Stability of the hydrophilic behaviour of oxygen plasma activated SU-8

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Abstract

The effect of O₂ plasma treatment on surface energy, topography and surface chemistry of the negative photoresist epoxy novolak SU-8 was investigated by contact angle goniometry, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Directly after plasma treatment, the surfaces were completely wetted by water with a contact angle between water and the SU-8 surface below five degrees. The surface free energy can be increased significantly depending on the plasma dose. The surfaces remained hydrophilic for several months showing a moderate hydrophobic recovery. The surface topography of the plasma treated SU-8 showed a formation of nanoscale aggregates. The rms-roughness of the topography was correlated with the plasma dose. An increased plasma dose induced aggregates of up to 200 nm in size. XPS measurements revealed changes in surface chemistry due to the oxygen plasma process and an increased antimony concentration on the surface.

Keywords: photo resist, SU-8, surface energy, plasma, hydrophilization, surface activation, antimony, roughness, XPS, contact angle, AFM

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1. Introduction

Bio micro-electro-mechanical systems (bio-MEMS) and microfluidic devices are usually built up from chemically inert materials such as silicon, glass, poly-dimethyl-siloxane (PDMS), poly-methyl-methacrylate (PMMA), or SU-8 [1-8]. SU-8 has turned out to be an advantageous material for fabrication of MEMS [4, 6, 8], rapid prototyping and cheap production, integration of sensors in a microfluidic system [5], or rapid 3-dimensional manufacturing of microfluidic systems using a scanning laser system [9].

For microfluidic systems used for nano-bio applications, it is decisive to be able to use water in the devices. Unfortunately, the native SU-8 surface is highly hydrophobic and has a low surface energy. This implies that microfluidic systems fabricated from native SU-8 require an active pumping mechanism. The polymer surface has to be rendered hydrophilic to enhance the capillary flow. To this end, wet chemical or plasma based processes may be used. A contact angle of \( \theta = 23^\circ \) can achieved with a wet chemical process [10]. Plasma processes can be used for resist stripping or activation of polymer surfaces. Oxygen plasma treatment with additional fluorinated gases allows for efficient stripping and removal of SU-8 [11, 12]. Also plasma activation of polymer surfaces is widely used and yields completely wettable surfaces with water contact angles of less than five
degrees [13-15]. Thus, it is attractive to employ a plasma process to achieve a highly hydrophilic SU-8 surface. In addition to the increased surface energy, plasma treatment of polymer surfaces often increases the surface roughness and induces nanoscale structures such as tiny bubbles which form at the surface [16-18]. Such structures can be attributed to a surface rearrangement during the plasma process, probably by cross-linking within the polymer-surface or by preferential etching [16].

We performed contact angle goniometry of SU-8 surfaces to characterize the wetting behavior of the plasma activated SU-8 as it is used in bio-MEMS devices. In order to address the shelf-life of microfluidic devices based on plasma treated SU-8 we investigated the hydrophobic recovery of the polymer surface over several weeks. The contact angle measurement with different liquids allows for calculating the surface energy which is needed to predict the contact angle and the capillary pressure of other liquids. We also investigated the effect of plasma treatment on the surface topography by atomic force microscopy (AFM). X-ray photoelectron spectroscopy (XPS) was used to investigate the influence of the plasma process on the surface chemistry.

2. Materials and Methods

Substrates and coating

Silicon (100) wafers with a three nanometer native oxide layer were used as substrates. Two different types of SU-8 (Microresist Technology GmbH, Berlin, Germany) were used in this study. SU-8 is delivered as an organic resin solution. We investigated SU-8 photoresists with the solvents γ -butyrolactone (GBL, trade name SU-8) and cyclopentanone (trade name SU-8 2000) in different concentrations (SU-8 10, 50, 100, SU-8 2025). For example, SU-8 10 solution contains 35-40 wt. % volatiles, 2.8 wt. % SbF$_6$ salt, and less than 1 wt. % Sb [19]. The photoactive lewis acidic catalyst triarylsulfonium hexafluoroantimonate acts as photo acid generator [20].

In the following, we describe the preparation for SU-8 10. The fabrication process followed the manufacturer’s recommendations. For the other types of SU-8 resists, the process parameters for soft-bake, exposure, post exposure bake, and hard-bake have to be modified accordingly. First, the substrate was cleaned by subsequently applying several milliliters of acetone and ethanol for 30 seconds at 5000 rpm. Then, approximately five milliliters of SU-8 were applied to the surface. The spin coating rate was ramped up in several steps to a maximum of 2500 rpm, resulting in a film thickness of about 12 micrometers. A pre-bake step was carried out for two minutes at 65 °C on a hotplate. The temperature was then ramped up to 95 °C and then kept constant for four minutes. Afterwards, the wafer was cooled down slowly to room-temperature. Then, the wafers were exposed in a mask aligner for two minutes (Süss MicroTec AG, Garching, Germany). After a post exposure bake with the same parameters as for the pre-bake, the wafers were developed in SU-8 XP (Microresist Technology GmbH) for two minutes. To allow for final cross-linking and to eliminate residual solvent, a hard-bake step was carried out at 160 °C for two minutes.

For the plasma treatment procedure, we used a microwave-plasma-generator (13.56 MHz, Plasma Technology, Rottenburg, Germany). An oxygen flow of 36 sccm at a pressure of approximately $2 \times 10^4$ bar was maintained with 0.8 V, 1.0 V, and 1.3 V potential, thus resulting a plasma power of 50 W, 110 W, and 150 W.

The plasma treated SU-8 samples were then stored in the laboratory under ambient conditions. Experiments have been conducted following two different strategies. The first batch of samples has been used for one set of measurements only and discarded afterwards. The others have been re-used
over the entire measurement period. These were cleaned after each contact angle measurement with acetone, isopropanol, and de-ionized water (18.2 MΩ). The second set mimics a long term laboratory usage, while set one resembles a long-term storage before use.

**Atomic force microscopy**

Surface topography was measured by atomic force microscopy (AFM) in a tapping mode (Dimension 3100, Veeco, Santa Barbara, CA). Silicon tips with a nominal resonance frequency of 300 kHz were used (MikroMasch, Tallinn, Estonia and BudgetSensors BS-TAP300). Image processing was done with the SPIP 4.3 software (Image Metrology A/S, Lyngby, Denmark). After a second order polynomial plane correction, the root mean square (rms) surface roughness was calculated by $r_{\text{rms}} = \left[ \frac{1}{N} \sum_{n=1}^{N} (z_n - \mu)^2 \right]^{1/2}$. Here, $N$ is the number of data points of the image, $z_n$ is the height data of the $n$-th point, and $\mu$ the average height. To determine the ratio between the surface area of the corrugated surface $A_r$ and the projected surface area $A_p$, the roughness factor (surface area ratio) $r = A_r/A_p$ was calculated using the corresponding SPIP 4.3 routine. Despite the high topographic resolution of AFM it should be noted that roughness measurements by AFM are affected by the choice of scan range and tip geometry [21]. To eliminate effects due to varying scan size, all images were taken at a scan size of $500 \times 500$ nm$^2$ with $512 \times 512$ pixel$^2$. With a pixel size of less than 1 nm$^2$, the nanoscale corrugations could be captured consistently.

**Contact angle measurements**

Contact angle goniometry was conducted to determine the surface energy of the specimens over time after the plasma treatments. We employed a DSA-10 contact angle goniometer (Krüss GmbH, Hamburg, Germany) using de-ionized water, glycerol, benzyl alcohol, ethylene glycol, and diiodomethane under ambient conditions (21 °C; relative humidity: 48-52%). In this implementation, the surface energy is determined by contact angle measurements of sessile drops on solid surfaces [22-24]. The automated analysis of the system is based on the Owens-Wendt-Rabel-Kaelble [23, 25, 26] method. A circular fitting algorithm was used for the identification of contact angles above five degrees. Angles below five degrees could not be evaluated precisely. Data of at least three drops per wafer were averaged for each liquid. The error bars represent the standard-deviation about the measured contact angles. The stored samples were characterized employing water and diiodomethane, whereas the re-used surfaces were tested with all five liquids.

The relation between the contact angle $\theta$ of the liquid at the solid interface and the surface energy of the liquid $\gamma_l$, the solid $\gamma_s$, and the interfacial energy $\gamma_{sl}$ between the solid and the liquid can be expressed by the Young equation [27]

$$\gamma_{sl} = \gamma_s - \gamma_l \cos(\theta) \tag{1}$$

One can separate the surface energies $\gamma_l$ and $\gamma_s$ into two components of interaction: the dispersive part $\gamma^d$ representing the van der Waals interaction and the polar part $\gamma^p$. The interfacial energy can then be calculated by subtracting the geometric mean of both polar (permanent dipoles) and dispersive (induced dipoles) contributions [22] leading to

$$\gamma_{sl} = \gamma_s + \gamma_l - 2 \sqrt{\gamma_s \gamma_l \gamma^p \gamma^d} \tag{2}$$

The extended equation can finally be transformed into a linear equation of the type $y = mx + b$ as:

$$\frac{1 + \cos(\theta)}{2} \frac{\gamma_l}{\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p \frac{\gamma_l^p}{\gamma_l^d} + \gamma_s^d}$$

$$\tag{3}$$
Since the surface tension parameters of the test liquids are known and the contact angle is being measured, both parameters $\gamma_s^p$ and $\gamma_s^d$ can be obtained from a linear least square fit. The surface energy of the solid is given by $\gamma_s = \gamma_s^p + \gamma_s^d$. Contact angles for other liquids can then be estimated using Young’s equation with known $\gamma_l$ and $\gamma_s$. The error bars in the surface energy calculations include only the standard deviation from this fitting procedure, they do not represent the statistical variation over several experiments.

For the rough surfaces the measured macroscopic contact angle $\theta_W$ is affected by the surface corrugations. Wenzel [28] suggested to correct for the surface roughness by introducing a roughness factor $r_W$ which represents the ratio between true surface area and projected surface area. The macroscopic contact angle is related to the contact angle of the smooth surface by

$$\cos(\theta_W) = r_W \cos(\theta_0)$$

(4)

This implies that the roughness amplifies the wetting properties of a surface. Kamusewitz and Possart showed that the geometric roughness factor $r = A_r/A_p$, obtained by AFM, and Wenzel’s roughness factor $r_W$, derived from contact angle measurements, are correlated with $r_W \approx r$ [29]. For rough low-energy surfaces the contact angle of the corresponding flat surface $\theta_0$ can reliably be obtained from dynamic contact angle measurements [29, 30]. However, for high energy surfaces with contact angles smaller than 15°, contact angle measurements are difficult. Close to complete wetting ($\theta < 5°$), we found that our measurements were not reliable. Thus, a reliable estimation of the contact angle by measurement of the contact angle hysteresis could not be obtained on freshly plasma activated SU-8 surfaces. Instead, the measured static contact angle was taken as an estimate for the contact angle $\theta_W$. Thus, the calculated surface energies could not be corrected for the surface roughness and the apparent surface energy is given.

**XPS measurement**

X-ray photoelectron (XPS) analyses were performed using a VG Theta Probe spectrophotometer (Thermo Electron Corporation, West Sussex, UK) equipped with a concentric hemispherical analyzer and a two-dimensional channel plate detector with 112 energy and 96 angle channels. Spectra were acquired at a base pressure of $10^{-8}$ mbar using a monochromatic Al-K$_\alpha$ source with a spot size of 300 µm. Differential charging on this highly isolating surfaces was compensated with a combined low energy electron-argon-ion flood gun. The instrument was run in the standard lens mode with electrons emitted at 53° to the surface normal and an acceptance angle of ±30°. The analyzer was used in the constant analyzer energy mode. Pass energies used for survey scans and detailed scans were 250 eV and 100 eV, respectively. Detailed scans were acquired for carbon C 1s, oxygen O 1s, antimony Sb 3d, and nitrogen N 1s. Under these conditions, the energy resolution (full width at half maximum height, FWHM) measured on gold Au 4f$_{7/2}$ is 1.95 eV and 0.82 eV, respectively. Acquisition times were approximately five minutes for survey scans and 30 minutes (total) for high-energy-resolution elemental scans. These experimental conditions were chosen in order to obtain an adequate signal-to-noise ratio in a minimum time and to limit beam-induced damage. All recorded spectra were referenced to the carbon C 1s signal with the lowest binding energy at 184.8 eV which was attributed to aromatic and aliphatic carbon of the SU-8 polymer. Data were analyzed using the program CasaXPS [Version 2.3.5, www.casaxps.com]. The signals were fitted using Gaussian-Lorentzian functions and least-squares-fit routines following Shirley iterative background subtraction. Sensitivity factors were calculated using published ionization cross sections [31] corrected for the attenuation length dependence with kinetic energy.
3. Results and Discussion

Several specimen subjected to different processing procedures were characterized in order to investigate the influence of the solvent and other process parameters. For resist films that were prepared following the standard procedure, the contact angle between water and SU-8 (solvent: GBL) and SU-8 2000 (solvent: cyclopentanone) were 74° and 90° directly after hard baking. The corresponding surface energies for the native surfaces of SU-8 and SU-8 2000 differ by $\Delta \gamma = 19$ mN/m (Table 1). Other variations in the manufacturing process such as different soft bake times, skipping the hard bake with or without development in SU-8 XP resulted in negligible variations of the contact angle of less than five degrees. Thus, the different surface energies of the native polymer surfaces have to be attributed to the respective solvents GBL and cyclopentanone, since the manufacturing process itself did not affect the surface energy. Directly after plasma treatment, the activated polymer surfaces were highly hydrophilic with a very small contact angle ($\theta < 5^\circ$). There was no measurable influence of the solvent GBL or cyclopentanone on the surface energy of a plasma activated SU-8 surfaces.

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\gamma_{\text{total}}$ (mN/m)</th>
<th>$\gamma_{\text{disperse part}}$ (mN/m)</th>
<th>$\gamma_{\text{polar part}}$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GBL (SU-8)</td>
<td>45.20 ± 0.88</td>
<td>38.69 ± 0.65</td>
<td>6.51 ± 0.23</td>
</tr>
<tr>
<td>Cyclopentanone (SU-8 2000)</td>
<td>26.48 ± 0.36</td>
<td>22.00 ± 0.23</td>
<td>4.48 ± 0.14</td>
</tr>
</tbody>
</table>

Table 1: Surface energy of the SU-8 samples fabricated with the solvents $\gamma$-butyrolactone (GBL) and cyclopentanone.

The hydrophobic recovery of the activated surfaces was monitored by contact angle and surface energy measurements over several weeks. To test the hydrophobic recovery of activated SU-8 under usage conditions, two sets of specimen were investigated. One set was stored until characterization, whereas the second set was cleaned after each measurement and re-used. After activation by $O_2$-plasma treatment (50 W) for several minutes (2 min, 4 min, 6 min, and 8 min), the evolution of the contact angle of water on a SU-8 surface was monitored as shown in Fig. 1. After one week the contact angles of the unused samples (Fig. 1 a) recovered slightly ($\theta = 17^\circ$, 11°, 9°, and 8°). The contact angle of the samples then slowly recovered to values between $\theta = 15^\circ$ (8 min exposure) and $\theta = 36^\circ$ (2 min exposure) after 74 days. Clearly, a higher plasma dose led to a more stable surface activation. For the same plasma parameters, the re-used specimen (Fig. 1 b) showed a rapid hydrophobic recovery ($\theta = 39^\circ$, 36°, 36°, and 32°) during the first week. After this initial fast recovery, the contact angles increased to values around 45° after 61 days. The final contact angle depended only weakly on the plasma dose.
The evolution of the surface energy was monitored for samples treated by a plasma with 110 W (stored samples, **Fig. 2 a**) and 150 W (cleaned and re-used samples, **Fig. 2 b**) intensity. Directly after plasma treatment, the surface energy was $\gamma_s = 79\pm1$ mN/m. Within the range of our experimental parameters, this value was independent from plasma treatment time and intensity. After 116 days, the surface energy of the stored samples had reduced slightly to values between 70 mN/m (8 min treatment) and 60 mN/m (2 min treatment). Here, we also observed a rapid initial recovery for the cleaned and re-used SU-8 samples. Within the first week, the surface energy decreased by about 10 mN/m. After 116 days, surface energies between 48 mN/m (2 min treatment) and 57 mN/m (8 min treatment) were reached. For both types of samples, unused and re-used, the decay was slower for surfaces treated with a higher plasma dose.

From the experiments it is evident that a higher plasma dose leads to a more stable modification. A comparison between the usage conditions highlights the noticeable long shelf life of the activated and stored SU-8 surfaces which remained hydrophilic for more than three months. Of course, usage reduces the shelf-life. The repeated use and cleaning processes lead to a faster increase of hydrophobicity, most probably due to contamination, swelling, and restructuring of the outermost polymeric surface. A reaction of surface hydroxy- or carboxy-groups with the test liquids such as diiodomethane is also possible.
As discussed before, a longer and more intense plasma treatment is helpful to stabilize the hydrophilic properties. The plasma treatment also affects the surface topography. The surface roughening was characterized by AFM. The untreated surface only exhibits small surface corrugations (Fig. 3 a). Depending on the plasma dose (power × treatment time), aggregates with a size between one nanometer (4.5 kWs) and more than 150 nm (72 kWs) were formed. A low dose plasma treatment (18 kWs) leads to a reorganization of the polymer-surface with round aggregates (Fig. 3 b). For an increasing plasma dose (54 kWs), the surface exhibits irregular structures due to plasma etching (Fig. 3 c). The topographic AFM data is represented by the height histograms in Fig. 4. With increasing plasma intensity the height distributions broaden and the average increases. For the 50 W plasma treatment, the height distribution is on the order of 10 nm to 80 nm (Fig. 4 a). For higher plasma intensities, the height distribution extends up to 200 nm (Fig. 4 b). The root-mean-square (RMS) roughness of the surface topography increases with the plasma dose as shown in
Due to the competition between etching and reformation, the RMS-roughness saturates for higher plasma doses. The relationship between plasma treatment dose and the topographic surface modification is reproducible as can be seen from the overlap of RMS values obtained on surfaces treated with 50 W and 110 W plasma power. This effect is more pronounced for the surface area ratio (Fig. 5 b). The surface area ratio saturates at approximately $r = 35\%$. Since the surface is highly hydrophilic, the surface roughness amplifies the wetting of water on SU-8. Thus, the increased surface roughness contributes to the stabilization of the hydrophilic properties of the plasma activated SU-8 surface.
In order to correlate the changes in surface energy and topography with the surface chemical composition, X-ray photoelectron spectroscopy (XPS) measurements were performed (Fig. 6). The atomic elemental composition is summarized in Table 2. For a non-plasma treated SU-8 film, the main two elements found were oxygen and carbon. This is expected from an aromatic polyether such as SU-8. A small trace of antimony, however, can be detected close to the detection limit of XPS. The high-resolution carbon 1s detail spectrum can be divided into three main components, aromatic carbon (C-C) at 284.8 eV, ether carbon (C-O) at 286.5 eV and a shakeup peak at 291.3 eV. The surface composition changes quite drastically after treatment with the oxygen plasma. An additional broad component in the carbon 1s detail spectrum centered at 289.2 eV can be attributed to carboxylic acids and aldehyde groups generated by partial oxidation. The amount of aromatic C-C groups is reduced and the aromatic shakeup peak is almost disappearing. In addition, an increase in the absolute amount of oxygen with an increase in full width at half maximum (FWHM) of this peak and a decrease of carbon was found (Fig. 6). The increase in the FWHM of the oxygen peak is a hint for different oxygen species present in the oxidized film. This is most probably due to a mixture of ether, aldehyde, and carboxylic acid functions. The small nitrogen signal might result from an imperfect oxygen atmosphere during the plasma process. A further change in the surface composition is the significant increase in antimony from 0.2 atom % to 2.6 atom %, most probably in the form of Sb$_2$O$_5$ [32]. This can be explained by a preferential etching of carbonaceous species during the plasma process and the formation of antimony oxide from the photo acid generator. It should be noted that antimony compounds are toxic. Thus, the accumulation of antimony on the surface due to the plasma treatment and possible adverse effects should be considered in bio-MEMS applications.

<table>
<thead>
<tr>
<th></th>
<th>Carbon (at%)</th>
<th>Nitrogen (at%)</th>
<th>Oxygen (at%)</th>
<th>Antimony (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>84.5</td>
<td>0.0</td>
<td>15.3</td>
<td>0.2</td>
</tr>
<tr>
<td>plasma treated</td>
<td>66.3</td>
<td>1.0</td>
<td>30.2</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Table 2: Normalized atomic elemental composition as obtained by XPS before and after plasma treatment.

Fig. 6 XPS survey and detail spectra of a SU-8 film before (a) and a film after two minutes oxygen plasma treatment (b). (1) survey spectra; (2) 1s and Sb 3d high resolution detail spectra; (3) C 1s high resolution detail spectra. Detail spectra are displayed after Shirley background subtraction.
4. Conclusions

We investigated changes of surface energy, topography, and surface chemistry of the natively highly hydrophobic photo-resist SU-8 that were induced by an oxygen plasma activation process. Contact angle measurements revealed an effective hydrophilization ($\theta < 5^\circ$) and, hence, a strong activation of the polymer surface. An increased plasma dose was found to improve the shelf-life of the hydrophilic SU-8. A more intense or longer plasma treatment also leads to an increased surface roughness which amplifies the wetting behaviour. The plasma process also affects the surface chemistry. The absolute amount of oxygen increases, while the amount of carbon decreases. This results in an activated surface. The analysis of the XPS spectra indicates the formation of different oxygen species in a mixture of ether, aldehyde, and carboxylic acid functional groups. Additionally, we found that antimony is enriched at the surface. The long term stability of the surface activation is another important aspect for the practical use of the plasma activation process in SU-8 microfabrication. We found that a moderate hydrophobic recovery occurs with the activated SU-8 surfaces remaining hydrophilic over several weeks.

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References


