

Fabricating and characterizing oblique polymer structures by electron beam writing on resist-coated SiO₂ wafers

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Abstract

We have successfully fabricated SU-8 materials having oblique structures by a new electron beam technology. We studied the contrast, sensitivity, etching, and thermal properties of SU-8, PMMA, and KrF resists to evaluate their suitability for the fabrication of oblique structures. Among these resists, SU-8 revealed the lowest contrast ratio, highest throughput, and best thermal stability, and so it became the candidate material for patterning the oblique structures. The technique we have developed involves five regional exposures of a thick SU-8 resist layer with various electron beam dosages. Furthermore, we discuss the surface morphology, reaction mechanism, and hydrophobicity after subjecting the SU-8 resist to a series of plasma treatments. The formation of surface nano-nodules during oxygen plasma treatment explains the surface hydrophobicity. We have carefully evaluated the effects of the electron beam writing dose and the design of the exposure area with respect to the inclined angle of the fabricated structure.

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1. Introduction

Microfabricated fluidic devices are potentially useful for multidimensional separations because small sample volumes can be manipulated and highly efficient separations can be achieved. Rapid progress in the production of micromechanic, microfluidic, and microoptic devices has propelled the development of new methods for the formation of binary high-aspect-ratio structures in relatively thick resist layers by X-ray and photolithography. Most fluid channels, however, are fabricated presently using optical or soft lithographic technologies [1–3]. The development of new techniques for preparing oblique microfluidic channels will benefit future bio-device applications [4]. Sloped microfluidic structures have the advantage of having smaller chip surface areas than do planar designs having the same flow distance.

Several lithographic techniques for the production of non-planar structures have been developed, such as stereo-lithography and focused ion-beam deposition. Stereo-lithography can be used to fabricate 3-D and high-aspect-ratio microstructures with low manufacturing costs and short fabrication times. Stereo-lithography also can customize the packages for microfluidics and microsensors to eliminate the dead volume of the reaction chamber [5]. The fabrication of MEMS packages on a wafer-level scale can decrease the manufacturing and assembly times. Stereo-lithography, however, uses an optical source to illuminate the resist and so the pattern resolution is restricted. Focused-ion-beam micromachining and focused-ion-beam deposition enable spatially selective and maskless patterning and processing of materials at extremely high levels of resolution [6–8]. State-of-the-art focused-ion-beam columns that are based on high-brightness liquid-metal-ion-source (LMIS) technology are capable of forming probes that have 10-nm dimensions, with the lower limit on spot size being set by the inherent energy spread of the LMIS

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and the chromatic aberration of the ion optical systems [9]. The printing speed of focused ion beam techniques, however, is very slow and time-consuming.

Electron beam writing, in comparison with optical or soft lithography, is a promising means for controlling and patterning small features, down to sub-100-nm, and for maskless processing [10,11]. The electron beam writing technology does not require a mask or mold for a pattern to be obtained, and such technologies have potential applicability for future mass production [12]. The development of electron beam resists for channel fabrication has focused on improving the sensitivity, resolution, and etching resistance of these materials.

Poly(methyl methacrylate) (PMMA) was the first, and is still the most popular, resist for electron beam applications for fabricating MEMS [13–15]. Moreover, PMMA is a positive radiation resist that has the highest resolution of all known resists, but the lowest sensitivity to irradiation, which limits its application in submicron microelectronics technologies. This deficiency may be overcome by chemical modification of the polymer to incorporate electron-accepting substituents into its macromolecular composition. The poor resistance to corrosive etching conditions and thermal instability may, however, restrict further applications [16]. The present KrF chemically amplified resist provides fast throughput, higher etching resistance, and better printing resolution [17], but the excellent contrast confines its applications to patterning oblique structures. An alternative, epoxy-based material, SU-8, is a solvent developed and chemically amplified resist system that has excellent sensitivity, thermal stability, and etching resistance. Conventionally, the SU-8 resist is used to fabricate planar and high-aspect-ratio patterns for micromachining systems [18]. To date, most research related to the SU-8 series of materials has concentrated on using thick or ultra-thick films, and has focused mainly on mechanical applications, using conventional UV or X-ray exposure [19,20]. Less attention, however, has been directed toward applying electron beam irradiation to manufacturing sloped structures [21,22] and thermal stability of polymeric film.

Initially, this paper describes a study that compares SU-8, PMMA, and KrF resists for their sensitivity, contrast, etching resistance, and thermal stability. Subsequently, we evaluated the surface properties and morphologies of SU-8 resists after their treatment with oxygen plasma. In addition, the electron beam writing strategy and the fabrication of oblique structures are proposed and discussed.

2. Experimental

The SU8-50 photoresist obtained from Microchem (MA, USA) was used to fabricate three-dimensional structures by electron beam writing. The ingredients of the resist, as provided by the vendor, are 50–70% epoxy resin, 25–50% γ -butyrolactone, 1–5% propylene carbonate, and triarylsulfonium hexafluoroantimonate salts. PMMA-A55 was also obtained from Microchem; KrF UV-86 resist

was obtained from Shipley (MA, USA). Electron beam exposure was performed on a Leica Weprint Model-200 stepper (Jena, Germany). The electron beam energy was 40 kV with a beam size of 20 nm and a beam current of 40 A/cm². The developer for the SU8-50 photoresist was 98–100% 1-methoxy-2-propyl acetate solution. The developer for the PMMA resist was a mixture of methyl isobutyl ketone and isopropanol, while that for the KrF UV-86 resist was 2.38% tetramethylammonium hydroxide solution.

The SU8-50 resists were spin-coated onto the SiO₂ film of a 6-in. silicon wafer—the resist thickness was 17 μ m at the spin rate of 6000 rpm for 0.5 min—followed by a two-step soft-baking process (10 min at 65 °C, then 2 min at 90 °C). The post-exposure baking (PEB) also proceeded in two steps: 30 min at 65 °C and then 10 min at 90 °C. The film outgassing was determined using a Hitachi (Tokyo, Japan) UG-21 thermal desorption system (TDS) in conjunction with a UG-400P atmospheric-pressure-ionization mass spectrometer (APIMS). The desorption temperature program was set from room temperature to 300 °C at ramp rate of 3 °C/min. Oxygen plasma treatment was carried out in a plasma-enhanced chemical vapor deposition (PECVD) chamber (STS, UK); the operating frequency was 380 kHz and the power was 250 W. The contact angle (First Ten Angstroms Model FTA-125, VA, USA) was measured by injecting water (100 μ L) on the sample surface. The spherulitic structure of the surface nano-lamellae was evaluated using an in-line Hitachi S-6280H SEM. The oblique morphology on the surface was evaluated using a Profiler P-10 (TENCOR, USA).

3. Results and discussion

3.1. Characterization of resist sensitivity

Characterization experiments for the three resists were carried out by electron beam exposure; the sensitivity and contrast of these resists was determined from the sensitivity curves displayed in Fig. 1. In general, the resist having the best contrast is most suitable for patterning planar structures, while a resist that exhibits low contrast is more suitable for fabricating oblique patterns. For practical mass manufacturing, the resist sensitivity can seriously affect the throughput and the cost. The samples of 17- μ m-thick SU-8 film on Si-substrate were exposed with square test structures, and we measured the resist heights as a function of the applied doses. The electron beam energy was 40 keV and the doses ranged from 1 to 15 μ C/cm² at regular increments. Subsequently, these samples were baked on a hot-plate and then developed. Fig. 1 displays the sensitivity curves for three types of electronic materials. We note that the SU-8 resist changes its sensitivity and contrast when the PEB process is applied. If the PEB process of the SU-8 resist is omitted, its contrast and sensitivity decrease. As mentioned above, lower contrast is beneficial for fabricating oblique structures. The SU-8 resist has negative tone

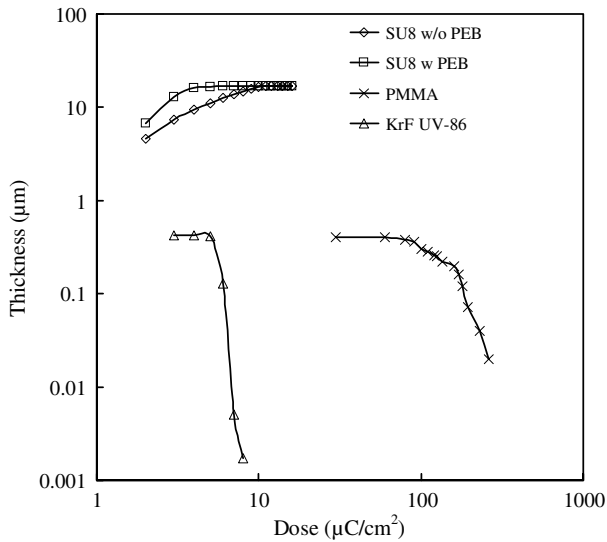


Fig. 1. The effect of the electron beam dose on the thickness of the resist.

behavior upon electron beam exposure, while both PMMA and KrF UV-86 resists display positive tone behavior. We see from Fig. 1 that the SU-8 resist has excellent sensitivity and lower contrast, regardless of its thickness. The KrF UV-86 resist has better contrast and sensitivity, while the sensitivity of the PMMA resist is too low. Therefore, of the three materials, the SU-8 resist has the best degree of flexibility in resist sensitivity and contrast and so it became our candidate for patterning oblique structures with high throughput.

3.2. Etching behavior of various films

The etching resistance of SU-8, PMMA, and KrF UV-86 resists against CF_4 mixture gas is illustrated in Fig. 2. Although the polymer backbones in these resists are quite different, both the SU-8 and the KrF UV-86 resists exhibit better resistance, relative to the PMMA resist, during sili-

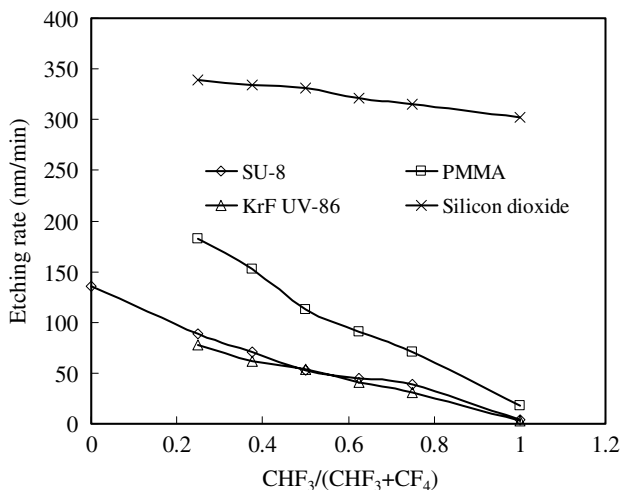


Fig. 2. The effect of the etching gas composition on the etching rate.

con dioxide etching. Increasing the CHF_3 ratio in the mixture of CHF_3 and CF_4 gases can decrease the resists' etching rates as a result of the capture of reactive fluorine radicals by hydrogen radicals in the plasma. The species generated from CHF_3 in the plasma are H^+ and CF_3^- , and the CF_3^- species can quench the activity of CF_3^+ in the plasma, which results in a decreased etching rate. Otherwise, the etching selectivity (i.e., the etching rate of silicon dioxide relative to that of the resist) increases upon increasing the CHF_3 ratio, and the etching selectivity for the SU-8 film reaches almost 100 when the etching gas is CHF_3 only.

3.3. Thermal stability with oxygen treatment

Thermal stability is another feature that favors SU-8 being used as the material, instead of the PMMA and UV-86 resists, for oblique structure fabrication. Fig. 3 displays the desorption behavior of various resists as determined by TDS-APIMS measurement. All of these films exhibit low out-gassing of NH_3 and C_3H_8 species. The PMMA and UV-86 films display higher H_2O desorption than does the SU-8 film during thermal stressing. The UV-86 film, when measured for C_2H_6 , is thermally unstable relative to the other films, as evidenced by the extremely high out-gassing peak. In contrast, the SU-8 film exhibits very low out-gassing upon its thermal stressing. To stabilize the SU-8 film even further, we propose a technique based on an additional oxygen plasma treatment in a PECVD chamber. The inset of Fig. 3 indicates that, after O_2 plasma treatment at 300°C , the SU-8 film exhibits the lowest out-gassing of NH_3 and C_3H_8 species. This finding suggests that the O_2 plasma reacts with unstable species in the SU-8 film. The emitted plasma stream can penetrate the resist film and stabilize the active chemical bonds by suppressing the out-gassing effect. Taking together both its thermal stability and high etching selectivity, SU-8

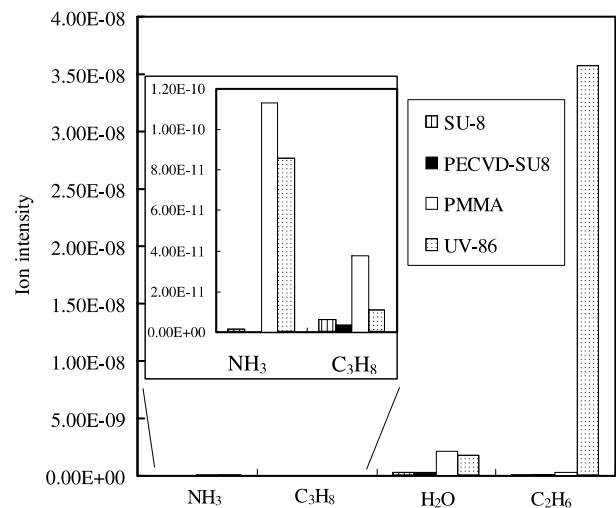


Fig. 3. The thermal stability of various resists (oxygen plasma treatment for SU-8 resist in a PECVD chamber at 300°C).

seems to be a beneficial material for use in either in fluidic channel walls or in the resist process.

3.4. Surface properties after plasma treatment

To apply the SU-8 polymer as a material for fabricating oblique channels, it is essential to understand its surface properties. The rule of thumb is that water-based solutions should flow through channels having hydrophilic surfaces, and nonpolar solutions in the channels that are hydrophobic. Fig. 4 displays the contact angles for SU-8 film after various degrees of oxygen plasma treatment. The film surface exhibits hydrophobicity after being treated for 0–10 s, but becomes hydrophilic with plasma-treatment times from 20 to 40 s. This observation suggests that oxygen plasma oxidizes the SU-8 resists and causes hydrophilicity through the formation of hydroxyl groups on its surface. Interestingly, the surface can be restored to its initial hydrophobic property after plasma treatment for 50–60 s. This observation suggests that oxygen plasma treatment does not just hydroxylate the surface, and that the microstructure of the film’s surface needs to be investigated in-depth. This oxygen treatment technology for SU-8 materials is a very simple and easy means of altering their surface hydrophilicity. The ability to control hydrophilicity will be a powerful tool when preparing the different types of channels in the future.

Fig. 5 illustrates SEM micrographs of the surface of the SU-8 resist after oxygen plasma treatment for 5, 20, 40, and 60 s. The morphology observed in Fig. 5a suggests that the treatment with oxygen plasma leads to the cross-linkage reaction and small cracks are formed on the surface. In Fig. 5b (20 s), the crack density has increased, which indicates that a large portion of the surface carbon atoms have become oxidized, and so the surface exhibits the hydrophilicity indicated in Fig. 4. In Fig. 5c, however, we observe nano-nodular structures have appeared after 40 s of plasma treatment. These nano-nodules have diameters of ca. 22 nm, and the surface is hydrophilic. When the film was plasma treated for 60 s, its surface reverted back to its hydrophobic character. The diameters of nodules increased to ca. 27 nm.

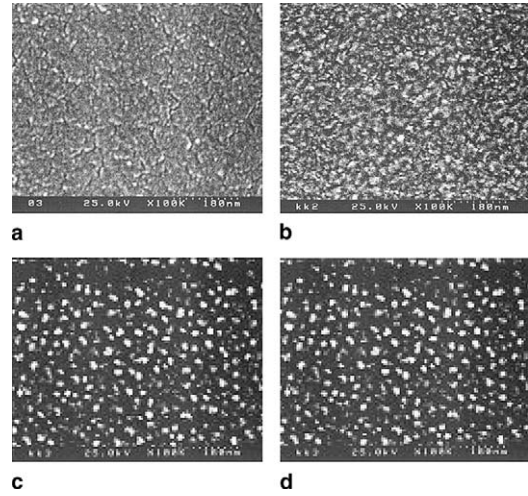


Fig. 5. SEM images (plan views; 10⁵ magnification) of oxygen plasma-treated SU8-50 resist films after treatment for: (a) 5 s, (b) 20 s, (c) 40 s, and (d) 60 s.

It is obvious that the density of the nano-nodules plays an important role in determining the surface hydrophilicity. The nano-nodules on the surface seem to possess hydrophobic character, while the other surface, possessing with hydroxyl groups after oxygen plasma treatment, exhibits hydrophilicity. In Fig. 5c, the role of the hydrophilic surface dominates over that of the nano-nodules, and the contact angle measurement indicates the surface’s overall hydrophilicity. In contrast, the nano-nodules in Fig. 5d cover a large portion of the surface, which, consequently, possesses hydrophobic character.

3.5. Fabrication of oblique structures

We propose a technique, illustrated in Fig. 6, for fabricating oblique structures. The method uses an electron beam to expose the desired area, which is divided into five dosage strips, named I, II, III, IV, and V. After much experimentation with the variables, we found that dosages of 2, 2.8, 3.6, 4.8, and 12 $\mu\text{C}/\text{cm}^2$ for these strips, respectively, cause an actual sloped structure to be created on the SU-8 material. The angle of inclination of the structure

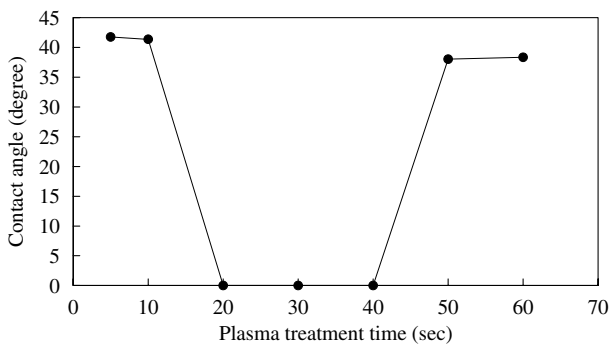


Fig. 4. The effect of oxygen plasma treatment time on the contact angle of the SU8-50 film.

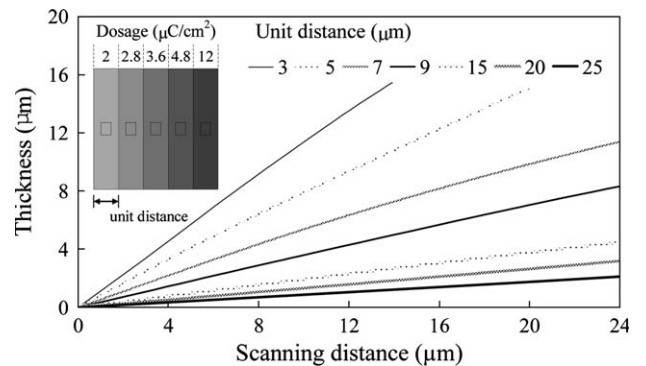


Fig. 6. Oblique profiles of the SU8-50 film designed by gradient electron beam exposure.

depends strongly on the unit distance; this angle decreases with increasing unit distance as a result of the dose absorption per unit area.

Table 1 lists the mathematical fitting of the various oblique lines in Fig. 6. The slope of the fitting equation can reflect the angle of inclination. The inclined angles for the unit distances of 3, 5, 7, 9, 15, 20 and 25 μm are 48.2°, 37.6°, 24.1°, 18.3°, 10.6°, 7.9° and 6.1°, respectively. The SEM micrographs presented in Fig. 7 provide further evidence that verifies the success of this unique technique. Clearly, oblique structures having a variety of inclined angles can be fabricated by electron beam exposure of the SU-8 material. These oblique structures are not easy to fabricate by conventional optical illumination methods. After their fabrication, these oblique patterns can be used as transfer molds for imprint technology or soft lithography. Together with the oxygen plasma treatment technol-

ogy mentioned earlier, the fabrication of oblique structures is a very promising technology for patterning hydrophilic and hydrophobic surfaces.

4. Conclusions

We have investigated the sensitivity curve, etching resistance, and thermal duration of SU-8, PMMA, and KrF UV-86 resists after electron beam lithography. The SU-8 resist demonstrates good performance in patterning oblique structures as a result of its lower contrast, higher throughput, better etching resistance, and excellent thermal properties, relative to the PMMA and KrF UV-86 resists. The surface of the SU-8 film displays interesting responses to oxygen plasma treatment. The initial surface, which is hydrophobic, becomes hydrophilic after plasma treatment for 20–40 s, but its hydrophobic character is restored after 50–60 s of plasma treatment. The formation of surface nodules, as evidenced by SEM, can be used to reasonably explain the transformations in surface hydrophobicity. We have demonstrated a novel gradient writing strategy that uses electron beam exposure to fabricate a sloped structure. The inclined angle of the structure was found to have an inverse relationship with respect to the dose received per unit area. Cross-sectional SEM images clearly indicate that the writing strategy we have proposed can be used successfully to fabricate obliquely patterned structures.

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Table 1
The fitting equation for various electron beam writing strategies

Unit distance (μm)	Fitting equation [Y: thickness (μm); X: scanning distance (μm)]
3	$Y = 1.118X$
5	$Y = 0.77X$
7	$Y = 0.448X$
9	$Y = 0.33X$
15	$Y = 0.188X$
20	$Y = 0.139X$
25	$Y = 0.107X$

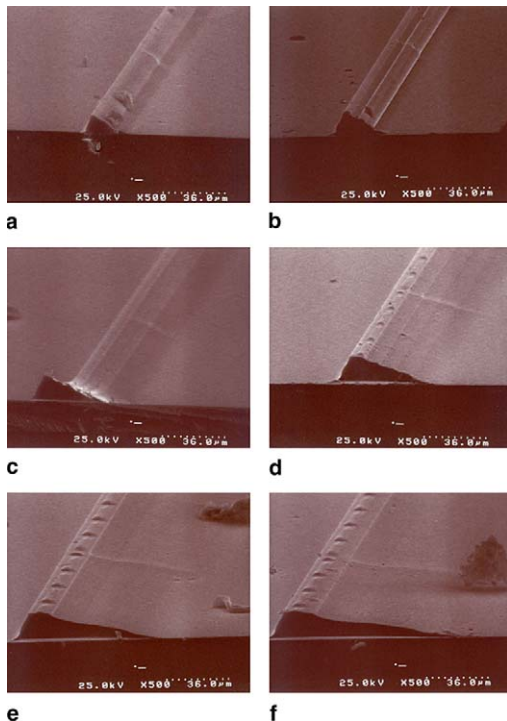


Fig. 7. SEM images of the oblique profiles of the SU8-50 film that were designed with sectional distances of: (a) 3 μm , (b) 5 μm , (c) 7 μm , (d) 9 μm , (e) 15 μm , and (f) 20 μm .

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