Optimized Surface Silylation of Chemically Amplified Epoxidized Photoresists for Micromachining Applications

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ABSTRACT: We explored the selective wet silylation of noncrosslinked areas of epoxidized photoresists using chlorosilanes. Emphasis was placed on the Si uptake of the epoxy films when controlled low levels of water were incorporated into the silylation solution. Fourier transform infrared measurements and oxygen-plasma resistance data with *in situ* laser interferometry and multiwavelength ellipsometry are presented. The fine tuning of the moisture level was found to be crucial for the generation of satisfactory and reproducible structures. The optimized version of the process was shown to be useful for epoxy-based dry micromachining. Overall, an attractive positive-tone process is presented as an alternative to the usual negative-tone process for commercial epoxy resists. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2189–2195, 2010

Key words: functionalization of polymers; microstructure; photoresists; selectivity

INTRODUCTION

Epoxy functionalized polymers are used extensively in microlithography as components of negative tone materials in a number of applications, including traditional electron-beam (e-beam) resists,[1] high-resolution chemically amplified resists for e-beam[2] or optical lithography,[3,4] and micromachining (e.g., SU8 resists[5]).

Silylation is defined as the replacement of the active hydrogen of a hydroxyl group (—OH), an amino group (—NH_2), or a sulfide group (—SH) by a silicon-bearing group. Some important applications that use the silylation of an organic compound include the following: (1) side-group protection in polymer synthesis (e.g., ref. [6]), (2) production of volatile products in gas chromatographic methods,[7] (3) chemical modification of surfaces for the improvement of certain properties (e.g., hydrophobicity),[8] and (4) opening of epoxy rings.[9]

Epoxy photoresists are widely used in micromachining applications because of their ability to form films in the thickness range 50–1000 μm. The silylation of epoxidized resists can be part of a positive-tone process offering the extension of resolution capabilities by the overcoming of high-absorbance problems in both optical lithography and micromachining.[10] Epoxidized resist silylation also finds applications in certain regimes of e-beam lithography[11–12] and low-energy e-beam exposure.[13] Finally, the same type of processing step can contribute toward the solution of certain micromachining problems through the use of a positive-tone process that takes advantage of negative resist benefits.[14]

In this study, we examined a positive-tone silylation process for a chemically amplified epoxidized resist. In line with our earlier experience,[15–18] we chose a liquid-phase silylation over the gas-phase version. However, if desirable, our findings can be adapted, at least in principle, to gas-phase silylation processes as well (e.g., refs. [19] and [20]).

A general concern regarding lithographic processes involving silylation steps is the frequently encountered limited reproducibility of the final structures;[21] the reproducibility problem appears to be a reflection of a puzzling humidity effect. Hence, in this study, the effect of humidity was considered in some detail. Instead of relying on the effect of air moisture, we used dry silylation solutions modified by the controlled introduction of minute amounts of water; the systematic variation of the latter suggested a complex response and revealed the existence of a level of moisture that was optimum for the lithographic applications in consideration.

The uncontrolled variation of water level stemmed from moisture found in starting materials or

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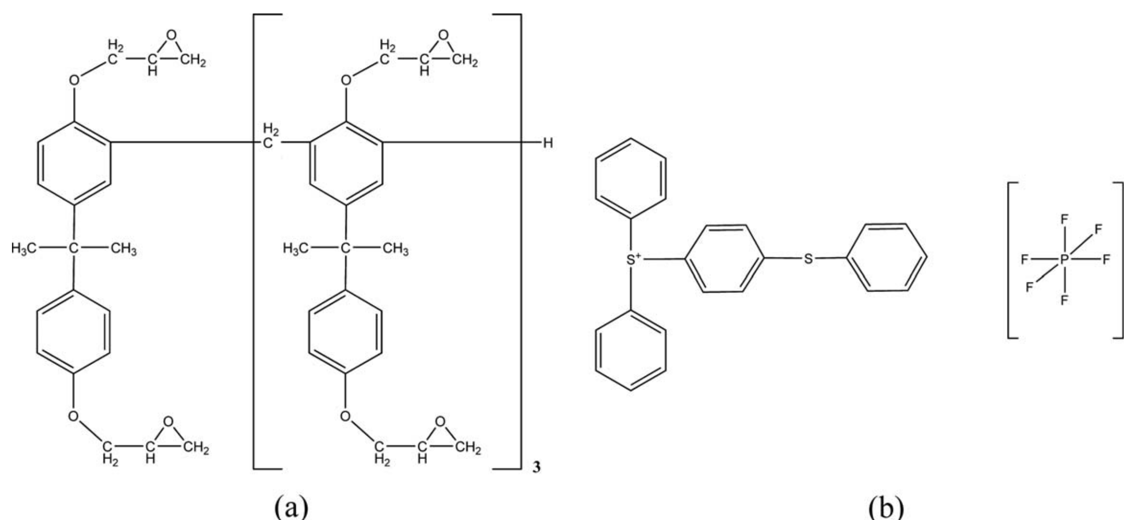

Figure 1 Structures of (a) EPON SU-8 and (b) Degacure KI 85.

introduced from the air and caused irreproducibility. The drying of the starting materials, controlled introduction of moisture to a specific level, and standard clean-room conditions (class 1000) led to optimum and reproducible results.

EXPERIMENTAL

Materials

The material selected for the silylation was EPON SU-8 [Shell Chemical Company, Los Angeles, CA; Fig. 1(a)]. EPON is the base polymer (oligomer) of the widely used commercial photoresist SU8 (MicroChem), which includes eight epoxy rings per polymer molecule. The photochemical acid generator used was Degacure KI 85 [Degussa; 5–10% w/w of the polymer; Fig. 1(b)]. Although antimonite salts are stronger acid generators and, thus, more effective chemical amplifiers, no antimonite-containing photochemical acid generator could be used in our case. This was because antimony oxides are nonvolatile, and thus, antimony-related residues (of the type known as *grass*) are observed upon resin etching in oxygen plasma.[17] Both materials were dissolved in propylene glycol methyl ether acetate (PGMEA) at concentrations chosen to lead to a desired film thickness. The maximum film thickness achievable with SU8 is about 2 mm, whereas the maximum aspect ratio is in excess of 50 for 365-nm lithography.[5] In this study, we covered the following film thicknesses: 0.5, 3, 15, and 100 μm; that is, the thickness was varied by more than two orders of magnitude.

Silylation process and dry development

The standard silylation process[17,22] consisted of the following steps (Fig. 2):

1. Substrate pretreatment (cleaning with acetone and isopropyl alcohol) and baking at 200°C for 20 min in a conventional oven.
2. Spinning of the resist at 500 rpm (acceleration = 100 rpm/s) for 30 s and, subsequently, at 1500–5000 rpm (acceleration = 300 rpm/s) for 30 s.
3. Prebaking for 1–5 min at 65°C and then for 4–30 min at 95°C.
4. Relaxation: The sample was left to cool at a temperature decrease rate of approximately 1.5°C/min.
5. Exposure to UV light (350–370-nm band obtained with a filter) through a mask (proximity printing) with doses falling into the optimum range for a negative-tone process with wet development. A KARL SUSS (Garching, Germany) MJB 3 mask aligner was used for this step.
6. Postexposure baking for 1–5 min at 65°C and then for 2–10 min at 95°C to crosslink exposed areas only.
7. Relaxation: The sample was allowed to cool at a rate of approximately 1.5°C/min.
8. Puddle wet silylation at room temperature for 2 min with a solution containing the silylating agent (5% v/v dichlorodimethyl silane), the resist solvent (10% v/v PGMEA), and an inert carrier (85% v/v *n*-decane).
9. Postsilylation baking for 5 min at 60–90°C
10. Dry development with oxygen-plasma etching.

Relaxation step 4 was essential, especially for thicker films, as it allowed for the formation of

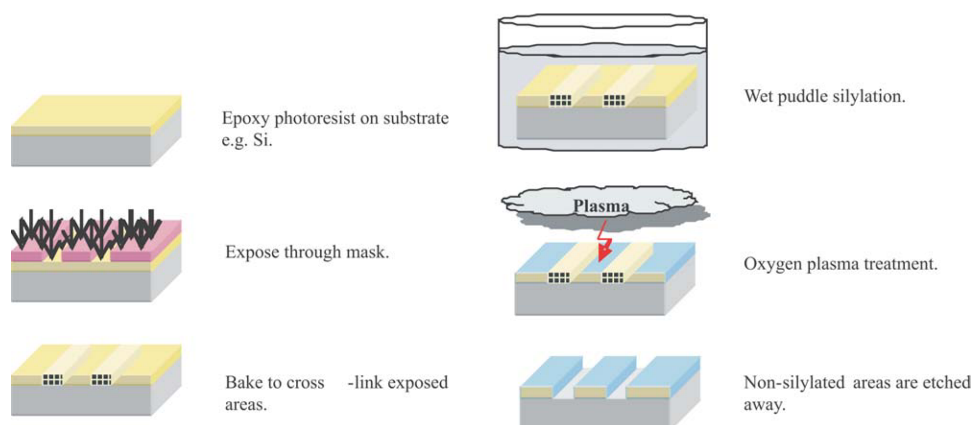

Figure 2 Process flow of epoxy resist silylation and plasma etching for micromachining applications. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

crack-free versions. In a similar vein, relaxation step 7 allowed for more efficient crosslinking; also, crack formation was suppressed.

In step 10, two types of plasma-processing units were explored: (1) reactive ion etching (RIE) and (2) inductively coupled plasma (ICP).

RIE was performed in a Nextral-Alcatel NE 330 etcher at 13.5 MHz, 10 mTorr, 400 W (0.57 W/cm^2), a bias voltage of 150 V, and an oxygen flow of 100 sccm. No sample temperature control was applied.

ICP was performed in an Adixen-Alcatel etcher (Annecy, France) at 10 and 15 mTorr with a source power of 400–2000 W, a bias voltage of 100 V, and an oxygen flow of 100 sccm. The temperature of the sample was controlled at 15°C by mechanical clamping and helium backside cooling.

In this study, we paid particular attention to the significance of step 8 and explored water-level variations of the standard process. A dry silylation solution was obtained by the addition of 4-Å molecular sieves in the form of 3.2-mm pellets (Merck) to each solution constituent before mixing. For the controlled humidity experiments, 0, 167, 333, 3333, and 5000 ppm deionized water were added in a dry silylation solution with a total volume of 30 mL. With this method, the results we obtained were quite reproducible.

All experiments were performed within the controlled conditions of a clean room. Strictly speaking, our dry silylation reference conditions were, in reality, conditions of a practically fixed and very low level of humidity. The latter, very low level of humidity was not determined, and we chose to perform experiments under laboratory conditions of practical significance. The findings reported later suggest that under the conditions used in this study, the reference humidity level was substantially lower than the one necessary for optimum results; hence, it was not necessary to attempt a further reduction of the moisture level of the molecular-sieve-treated solution that was processed in a clean-room environment.

Structures were imaged with a Philips (Eindhoven, Holland) 515 scanning electron microscope.

Characterization techniques

A laser interferometer (XENON, Athens, Greece) (equipped with a red laser at 328 nm) was used for the *in situ* measurement of thickness loss when etching was performed in the RIE reactor. A spectroscopic ellipsometer was used for *in situ* etch rate measurements [M2000F (EC400), J. A. Woolam Co., Inc., Lincoln, NE] with the ICP reactor. Finally, infrared spectroscopy measurements were performed with a Nicolet Fourier transform infrared (FTIR) Magna IR Spectrometer 550.

RESULTS AND DISCUSSION

Effect of the humidity on the silylation reaction and Si incorporation

The effectiveness of the silylation reaction was tested (1) *in situ* by laser interferometry and ellipsometry under RIE and ICP conditions, respectively, and (2) *ex situ* by FTIR spectrometry.

Figure 3 shows the results from the ellipsometry measurements during ICP etching for silylation solutions containing 0, 33, 167, and 333 ppm water. Polymers silylated with solutions containing 0–167 ppm water exhibited a constant thickness loss, which reflected an etching rate comparable to that observed for the nonsilylated polymer (EPON SU8). On the other hand, for polymers silylated with solutions containing 333 ppm water, the etching rate was substantially lower, which meant that the silylation reaction was quite effective. We evaluated the etching rates of the silylated materials, as shown in Figure 3. For nonsilylated EPON SU8, the etch rate

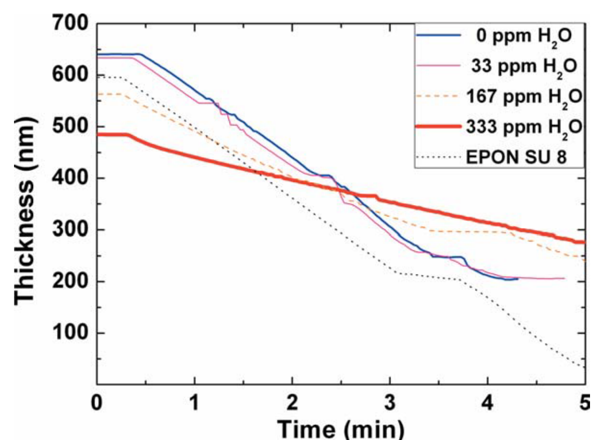

Figure 3 Absolute thickness loss from ellipsometry for polymers silylated with various water content solutions and for the nonsilylated polymer (SU8). Among the samples shown, the etch rate was at a minimum for the sample with 333 ppm H_2O. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was 133 nm/min. With silylation treatment, the etch rates were 126, 124, 82, and 45 nm/min for 0, 33, 167, and 333 ppm water, respectively; the selectivity in the last case was 3 : 1. The etch rate was high and comparable to that for nonsilylated EPON SU8 for silylation solutions with 0–33 ppm water, dropped for solutions with 167 ppm water, and underwent a substantial further reduction for solutions with 333 ppm water. All experiments conducted were measured within the typical experimental error deviation in etch rates (±15%) and showed good reproducibility of the silylation of the polymer surface.

We observed a difference in the initial film thickness for the selected samples in the plot (Fig. 3). Indeed, after silylation, the films were not uniform and some presented a loss of thickness instead of the expected swelling observed in the films after the silylation process. This was apparently due to a removal of material from the film surface as a result of the action of PGMEA (15 v/v % content in this first experiment) as a solvent; this problem was minimized upon reduction of the PGMEA content to 10% v/v.

The effectiveness of the silylation reaction for silylation solutions with a variety of water contents (0–5000 ppm) was also probed via laser interferometry during the oxygen-plasma step. Figure 4 shows the interference intensity versus etching time. Laser interferometry showed qualitatively the etching resistance of the samples. Indeed, the resistance between two peaks corresponded to a thickness loss of $\lambda/2n$, where λ(wavelength) $= 632.8$ nm of the He–Ne laser and $n = 1.67$ is the refraction index for the selected material (EPON SU8). Thus, the etch rate was $(\lambda/2n)/\Delta t$, where t is the etching time. Figure 4 suggests that the nonsilylated film and the film silylated with zero humidity exhibited almost the same etch rates, as mentioned before. For the rest, we only observed less than one period; this meant that the thickness loss was reduced to less than one period and that an oxide was formed on the surface. The roughness of this oxide caused signal loss and noise (by scattering).

When we measured the final thickness of the etched films via profilometry, we observed that for water contents exceeding 333 ppm, the reaction was effective, and the silylated film was not etched away (the remaining thickness was almost identical to the initial one). At around 500 ppm water, we observed that the silylation solution dissolved the film before etching, that is, the effect of silylation was a complete thickness loss instead of oxygen-plasma etching resistance.

Silicon incorporation was also studied via FTIR spectrometry (Fig. 5). As a result of the progress of silylation, the following were observed:

1. A reduction of the signal corresponding to characteristic epoxy-ring bands, namely, the band at 860 cm^{-1}, representative of the epoxy-ring vibrations, and the band at the 910 cm^{-1}, indicative of the glycidyl ether functionality.
2. New broad bands at 806 cm^{-1} due to the formation of Si—C and Si—O—Si bonds and in the vicinity of 1085 cm^{-1} due to a Si—O bond in the silylated resist; this bond was indicative of successful silicon incorporation.

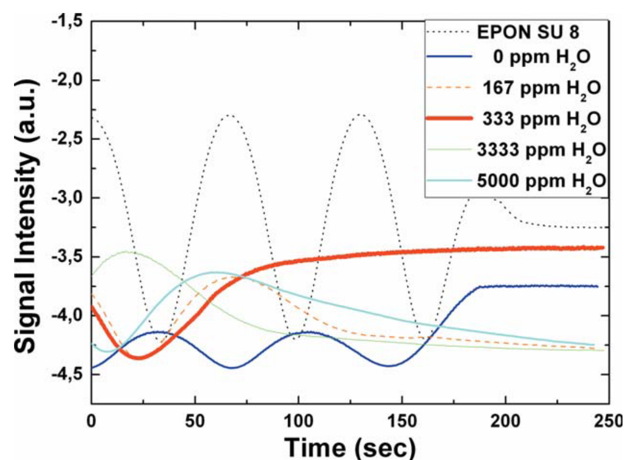

Figure 4 Interference intensity during etching for polymers silylated with various solutions of various water contents (inset) and for the nonsilylated polymer (SU8). The silylated zero-humidity sample exhibited the same etch rate as the nonsilylated sample. All other samples showed some resistance to etching. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

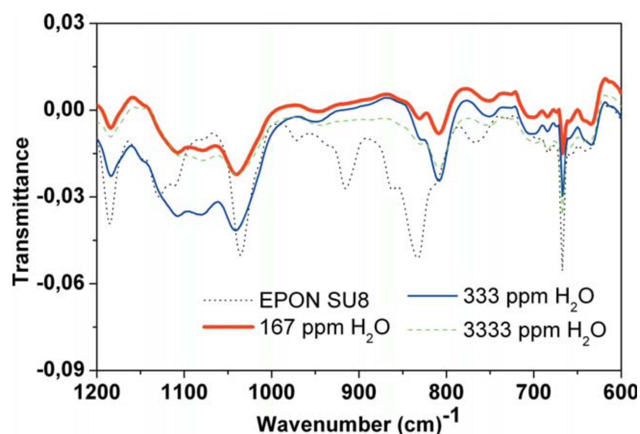

Figure 5 FTIR spectra of the epoxy film (SU8), the silylated film with a silylation solution containing 167 ppm (5 μL), 333 ppm (10 μL), and 3333 ppm (100 μL) water. The sample silylated with 333 ppm water exhibited enhanced peaks at 806, 860, 910, and 1085 cm^{-1}; this suggested an optimized (maximum Si uptake) humidity content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The FTIR spectra clearly showed that around 333 ppm water in the silylation solution, a more effective surface silylation of the polymer film was possible. This finding was compatible with all data from the preceding characterizations (ellipsometry and laser interferometry); hence, it appeared reasonable to pursue the lithographic process outlined in Figure 2 in a version with a silylation solution incorporating 333 ppm water.

The same results, with regard to the effectiveness of the silylation solution containing 333 ppm water, were obtained when the time elapsed between the preparation of the silylation solution and its application to the resin was varied from 1 min to 24 h; elapse times of 1 min, 30 min, 1 h, 3 h, and 24 h were examined. The latter finding meant that the lithographic outcome was insensitive to the age of the silylation solution containing the optimum level of moisture; thus, enhanced reproducibility is guaranteed, at least when the silylation solution is reasonably fresh and no additional moisture accidentally enters the solution.

Humidity effect interpretations

This study of the humidity effect in the silylation solution demonstrated the significance of the precise control of moisture level for a successful and reproducible silylation-aided lithography of an epoxidized resist; for example, the zero-moisture solution was found incapable of introducing a substantial level of silylation to the polymer films. Humidity appeared to act in a beneficial way for the silylation of the polymer film but only within a narrow concentration window. The maximum value of humidity inside the silylation solution—as to whether it could perform silylation on the surface of the polymer film—was 333 ppm.

Although not important for practical purposes, the potential mechanism leading to the herein reported unusual dependence of silylation level on moisture content is of materials science interest, and we briefly discuss two alternatives:

1. Humidity leads to the hydrolysis of the silane, and condensations follow. In the case of $(CH_3)_2SiCl_2$, hydrolysis may either lead to cyclic siloxanes (mostly trimers and tetramers) or to linear siloxane oligomers of various lengths.[23] The new siloxane species might react near the surface with the molecules of the resin, whereas their availability and ability to react in the interior of the film will depend on both their amount and their mobility (which will be lower for larger species size). Very low humidity levels might have a limited effect in view of the limited amount of siloxane species that can be generated. On the other hand, an excessive amount of humidity might create siloxane species of very low mobility. Hence, an optimum level of moisture might arise when the resulting siloxane species are simultaneously sufficiently fast and numerous.
2. Water in small amounts weakens the Si—Cl bond via hydrogen bonding (Si—Cl. . .H—O—H; Figs. 6, 7) or facilitates the epoxy ring opening (Fig. 8).

The second alternative mentioned above is further illustrated in Figures 6, 7, and 8. In Figure 6, it is shown that H_2O attack renders Si strongly electropositive (δ^+) and thus, is attacked by the oxygen of the epoxy ring. On the other hand, the chloride ion that is released can attack the epoxy-ring carbon (preferably, the secondary carbon) and may either remain there (case 1, shown in Fig. 7(b)) or escape as HCl gas leaving a double bond behind (case 2, shown in Fig. 7(a)).

Both of these mechanisms are possible in principle, but because during our experiments the evolution of HCl was apparent, either the second alone or both mechanisms operated.

In Figure 8 it is shown that the oxygen of water can also attack one of the epoxy-ring carbons, rendering the epoxy-ring oxygen strongly negative and,

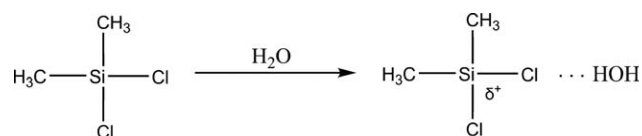

Figure 6 Hydrogen bonding weakening the Si—Cl bond.

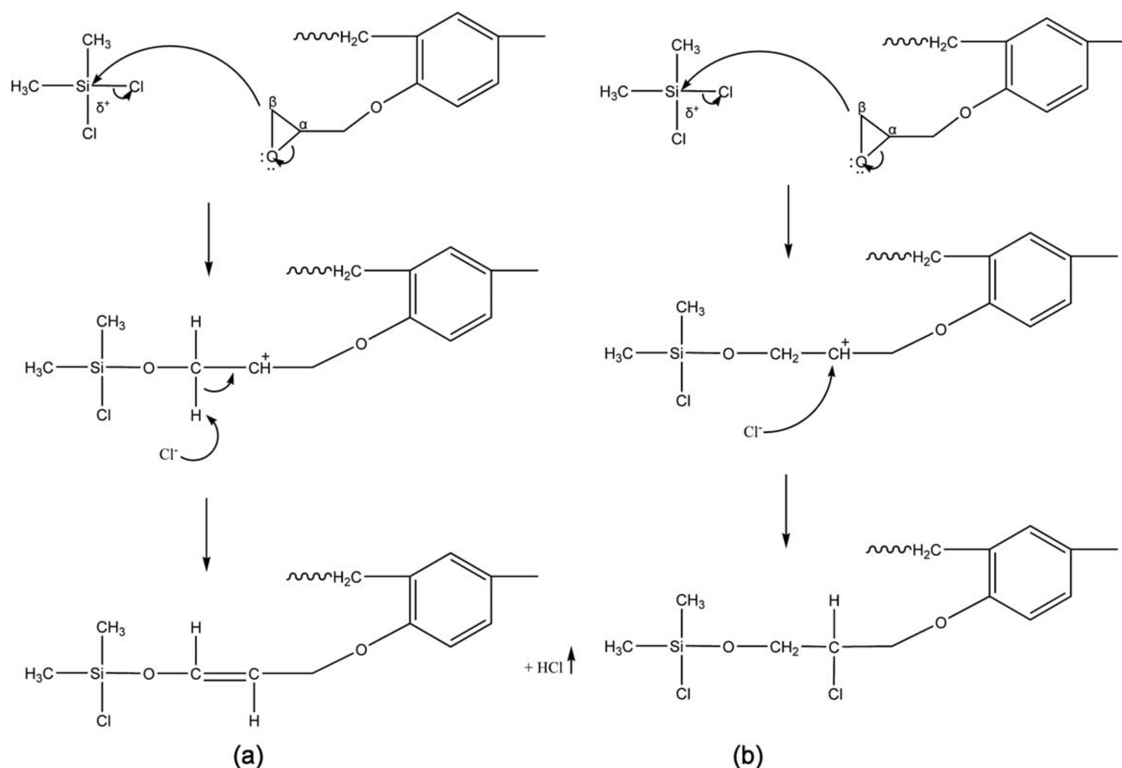

Figure 7 (a) Chloride ion escaping as HCl gas. (b) Chloride ion remaining after attacking the epoxy (secondary) carbon.

thus more efficient to attack Si; this would lead to epoxy-ring breakage and oxygen silylation. In this case, the —OH group sticks to the carbon and a proton is released, which forms HCl with the Cl^- released by the Si compound (Fig. 8).

When the water content is very low, the previous sequence of reactions is not possible. On the other hand, when excessive water is present, it hydrolyzes the chlorosilane [dimethyl-dichloro-silane (DMDCS)], that is, Si—Cl bonds break, and Si—OH bonds (and, possibly, upon condensation, Si—O—Si bonds plus water) form, whereas HCl evolves. The new combination is less drastic and does not attack the oxygen of the epoxy ring; that is, no chemical silylation takes place (Fig. 9).

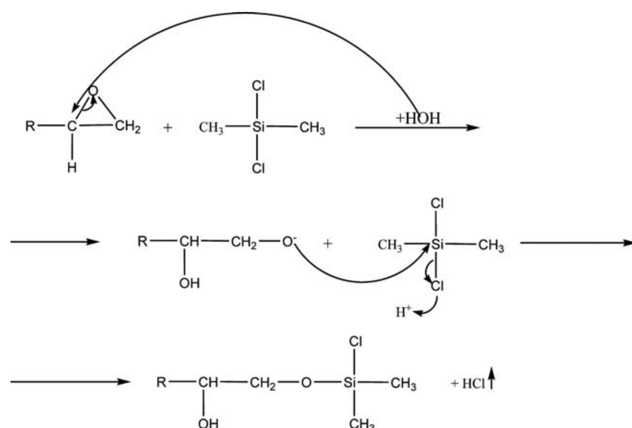

Figure 8 Alternative reaction: oxygen silylation and epoxy-ring breakage.

The second alternative (Figs. 6, 7, 8) was supported indirectly by the experimental fact of the nondestruction of the silylation solution after several hours, although a parallel contribution to the overall phenomenon from the first alternative (silane hydrolysis and condensation) could not be excluded.

Lithographic evaluation

Figure 10 shows the resist lines after UV contact printing and wet development, whereas Figure 11 shows the resist lines after UV contact printing, silylation, and dry development (ICP etcher).

The outcome of the standard lithography process appears in Figure 10. Undesirable features included a substantial level of residues and a curvature of features intended to have a flat form. The outcome of the optimized silylation process considered in this

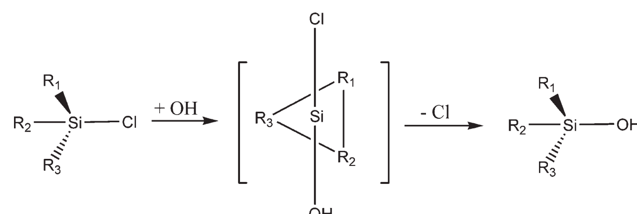

Figure 9 Hydrolysis of DMDCS.

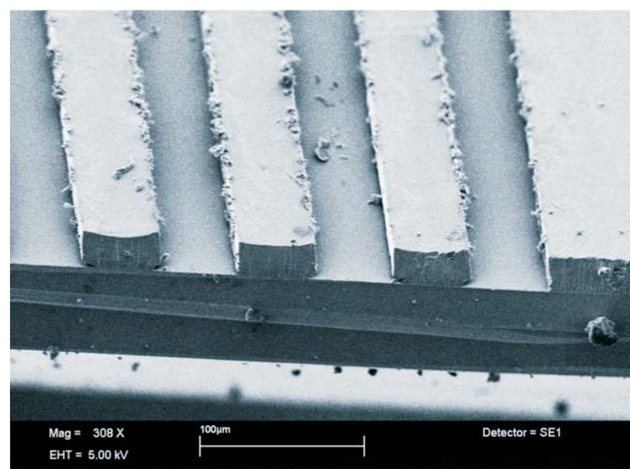

Figure 10 Standard lithography process with epoxy resist (conditions: 5% sensitizer, 10-μm film thickness, 50 μm wide lines, and 190 mJ/cm^2 dose). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

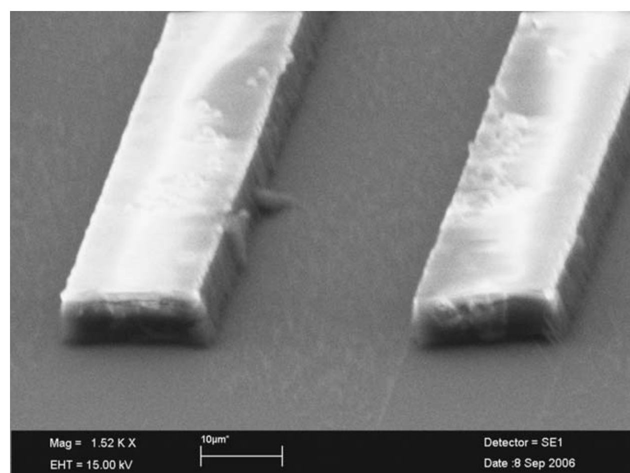

Figure 11 Wet silylation process and dry development process (conditions: 5% sensitizer, 7-μm film thickness, 20 μm wide lines, 210 mJ/cm^2 dose). See the text for the silylation and ICP etcher conditions.

work is shown in Figure 11: the curvature was removed, and the level of residues was drastically reduced. The broken ends allowed for an observation of the silylation depth, indicated by a color difference (silylated light portion vs nonsilylated dark portion).

CONCLUSIONS

We presented and optimized an epoxy-based lithographic route incorporating a silylation step. Reproducible results were obtained by the control of the amount of humidity inside the silylation solution. The presence of a low level of water within a rather narrow range of concentrations was necessary for the reaction to take place inside the film at a satisfactory level.

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