were etched completely and all the visible residues of the irradiated area had been removed. After rinsing the patterned sample in DI water and letting it dry, sometimes small crystals could be seen on the surface of the sample. Energy-dispersive X-ray spectroscopy (EDS) investigations showed that these small crystals contain potassium and sodium which indicates that these are residues of the etchant. To remove these crystals and achieve a clean surface, the samples, were immersed into 5:1:1 $H_2O$:$H_2O_2$:HCl decontamination solution for 2 min and then they were rinsed in distilled water.

The etched structures were investigated by optical microscopy and scanning electron microscopy (SEM).

## 3. Results and discussion

A fluence test sample, that was irradiated with fifteen parallel lines and each line received different fluences, was attempted to etch at room temperature in 30 wt% KOH and 30 wt% NaOH. The etchant was stirred continuously and the progress of etching was recorded in every 5 min. After 50 min, no etching was observed at any fluences in either etchants.

This experiment was repeated at elevated temperatures. The observations show that in this case both KOH and NaOH etches effectively the irradiated areas of the cured PDMS while the unirradiated parts do not etch away. This indicates that the etching rate of the irradiated PDMS is highly dependent of the temperature of the KOH and NaOH solutions. The etching in both cases was found to be isotropic and homogenous.

The mictostructures were investigated with an optical microscope before and after etching and swelling has not been observed. Apparently, aqueous solutions of KOH and NaOH do not swell PDMS unlike numerous organic solvents [21].

### 3.1. Etching with potassium hydroxide (KOH)

A fluence test sample was taken out from the KOH solution after certain period of times. After each time, the advancement of the etching process have been investigated. The cured PDMS is quite resistant to the KOH solution, while the irradiated areas etch quickly. After 2 min of etching, the lines with $5.31 \times 10^{15}$ ion × $cm^{-2}$ (8500 nC × $mm^{-2}$), $6.53 \times 10^{15}$ ion × $cm^{-2}$ (10,450 nC × $mm^{-2}$), $8.02 \times 10^{15}$ ion × $cm^{-2}$ (12,830 nC × $mm^{-2}$), $9.09 \times 10^{15}$ ion × $cm^{-2}$ (14,550 nC × $mm^{-2}$) fluences were etched completely to the substrate (Fig. 1). Higher magnification images show, that the lines with $5.31 \times 10^{15}$