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The effect of soft bake temperature on the polymerization of SU-8 photoresist

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Abstract

This paper presents the results of an investigation of the influence of soft baking temperature on the lithographic performance of the negative photoresist SU-8. The work was initiated in order to obtain a lithographic resolution suitable for integration of diffractive optical components for near-infrared wavelengths. The study was carried out on 40 μ m SU-8 layers on thermally oxidized silicon wafers, a widespread platform for integration of microfluidic systems and waveguides. A series of experiments covering soft bake temperatures in the range 65-115 °C were performed under otherwise identical processing conditions. The influence of the soft bake temperature on polymerization temperature as well as cracking, lithographic resolution and hardness of the resist was investigated. The kinetics of the polymerization process were observed to change with soft bake temperature, leading to changes in sensitivity and contrast of the resist, as well as changes in the material strength of the developed structures. Soft baking at 65 °C proved superior with respect to all the inspected properties, providing a sample showing full resolution of 3.8 μ m wide trenches and no stress-related cracking.

1. Introduction

The photoresist SU-8 was developed at IBM in the late 1980s. One of the first applications suggested was to replace the expensive x-ray lithography step in the LIGA process with SU-8 and near-UV lithography [1]. SU-8 is widely used as a structural material in itself, in order to realize microfluidic circuitry [2] or as the molding material for replication in PDMS (polydimethylsiloxane) [3]. Due to its high refractive index, SU-8 can serve as the waveguiding material in integrated optics for lab-on-a-chip applications [4].

SU-8 is a chemically enhanced, negative tone photoresist, based on the EPON[®] SU-8 epoxy resin. The resin is made photosensitive by the addition of an onium salt [1], which acts as a photo-acid generator (PAG). When exposed to UV light, the onium salt decomposes and generates a strong acid [5], which initiates cationic polymerization by ring-opening

and subsequent cross-linking of the epoxy groups [6]. The mixture is usually dissolved in an organic solvent in order to enable spin coating. SU-8 has a high functionality (each SU-8 molecule has eight reactive epoxy groups), which yields good sensitivity, and a low molecular weight, providing high contrast and high solubility [6]. These properties combined with a good UV transparency (46% transparency at 365 nm for a 100 μ m film [7]), makes SU-8 a popular choice for fabrication of high aspect ratio structures.

A typical SU-8 process consists of spin coating, exposure, polymerization and development [8]. The SU-8 is spin coated onto a substrate and soft baked in order to evaporate the solvent. In the exposure step the SU-8 film is exposed to near-UV light through a mask. Once initiated in the exposure, the polymerization process is assisted by thermal energy in the so-called post-exposure bake, or PEB. Finally the unexposed SU-8 is dissolved by an organic solvent, leaving only the crosslinked SU-8 structures on the substrate.

High aspect ratio SU-8 structures, such as aspect ratio 10 in 200 μ m tall structures, have been reported since the

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first reports of SU-8 structures [1, 7]. As the coatings became thicker, this figure grew to 20 and above [9, 10]. Recently, aspect ratios of 40 have been reported [11]. Although conceptually a simple process, the realization of SU-8 structures proved very sensitive to processing conditions. Many have investigated the influence of various processing parameters on the outcome of SU-8 processing [12–14], but the soft bake temperature was fixed (usually at 95 °C) in all investigations. While other exposure techniques such as two-photon lithography [15] and electron–beam lithography [16] have been employed in order to obtain nanometer resolution in SU-8, this study focuses on near-UV lithography of coatings with a thickness suited for simultaneous integration of optical and microfluidic systems.

A significant problem in SU-8 processing is the formation of cracks. The cracks form due to tensile stress in the SU-8, which builds up during processing, and are initiated during the development. Cracked structures may lead to leakage in microfluidic systems, and unwanted scattering and increased propagation loss in optical systems. Apart from optimization of the processing parameters, cracking problems can be solved through restricted design by reducing the area of exposed SU-8 [17], thus reducing the level of stress in the structures, and by avoiding sharp concave corners, which act as crack nucleation points.

We present the results of an investigation of the influence of soft baking temperature on the lithographic performance of SU-8. The study is carried out on 40 μ m SU-8 on thermally oxidized silicon wafers, and forms part of a broad investigation of the SU-8 fabrication process. These efforts aim at optimization of the reproduction fidelity in order to realize integration of diffractive optical components for use in lab-on-chip systems [18].

2. Experimental details

In order to investigate the influence of the soft bake temperature on the lithographic performance of SU-8, six coated substrates were soft baked at temperatures of 65 °C, 75 °C, 85 °C, 95 °C, 105 °C and 115 °C. All other parameters in the processing were kept equal throughout the series.

The SU-8 used in the described experiments is the NANO SU-8 25 formulation (MicroChem Corporation, MA, USA). The solvent in this formulation is γ -butyrolactone (GBL). The resist is refrigerated in between use in order to prolong the shelf life.

The SU-8 fabrication process, which is carried out in a class 100 cleanroom, involves more than 30 parameters and is executed over a period of 2 to 3 days. The details of the processing are described in the following.

SU-8 is coated onto dehydrated, thermally oxidized 100 mm diameter silicon wafers (Topsil, Denmark) using a Karl Süss spin coater model RC8 with integrated hotplate (Karl Süss, France). A volume of approximately 4 ml of SU-8 is deposited at the center of the wafer, which is subsequently spun at a maximum speed of 1250 rpm for 30 s, producing a coating of approximately $40 \,\mu$ m thickness (after soft bake). In order to enable edge bead removal, or EBR, the solvent level in the coating is reduced for 10 min at 50 °C on the integrated spinner hotplate. EBR is performed using propylene glycol

monomethyl ether acetate (PGMEA) as the solvent in the EBR function of the RC8 spinner.

Once the edge bead has been removed, the substrates are soft baked on PID-controlled hotplates (Harry Gestigkeit GmbH, Germany). The temperature cycle consists of a 6 min ramp to the soft bake temperature and baking for 5 min. After the bake the hotplate is allowed to cool to room temperature (1.5-2 h) before the substrates are removed. Although this cooling procedure may be excessively long, it provides an easy way to ensure a reproducible cooling of the substrates.

Mask transfer to the SU-8 is carried out in hard contact mode on a Karl Süss MA6/BA6 aligner (Karl Süss, Germany) using the i-line from a mercury arc lamp (365 nm) with a constant intensity of 9.0 mW cm⁻². A dose of 225 mJ cm⁻² is administered in a single exposure (25 s). The aligner is fitted with an i-line filter (365 nm, 20 nm FWHM) as the increased SU-8 absorption at shorter wavelengths would otherwise jeopardize the resolution [1, 7]. The mask used is a chrome-on-quartz mask (Compugraphics International, UK) fabricated using an address spot size of 0.025 μ m.

In order to limit photo-acid diffusion, post-exposure bake is performed shortly after exposure (usually within 15 to 30 min) on the same hotplates used for the soft bake. The substrates are ramped to 65 °C in 6 min, baked for 30 min and cooled slowly to room temperature (approx. 1.5 h). The substrates are allowed to relax overnight before development by immersion in agitated PGMEA for a total of 5 min, followed by a rinse in isopropanol. Rinsing with isopropanol speeds up the drying procedure, but also replaces the relatively high surface tension PGMEA with a lower surface tension solvent. As the contact angle between SU-8 and the two solvents is comparable (measured to be $2.6 \pm 0.9^{\circ}$ and $5.4 \pm 0.9^{\circ}$ for PGMEA and IPA, respectively, on a DSA10 from Krüss, Germany), this reduces collapse of high aspect ratio structures [19].

During the post-exposure bake, the exposed resist polymerizes by cross-linking of the SU-8 monomers. The rate at which polymerization occurs and the resulting crosslink density depends on the processing conditions. The polymerization temperature reported here is based on an observation of the temperature in the post-exposure bake at which the image of the mask first becomes visible on the substrates. The polymerization temperature is recorded from the hotplate controller. As the polymerization is a kinetic process, the observed polymerization temperature will depend on the time between exposure and PEB initiation, as well as on the temperature ramping rate during the PEB.

Once post-exposure baked and developed, the fabricated structures are inspected in order to determine the lithographic resolution, the structural height and the crack density.

The resolution is determined by inspection of two monitor structures in an optical microscope. Figures 1(a) and (b)show close-up pictures of trench and ridge resolution monitors, respectively. The trench resolution monitor consists of three trenches 50 μ m apart with a width which is varied in 0.2 μ m steps. The ridge resolution monitor is a series of seven ridges anchored at one end. The ridges are separated by a space equal to the width, and the width is varied in steps of 0.5 μ m. In both cases, the structures extend to a length of 5 mm. A trench resolution of 3.4 μ m signifies that the narrowest trench



Figure 1. Optical microscope pictures of monitor structures used to assess the resolution of (*a*) trenches and (*b*) ridges (soft baked at 75 °C). While the 4.5 μ m ridge structure is seen to be fully resolved, the trench resolution is more unclear. However, microscope inspection reveals that the 3.4 μ m trench structure is fully resolved.

that is resolved all the way to the substrate is the 3.4 μ m trench. A ridge resolution of 4.5 μ m signifies that the 4.5 μ m ridge structure is the smallest ridge structure which is fully resolved and structurally stable. The observed resolutions were confirmed using scanning electron microscopy (SEM). Scanning electron micrographs were obtained from cleaved, gold coated monitor structures using a JSM 5500LV SEM (JEOL, Japan).

The structural height is measured across a 50 μ m wide ridge using a P1 Stylus Profilometer (KLA Tencor, USA). A total of eight points on each wafer were measured. The highest realizable trench and ridge aspect ratios are obtained as the ratio of the average height to the resolution of the trench and ridge structures, respectively.

During the bake processes, the difference in thermal expansion between the SU-8 and the substrate, and possibly shrinkage due to polymerization, causes tensile stress to build in the structures. Depending on the stress level, the material strength, and the strength of the bond between material and substrate, one of two scenarios may occur. The material may retain the stress and remain intact, or it may release the stress either by delaminating from the substrate or by the formation of cracks. The crack density is determined by image analysis. A grayscale picture of the central part of a 5 by 5 mm square structure is obtained by optical microscopy, and cracks are colored using standard image editing software. The density of cracks is then computed as the ratio of the number of colored pixels to the total number of pixels. The crack density can never reach 100%, and in practice it will not exceed 50% as cracking releases the stress in the surrounding material. Two structures on each wafer were analyzed, and the crack density computed as the arithmetic mean of the two densities.



Figure 2. Observed polymerization temperature as a function of the soft bake temperature. The error bars represent the readout precision. The dashed line serves as a guide to the eye. At low soft bake temperatures, the polymerization temperature is disturbed by the fact that the ambient temperature sets the lower limit.

In addition to these inspections, the strength of the crosslinked SU-8 was probed using a FM-700 micro-hardness tester (Future-Tech, Japan). The micro-hardness tester was operated in Vickers hardness mode, using a test load of 10 g and a load keeping time of 5 s. In order to avoid any influence from the substrate, the test load was selected to give a permanent indentation depth of approximately one tenth of the SU-8 thickness. The hardness of the SU-8 was tested in five different locations, separated by at least 100 μ m while avoiding cracks, within the same 5 by 5 mm square structure used in the cracking inspection.

3. Result and discussion

The observed polymerization temperature as a function of soft bake temperature is presented in figure 2. At the lowest soft bake temperatures, cross-linking was already evident when the PEB was initiated. The polymerization temperature is thus set to the temperature of the processing ambient (22 °C). However, while the image on the sample soft baked at 75 °C took approximately 15 min to develop, faint traces were visible directly upon exposure of the wafer baked at 65 °C, indicating that polymerization would have been initiated even at a lower temperature. The apparent plateau at low soft baking temperatures is thus an artifact due to the temperature of the processing ambient. At higher soft bake temperatures, the polymerization temperature rises, saturating at 39 °C for soft bake temperatures of 95 °C and above.

The increase in polymerization temperature with increasing soft bake temperature suggests solvent level dependent polymerization kinetics. As the soft bake temperature increases, the solvent concentration in the soft baked SU-8 decreases, reaching an apparently constant level at temperatures of 95 °C and above. The faster kinetics at low soft bake temperature could be explained by higher mobility in the SU-8 matrix, due to the higher solvent concentration. However, the solvent concentration may also affect the photo-acid generation process. During exposure, the organic cation of the onium salt is destroyed and the salt decomposes [5]. The anionic part reacts with solvent, monomer, or impurity molecules in the resist and forms a



Figure 3. Cross-sectional scanning electron micrographs of the smallest fully resolved and structurally stable ridge structure (*a*) for the sample soft baked at 65 °C and (*b*) for the sample soft baked at 95 °C.

strong acid [20]. An increased solvent content may facilitate this process, thus increasing the effective concentration of the actual polymerization catalyst, in essence increasing the sensitivity of the resist. Both effects of the increased solvent concentration, in particular the latter, would result in a higher cross-link density and thus a stronger material.

Figure 3 shows scanning electron micrographs of the smallest resolved and structurally stable ridge structure for the samples soft baked at 65 °C and 95 °C, respectively. The inspection confirmed the optical inspection described in the former section, showing the smaller structures to be failed, either by collapsed or wriggly ridges. The samples soft baked at other temperatures were similar.

Selected micrographs from the inspection of trench structures may be seen in figure 4. Again the inspection confirmed the optical inspection, showing the narrower trenches to be partially obstructed. The sample soft baked at 65 °C (see figure 4(a)) shows smooth, near vertical sidewalls. The sample soft baked at 95 °C (figure 4(c)) shows slightly more sloped and rough sidewalls. It is seen in figure 4 that the smallest resolved trench in the case of soft baking at 65 °C is narrower than in the case of a 95 °C soft bake. This is in contrast to the trench resolution established from optical microscope inspection, i.e. the size of the mask feature responsible for the trench, which shows a resolution of 3.8 μ m and 3.4 μ m for soft baking at 65 °C and 95 °C, respectively. The samples soft baked at 65 °C and 75 °C are overexposed while the samples soft baked at 95 °C, 105 °C and 115 °C are underexposed, suggesting an increased sensitivity at low soft baking temperatures.

Figure 5 shows the result of the height measurements along with the highest realizable aspect ratio for the trench and



Figure 4. Cross-sectional scanning electron micrographs of the smallest fully resolved trench structure for the sample soft baked (*a*) at 65 °C, (*b*) at 75 °C, (*c*) at 95 °C and (*d*) at 115 °C. The size of the mask feature responsible for the trench is indicated by a black bar at the top of the trench. The actual width of the trench is indicated by the arrows.



Figure 5. The structural height and highest realizable aspect ratio as a function of soft bake temperature. The error bars correspond to one standard deviation. The dashed lines serve as guides to the eye.

ridge structures, respectively. The structural height initially decreases from a value of almost 40 μ m at a soft bake temperature of 65 °C to slightly below 36 µm at 85 °C. At higher soft bake temperatures there is a slight increase in the structural height. The trench aspect ratio is initially constant at 10.5, but decreases at temperatures above 95 °C. The ridge aspect ratio is initially 8, then decreases toward a value of 4 at 105 °C, and finally increases slightly at 115 °C. While the trench resolution is equal to the minimum obtainable line width, the ridge resolution is affected by both line width and structural stability, as the surface tension of the evaporating solvent following development will tend to collapse the ridges [19]. In fact, recent investigations have shown that adding a final rinse in water to the development process has a positive effect on the ridge resolution [21]. The decrease in trench aspect ratio suggests a decrease in resist contrast at elevated soft bake temperatures. A decrease in contrast may be explained by thermal activation of the photo-acid generator during soft bake. The amount of released polymerization catalyst is not enough to fully polymerize the SU-8, but the resulting background cross-link density lowers the effective dose contrast between exposed and unexposed areas of the resist, and causes line broadening. The initial decrease in ridge the aspect ratio suggests a decrease in the structural strength of the resist, possibly due to a decrease in the crosslink density as a result of decreasing sensitivity. The rate at which the cross-linked SU-8 deteriorates in the developer must be expected to increase with a decrease in cross-link density. This may explain the initial decrease in structural height. The increase in height at higher soft bake temperatures is consistent with an increase of cross-link density due to thermal PAG activation.

In figure 6 the result of the crack inspection and hardness measurements is presented. No cracks were observed in any of the structures on the sample soft baked at 65 °C. The crack density is thus set at 0%. The crack density increases with increasing soft bake temperature up to 105 °C, then drops significantly. The hardness of the SU-8 decreases with increasing soft bake temperature, from a Vickers hardness number of almost 24 at 65 °C to below 21 at 105 °C. At a soft bake temperature of 115 °C the hardness increases to 22. A Vickers hardness number of 25 has previously been reported to be sufficient for SU-8 to be used as a master mould for PDMS



Figure 6. Crack density and Vickers hardness as a function of soft bake temperature. The error bars on the crack density represent the range of measurements, while those on the hardness correspond to one standard deviation. The dashed lines serve as guides to the eye.

soft lithography [3]. It is important to note that the Vickers method is only really suitable for quantitative characterization of samples with similar ductility, which is not necessarily true for these films. The method is thus not well suited for polymeric samples, and the measurements presented here only serve as a qualitative comparison of the samples.

As observed in figure 6, the crack density increases with increasing soft bake temperature while the hardness decreases. The decrease in hardness suggests a decrease in cross-link density, again as a result of the degrading resist sensitivity. In the case of the crack density, a decreasing material strength would make the resist more prone to cracking. However, the driving force behind cracking is the residual stress in the polymerized structures. As all the samples were post-exposure baked at 65 °C, the stress induced during PEB due to thermal mismatch must be expected to be similar for all samples. In our view the residual stress changes as a function of the stress in the film at the point of polymerization, i.e. the level of stress induced during soft baking. For samples soft baked at low temperature the mobility is high enough to relax the coating, owing to the high solvent content. The low crack density at low soft bake temperature can thus be explained by the combined effect of an intrinsically stronger material and a lower residual stress. At 115 °C the hardness increases, probably due to thermal PAG activation, causing the crack density to decrease. While this effect may continue to decrease the crack density at higher soft bake temperatures, the lithographic resolution would suffer, as indicated in figure 5.

All of the above observations point toward degrading lithographic performance and material properties with increasing soft bake temperature. One must, however, keep in mind that while the optimal post-soft bake processing conditions must be expected to change with soft bake temperature, they were kept constant in this investigation. The post-exposure bake temperature of 65 °C is best suited for samples soft baked at low temperature, for which a large part of the polymerization occurs at low temperature. Increasing the temperature in the post-exposure bake of samples soft baked at higher temperatures would cause the polymerization to progress further, increasing the cross-link density. The result would be an increase of the material strength, and thus an increase of the hardness and a decrease in the crack density.

This would also increase the realizable ridge aspect ratio, while the realizable trench aspect ratio probably would decrease due to line broadening. Increasing the PEB temperature in the case of a low soft bake temperature would lead to a higher level of residual stress and consequently increased delamination risk. The exposure dose, on the other hand, was optimized for soft baking at 95 °C. At lower soft bake temperatures higher sensitivity leads to overexposure, which causes the trench resolution to degrade. Thus, a lower exposure dose at the low soft bake temperatures is expected to improve the minimum line width.

4. Conclusion

The effect of the soft bake temperature on the lithographic performance and cracking of SU-8 25 was investigated. We have shown how soft baking at a low temperature causes the exposed SU-8 to polymerize at a faster rate and to a further degree compared to traditional soft baking at 95 °C. This results in increased sensitivity and a higher realizable aspect ratio. Soft baking at a low temperature also reduces the level of stress induced due to a thermal mismatch between the SU-8 and the substrate. Combined with an increased material strength due to a higher cross-link density, this prevents cracking. In fact, a soft bake temperature of 65 °C results in completely crack free structures with aspect ratios of 10 and 8 for trench and ridge structures, respectively. This represents a large improvement compared to the result of processing at the standard soft bake temperature of 95 °C.

In conclusion, the soft bake temperature cannot be ignored while optimizing SU-8 processing as it has profound influence on the lithographic performance and the material properties of the resist.

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References

- La Bianca N and Gelorme J D 1995 Advances in resist technology and processing XII Proc. SPIE 2438 846–52
- [2] Jakeway S C, de Mello A J and Russel E L 2000 Fresenius J. Anal. Chem. 366 525–39
- [3] Chan-Park M B, Zhang J, Yan Y and Yue C Y 2004 Sensors Actuators B 101 175–82
- [4] Mogensen K B, El-Ali J, Wolff A and Kutter J P 2003 Appl. Opt. 42 4072–9
- [5] Crivello J V and Lam J H W 1979 J. Polym. Sci. A 17 977–99
- [6] Shaw J M, Gelorme J D, LaBianca N C, Conley W E and Holmes S J 1997 IBM J. Res. Develop. 41 81–93
- [7] Lee K Y, LaBianca N, Rishton S A, Zolgharnian S, Gelorme J D, Shaw J and Chang T H-P 1995 J. Vac. Sci. Technol. B 13 3012–6
- [8] MicroChem 'NANOTM SU-8 Negative Tone Photoresist Formulations 2–25', Datasheet Rev. 2/02 (http://www.microchem.com)
- [9] Lorenz H, Despont M, Fahrni N, Brugger J, Vettinger P and Renaud P 1998 Sensors Actuators A 64 33–9
- [10] Ling Z, Lian K and Jian L 2000 Advances in resist technology and processing XVII Proc. SPIE 3999 1019–27
- [11] Williams J D and Wang W 2004 J. Microlith. Microfab. Microsyst. 3 563–8
- [12] Eyre B, Blosiu J and Wiberg D 1998 Proc. MEMS '98 pp 218–22
- [13] Zhang J, Tan K L, Hong G D, Yang L J and Gong H Q 2001 J. Micromech. Microeng. 11 20–6
- [14] Hong S J, Choi S, Choi Y, Allen M and May G S 2004 Proc. ASMC '04 pp 404–8
- [15] Juodkazis S, Mizeikis V, Seet K K, Miwa M and Misawa M 2005 Nanotechnology 16 846–9
- [16] Akatry M, Jensen M O, Westra K L, Brett M J and Freeman M R 2003 J. Vac. Sci. Technol. B 21 5–7
- [17] Lin C-H, Lee G-B, Chang B-W and Chang G-L 2002 J. Micromech. Microeng. 12 590–7
- [18] Hübner J, Jorgensen A M, Anhoj T A and Zauner D A 2005 Integrated optics: devices, materials, and technologies IX *Proc. SPIE* 5728 269–77
- [19] Tanaka T, Morigami M and Atoda N 1993 Japan. J. Appl. Phys. 32 6059–64
- [20] Crivello J V 1999 J. Polym. Sci. A 37 4241-54
- [21] Kondo T, Juodkazis S and Misawa H 2005 *Appl. Phys.* A **81** 1583–6