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Letter

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printing

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# Patterning of a polysiloxane precursor to silicate glasses by microcontact printing

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## Abstract

A polysiloxane precursor to silicon dioxide was used to generate silica patterns on a flat surface. The conversion of a thin film of this polymer to silica was done either by photolithography or by printing an organic acid on the film. The former technique allowed the formation of structures with thickness as large as 2  $\mu\text{m}$ . The latter method could generate patterns with sub-micron resolution and thicknesses smaller than 0.2  $\mu\text{m}$ . These structures could be used as resists for  $\text{O}_2$  reactive ion etching (RIE). © 1998 Published by Elsevier Science S.A.

*Keywords:* Glass photoresist; Microcontact printing; Polysiloxane

## 1. Introduction

This paper describes a new method to generate  $\mu\text{m}$ -scale patterns of silicate glass on flat and non-planar substrates. The precursor material is a polysiloxane polymer (spin-on glass), which can be crosslinked into silica by exposure to protons. Two different methods can lead to the formation of silica structures. The first method—which has been described in the literature [1]—involves the sensitization of the polysiloxane by a UV acid generator and produces patterns by photolithography. The second, non-photolithographic technique that we describe converts the polymer to silica by bringing an elastomeric stamp bearing the desired pattern and inked with a suitable acid into contact with it. This method—microcontact printing ( $\mu\text{CP}$ ) of acids—is a useful variant of ‘soft lithography’ [2].

Layers of silicon dioxide or spin-on glass are commonly used in VLSI fabrication. They have good planarization and dielectric properties [3]. They are also used as resists for etching metallic and organic layers [4]. Chemically amplified glass photoresist (GP) [1] has given conventional spin-on glass the capability to accept patterning, and has been used as a resist in multilevel processing.

Microcontact printing ( $\mu\text{CP}$ ) has been developed to pattern self-assembled monolayers (SAMs) on gold and silver [5], and, with more difficulties, on  $\text{Si}/\text{SiO}_2$  and

other substrates [6]. These monolayers can act as resists for wet etching and allow the fabrication of microstructures [7]. The combination of acid-sensitive spin-on glass and  $\mu\text{CP}$  provides a useful new capability to form silica microstructures.

Here, we present a method to fabricate a patterned glass film. A film of acid-sensitive spin-on glass on a silicon wafer is stamped with a suitable acid. The acid diffuses into the film and induces the transformation of the polymer into a precursor to silica. After removing the unreacted polymer and curing, a silicate glass pattern is produced. Although films as thick as 2  $\mu\text{m}$  (after processing) have been patterned by UV exposure of the polysiloxane precursor, the thicknesses of the films that can be patterned by stamping did not exceed 0.2  $\mu\text{m}$ , reflecting, we presume, the requirement that the protons diffuse from the surface into the bulk of the thin film. Nevertheless, films patterned by stamping were sufficiently thick to act as resists for  $\text{O}_2$  reactive ion etching (RIE) of an underlying polymer film.

## 2. Experimental

### 2.1. Materials

Polished silicon wafers (Silicon Sense, MA) were cleaned before use by sonication in trichloroethylene, acetone and methanol. Aluminum-coated wafers were pre-

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pared by e-beam evaporation of  $\sim 100$  nm of Al (99.99%, Alfa). Diacetoxy-di-*t*-butoxysilane and methyltriacetoxysilane (United Chemicals) were used as received. Tetrahydrofuran (THF), 4-methyl-2-pentanone (MIBK), *t*-butyl methyl ether, 2-propanol (IPA), and triethylamine were used without further purification. Triphenylsulfonium hexafluoroantimonate (50% in propylene carbonate) was used as received. The elastomeric molds used in  $\mu$ CP were prepared by casting a silicone precursor (Sylgard 184, Dow Corning, NY) on masters prepared by conventional photolithography [8].

## 2.2. Formation of the *n*-alkylsulfonic acids

The commercially available (Aldrich) sodium salt of the respective sulfonic acid (1 g) was suspended in anhydrous Et<sub>2</sub>O (50 ml), and HCl was bubbled in under cooling. After 15 min, the volatiles were removed in vacuo, and the residue was resuspended in anhydrous Et<sub>2</sub>O and filtered. The clear organic phase was evaporated to dryness, yielding the corresponding sulfonic acids as colorless oils or solids. Yields were generally above 90%.

## 2.3. Synthesis of glass photoresist

Synthesis of the glass photoresist followed the literature [1]. Briefly, a solution of 46.2 g of diacetoxy-di-*t*-butoxysilane in 1.5 l of MIBK was cooled to  $-10^\circ\text{C}$  under nitrogen atmosphere, and 68 ml of triethylamine was slowly added to it. A solution of deionized water in 80 ml of THF was added dropwise, and the mixture was heated to  $70^\circ\text{C}$  for 4 h. The silane polymerized by hydrolysis and condensation of the acetoxy groups, the *t*-butoxyl groups remaining intact. We used a 3:1 molar ratio of water:silane, which corresponds to six equivalents in the polymerization reaction. After cooling and rinsing the solution with water, the product was purified through a short silica column.

The methyl-doped GP (GP:Me) was prepared with the same procedure as the undoped polysiloxane, except that 4 g of methyltriacetoxysilane was added as a 10% solution in MIBK at the end of the polymerization reaction and left to react at  $70^\circ\text{C}$  for another hour. This corresponded to a 10% molar ratio of methyl to silicon.

## 2.4. Priming

The silicon wafers were primed before spin-coating of the GP films. Priming increased the adhesion between the exposed GP and the wafer and prevented the film from cracking. A freshly prepared 1:1:10 mixture of diacetoxy-di-*t*-butoxysilane, triethylamine, and MIBK was spin-coated on the wafers at 3000 RPM. The wafers were then rinsed with IPA and deionized water. The contact angle of water with the primed surface was ca.  $40^\circ$  at this stage, showing that the wafer was partly covered with *t*-butoxyl groups.

## 2.5. UV exposure

For UV exposure, the glass photoresist GP:Me was sensitized with 2% molar of triphenylsulfonium hexafluoroantimonate [1]. After exposure of the films through a chrome mask with a mercury lamp (main wavelengths: 365 nm and 405 nm), the wafers were baked at  $100^\circ\text{C}$  for 2 min. They were then developed in anisole for 30 s with strong agitation and blown dry with nitrogen.

## 2.6. Microcontact printing

The procedure used in patterning of GP films by  $\mu$ CP is depicted on Fig. 1. An elastomeric stamp was inked by soaking for 1 s in a 10-mM solution of hexadecanesulfonic acid in a 1:1 mixture of *t*-butyl methyl ether and IPA. The stamp was blown dry for 1 min. It was then put in contact with the GP-coated wafer for 1 min, and the wafer was baked on a hot plate at  $130^\circ\text{C}$  for 20 min. Development was carried out in anisole for 20 s.

## 2.7. Reactive ion etching

A  $1.4\text{-}\mu\text{m}$  thick film of polyimide (Pyralin PI 2556, du Pont) was spun onto a wafer and cured at  $350^\circ\text{C}$  for 30 min. The surface of the film was then oxidized in an O<sub>2</sub> plasma for 20 s, and GP was spin-coated at 2500 RPM from a 10% MIBK solution. Microcontact printing and development of GP were performed as described above. Following development, the wafer was etched in an O<sub>2</sub>

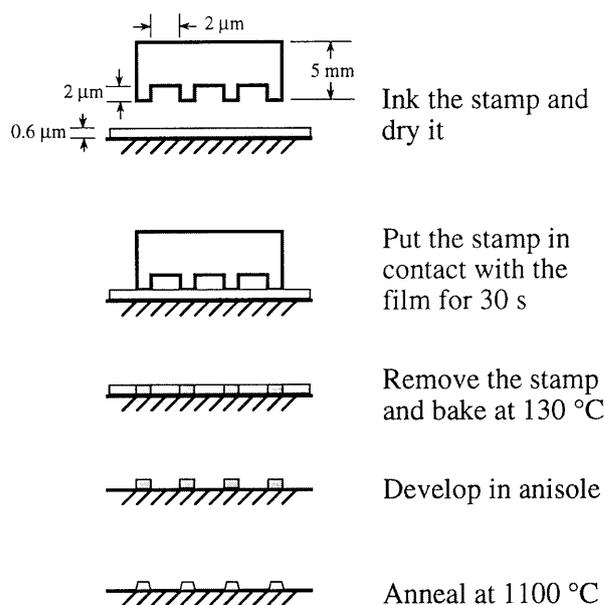


Fig. 1. Schematic outline of the method used to fabricate patterns on a glass photoresist film by microcontact printing. The silicone stamp is briefly soaked in a 10 mM solution of hexadecanesulfonic acid in *t*-butyl methyl ether. It is then blown dry for 1 min and put in contact with a wafer coated with  $0.6\text{-}\mu\text{m}$  thick GP film for 30 s. The wafer is baked for 10 min at  $130^\circ\text{C}$  on a hot plate and developed for 20 s in anisole.

RIE (25 sccm, 150 mTorr, 100 W,  $-600 V_{\text{bias}}$ ) for 12 min.

### 3. Results

#### 3.1. UV exposure

A maximum thickness of ca.  $1 \mu\text{m}$  before exposure and  $0.3 \mu\text{m}$  after exposure was reached for conventional glass photoresist, as reported in the literature [1]. Thicker films cracked either during spin-coating or during post-exposure baking. Doping silica precursors with methyl groups is known to increase the compliance and decrease the tendency of the silica structures to break during annealing [9]. Commercial spin-on glass contain methyl groups for this purpose. The methyl-doped glass photoresist that we used allowed us to reach thicknesses of  $6 \mu\text{m}$  by spin-coating a

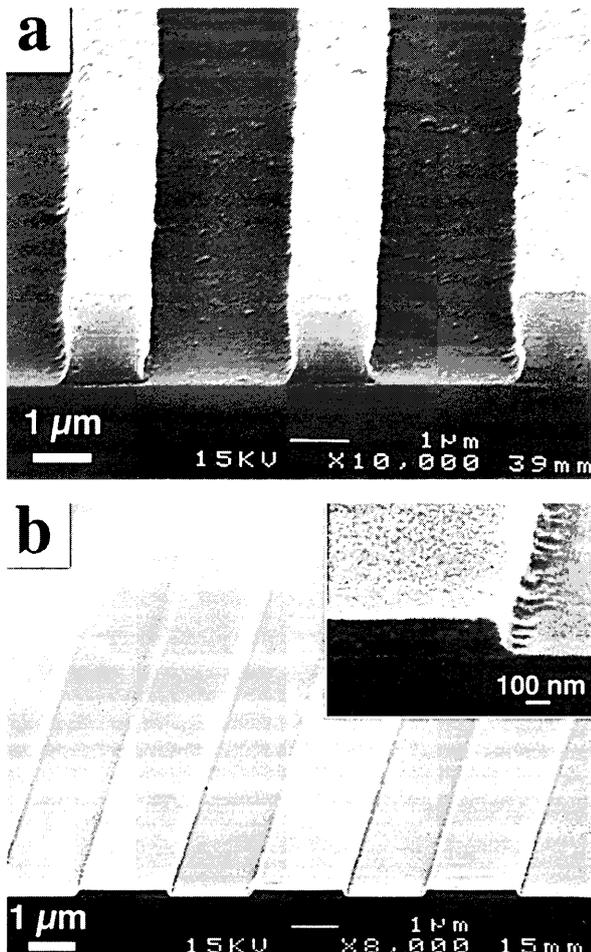


Fig. 2. SEMs of patterned silica structures. (a) These structures were generated by photolithography on a  $6\text{-}\mu\text{m}$  thick GP:Me film using a chrome mask patterned into  $2\text{-}\mu\text{m}$  lines separated by  $2 \mu\text{m}$ . After development, the wafer was annealed at  $400^\circ\text{C}$  for 1 h in air. The resulting lines were  $2 \mu\text{m}$  high and  $1.5 \mu\text{m}$  wide. (b) These structures were generated by  $\mu\text{CP}$  on a  $0.6\text{-}\mu\text{m}$  thick GP film with a silicone stamp bearing  $2\text{-}\mu\text{m}$  lines separated by  $2 \mu\text{m}$ . The lines were annealed at  $400^\circ\text{C}$  for 1 h in air.

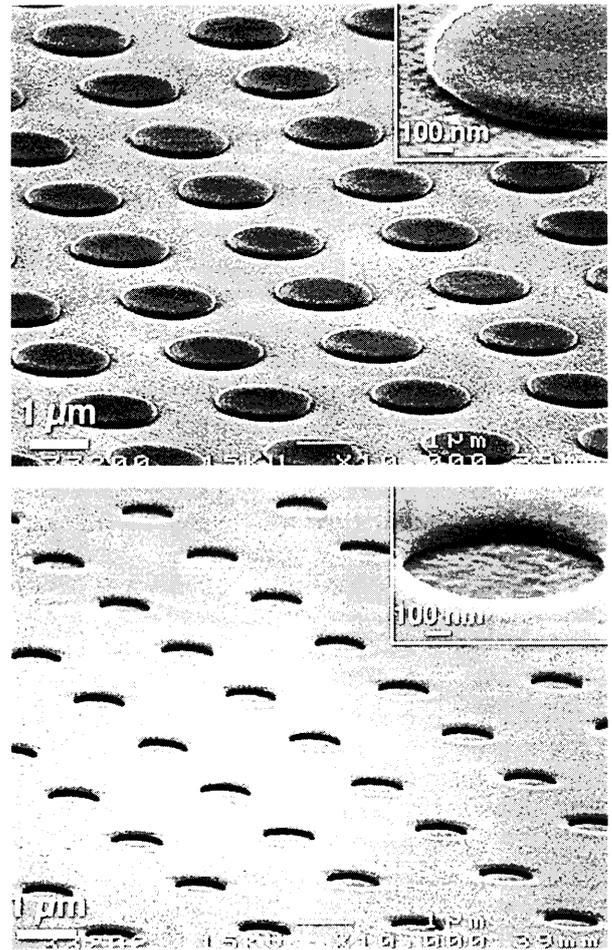


Fig. 3. SEMs of silica patterns fabricated by stamping a  $0.6\text{-}\mu\text{m}$  thick GP film on an Al-coated wafer. The ink was a  $10 \text{ mM}$  solution of hexadecanesulfonic acid in *t*-butyl methyl ether. The wafer was baked for 10 min at  $130^\circ\text{C}$  on a hot plate and developed for 20 s in anisole.

$45\%$  MIBK solution of GP:Me at 2500 RPM. The patterns generated after exposure did not break and had a thickness of  $2 \mu\text{m}$ . The conversion of GP into dense silica gives rise, in theory, to a shrinkage of a factor of 7 in volume (the ratio of the molar volumes of these materials). In practice, this shrinkage takes place mainly in the direction perpendicular to the substrate for thin-film structures. Thus, the thickness of the pattern is much smaller than that of the non-exposed film.

Fig. 2 shows structures generated by photopatterning using a chrome mask bearing a pattern of  $2\text{-}\mu\text{m}$  lines and spaces, after developing with anisole and annealing at  $350^\circ\text{C}$  for 1 h. The resulting lines are  $2 \mu\text{m}$  high and  $1.5 \mu\text{m}$  wide; these dimensions show that shrinkage occurred both perpendicularly to the surface and in the plane of the surface, perpendicularly to the line. Assuming that all the exposed material is converted to silica, this gives a volumetric shrinkage factor of ca. 4. This number, smaller than the theoretical shrinkage, suggests that some cross-linking was already present in the polymer.

### 3.2. Microcontact printing

Films with a thickness of  $0.6\ \mu\text{m}$  were spin-coated at 2500 RPM using a 10% solution of GP in MIBK. These films were printed with acids using  $\mu\text{CP}$  and an elastomeric silicone stamp. Different acids were tried, using the same procedure for  $\mu\text{CP}$ . Oxalic acid, boric acid, and polyacrylic and polystyrene sulfonic acids did not produce any observable crosslinking. Stamping with pentanesulfonic acid, which is a liquid at room temperature, converted the entire film to silica and did not give any pattern; we suppose that this result reflects the high mobility of this acid. Hexadecanesulfonic acid is a solid at room temperature and gave the best result. We observed that the contact time between the stamp and the film was the parameter that limited the resolution that could be achieved. Contact times longer than 2 min resulted in blurred patterns. This blurring is probably due to the diffusion of the acid that might occur at this stage. Surprisingly, the post-exposure baking (PEB) time did not seem to have much influence on the resolution: PEB times from 20 to 60 min gave similar results. If the PEB was shorter than 15 min, the polymer did not cross-link all the way to the substrate, and the silica pattern lifted off from the substrate during development. We interpret these observations as suggesting that lateral diffusion of the hexadecanesulfonic acid takes place during printing and determines the resolution. Then, during PEB, the acid diffuses isotropically into the polymer and catalyses the cross-linking in the bulk. Fig. 2b Fig. 3 show different patterns obtained by stamping a  $0.6\text{-}\mu\text{m}$  thick film. The irregularity in the profile of lines was approximately 100 nm. The lateral diffusion of the acid led to an increase of the width of the pattern by ca. 100 nm, uniform on the whole area of the sample ( $1\ \text{cm}^2$ ).

### 3.3. RIE

Silicon wafers bearing a  $0.6\text{-}\mu\text{m}$  thick film of GP on top of a  $1.4\text{-}\mu\text{m}$  thick layer of polyimide were printed with

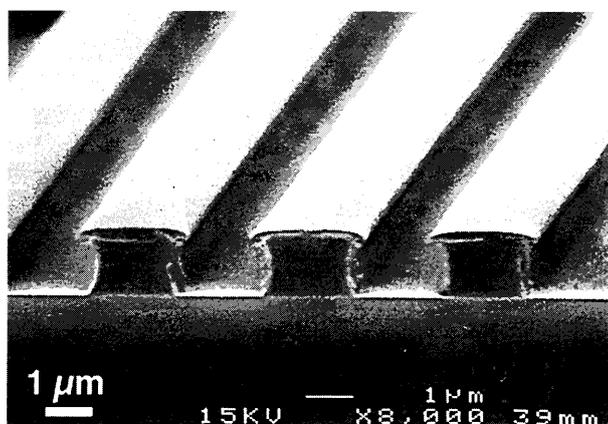


Fig. 4. SEM of lines generated by  $\text{O}_2$ /RIE on a  $1.4\ \mu\text{m}$ -thick polyimide film. The resist was a  $0.2\text{-}\mu\text{m}$  thick GP film that had been patterned by  $\mu\text{CP}$  of hexadecanesulfonic acid into  $2\text{-}\mu\text{m}$  lines separated by  $2\text{-}\mu\text{m}$  spaces.

hexadecanesulfonic acid and developed as described above to generate a pattern of  $2\text{-}\mu\text{m}$  lines and spaces. This pattern was transferred to the polyimide film by  $\text{O}_2$  RIE (Fig. 4).

## 4. Conclusions

A polysiloxane-based chemically amplified photoresist was used to produce silica patterns on flat substrates. Two different methods of exposure were applied. A regular UV exposure gave features as thick as  $2\ \mu\text{m}$  after annealing, with a quarter-micron edge resolution. The exposure was also carried out by stamping a photoresist film with hexadecanesulfonic acid. The thickness of the patterns was smaller than  $0.2\ \mu\text{m}$  in this case. The patterns were successfully transferred to an underlying polyimide film by  $\text{O}_2$  RIE. Although the maximum achievable thickness is small, we believe that  $\mu\text{CP}$  of a polysiloxane is a promising complement to conventional use of photolithography for production of patterned glass films. The deformability of the elastomeric stamp obviously must be controlled for structures requiring long-range order: the limits to registration and achievable pattern resolution in  $\mu\text{CP}$  have not yet been quantified.

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## References

- [1] T. Ito, M. Sakata, A. Endo, H. Jinbo, I. Ashida, *Jpn. J. Appl. Phys.* 32 (1993) 6052.
- [2] J.L. Wilbur, E. Kim, Y. Xia, G.M. Whitesides, *Adv. Mater.* 7 (1995) 649.
- [3] T. Nakano, T. Ohta, *J. Electrochem. Soc.* 142 (1995) 918.
- [4] J.M. Moran, *Solid State Technol.* 24 (1981) 195.
- [5] A. Kumar, H.A. Biebuyck, N.L. Abbott, G.M. Whitesides, *J. Am. Chem. Soc.* 114 (1992) 9188.
- [6] Y. Xia, M. Mrksich, E. Kim, G.M. Whitesides, *J. Am. Chem. Soc.* 117 (1995) 9576.
- [7] N. Abbott, A. Kumar, G.M. Whitesides, *Chem. Mater.* 6 (1994) 596.
- [8] A. Kumar, G.M. Whitesides, *Appl. Phys. Lett.* 63 (1993) 2002.
- [9] Y. Haruy, S.E. Webber, *MRS Symp. Proc.* 271 (1992) 297.