PMMA as an etch mask for silicon micromachining–a feasibility study[†]

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Abstract

Silicon micromachining requires a proper etch mask, which can withstand the action of etchant during the fabrication of typical structures. Widely used etch mask materials are SiO_2, Si_3N_4, gold (Au), chromium (Cr) and boron diffusion. Deposition of these on substrates requires expensive equipment. Mihaela Ilie *et al*. [*Proc. SPIE Materials and Device Characterization in Micromachining*, 1998, 3512, 4221] reported PMMA as a mask layer on the backside during silicon etching by KOH solution. This etch mask is cheap and is easy to use. In the present work, PMMA is deposited on silicon substrate with a simple technique of spin-coating. The adhesion of spin-coated film of PMMA on silicon wafer is an important parameter for its use as an etch mask, while etching in aqueous KOH solution for silicon micromachining. Pre- and posttreatments have been performed on silicon substrate and the mask layer to achieve greater adhesion of the mask material. Feasibility is demonstrated of the use of PMMA as etch mask.

Keywords: Silicon micromachining, etch mask, PMMA.

1. Introduction

Silicon technology has reached the level of subsubmicron size and added 'smartness' by integrating sensors and actuators (the moving parts) with the devices. This has become possible with the silicon micromachining technology which extensively uses anisotropic etching of silicon in KOH,[1–3] KOH+IPA[4] and EPW.[3] Typical micromachined structures include thin membranes, deep and narrow grooves, cantilevers, diaphragms, high-precision nozzles, gratings, etc.[5,6] The etch masks used are silicon dioxide (SiO_2), silicon nitride (Si_3N_4), gold (Au), chromium (Cr),[7–11] and boron (B),[11] the former two being extensively used. These are grown, deposited or diffused using commerically available equipment/techniques. Silicon dioxide is normally grown at elevated temperature at 1100°C, while silicon nitride is deposited by chemical vapour deposition (CVD) at around 800°C.

Fabrication of typical antireflection grating requires silicon etching till a depth of 0.3 μm, whereas a typical cantilever structure requires etching to a depth of 250 μm. Etching rate of silicon in 20% by weight KOH solution at 80°C is 86 μm/h.[1] Thus, 0.3 μm-thick silicon for grating can be etched in a few minutes, whereas it takes about 3 h for 250 μm cantilever. Further, the etching rate of SiO_2 is 0.268 μm/h in 20% weight KOH at 80°C. In order to mask silicon for complete fabrication

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of grating, 0.2 μm-thick SiO_2 needs to be grown. Likewise, for a cantilever structure, 0.8 μm-thick SiO_2 needs to be grown. The growth process requires less than an hour for a grating and about 8 h for a cantilever structure at the above-mentioned temperature (deposition rate 0.1 μm/h).[12] Similar is the case with Si_3N_4. The above values indicate that the process of SiO_2 or Si_3N_4 deposition is expensive and time-consuming. Also, if the thickness of SiO_2 or Si_3N_4 is not uniform, the yield for the fabrication process will be reduced.

While working with PMMA for other applications, we learnt that it possesses characteristics like easy to cast films, low (negligible) etching rate in KOH and good temperature resistance, which are suitable as an etch mask for micromachining. Ilie *et al*.[13] have reported the use of PMMA as etch mask. The main problem they encountered is the adhesion of PMMA on to the substrate. Commercially available PMMA has poor adhesion. Good adhesion is because of the attractive interaction between the layer and the substrate and to improve it attractive interaction should be strengthened. Ilie *et al*.[13] used primer layers between the substrate and the PMMA to improve adhesion.

The present paper reports the experiments carried out to examine the feasibility of spin-coated PMMA as an etch mask. Pre- and posttreatments on silicon substrate and PMMA are done to improve adhesion and therefore masking characteristics. Results obtained are reported and discussed on the basis of available literature.

2. Experimental

N-type, 500 μm-thick silicon substrate of (100) orientation was used in the present experiments. The silicon substrate was cleaned by dipping in HF solution and then washing with acetone.[14] A simple technique of spin-coating was used to coat a film of PMMA on to silicon substrate to test its feasibility as an etch mask. For the spin-coating, the solution of PMMA was prepared by dissolving grains of commercially available PMMA in chloroform ($CHCl_3$). The concentration of the solution was varied by dissolving different weights of PMMA grains in 100 cc of $CHCl_3$. The solution of PMMA was poured on the silicon wafer and was spun at 3000–4000 rpm for 1½ min. The coated samples were then baked in an oven to increase the adhesion. The baking temperature and baking time were varied from 70°C to 90°C and from 15 min to 60 min, respectively, to observe the variation of masking durability.

The sample was then dipped in KOH solution. The solution of KOH was prepared by dissolving KOH pellets in de-ionized (DI) water. The concentration of KOH was varied starting from 5% to 20% by weight dissolved in DI water. Durability of PMMA was tested as an etch mask measured in minutes at different KOH concentrations and temperatures (from 60°C to 80°C) of KOH.

3. Results and discussion

The data collected for demonstrating the feasibility of PMMA as an etch mask for silicon micromachining are presented here. To start with, 2.5 g of PMMA was dissolved in 100 cc of $CHCl_3$ and used in the present experiments. This was chosen out of experience gained during the work being carried out in our laboratory on other applications of PMMA. Films of PMMA spin-coated on silicon substrates were dipped in KOH solution of 5% by weight in DI water at room temperature. This concentration was selected as the durability of PMMA in KOH was not known. It was found that the films peeled off within 5 min.
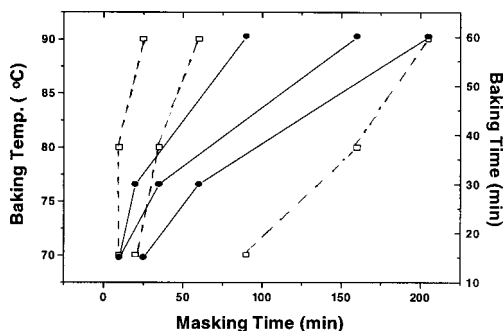
FIG. 1. Variation of masking time of PMMA with baking temperature and baking time when dipped in KOH at RT. □--□: Variation with baking time 15, 30 and 60 min; ●–●: Variation with baking temperatures of 70, 80 and 90°C.

In order to increase the time taken for peeling off (masking time), the adhesion of PMMA with silicon substrate needs to be improved. The adhesion of polymer resists to the substrates in lithography process is improved by baking the resist at specific temperature and for specific time.[15] The same procedure was adopted in the present work. The results of variation of masking time of PMMA with baking temperature (70°C to 90°C) and baking time (15 to 60 min) when dipped in KOH at room temperature (25°C), 60°C and 80°C are shown in Fig. 1. Baking temperature above 90°C was not used because the glass transition temperature of PMMA is 105°C. Concentrations of KOH and PMMA were kept constant for the experiments.

From Fig.1 it can be seen that for constant baking time (-□- three different times), the masking time increases with increase in baking temperature. Further, the masking time also improves with increase in baking time at constant baking temperature (•-•-•: three different temperatures). Maximum masking time of 205 min is achieved at a baking temperature of 90°C and baking time of 60 min. Increase in masking time with baking temperature can be attributed to improved adhesion of PMMA on to the silicon substrate.[16]

This was further confirmed by IR spectroscopy. IR spectra obtained for the baked and unbaked samples are shown in Fig. 2. The peak values observed at 2995, 2946, 1731, 1447, 1149, 986, 610 cm^{-1} are attributed to CH_2, CH_2 stretch, carbonyl group, C-CH_3, CH bend in ester group, SiH_4 and silicon, respectively. These peaks agree well with the standard peak values of PMMA,[17] which confirms that there is no change in the compound coated on the substrate even after baking. In addition to these peaks, peaks are observed at 1384, 1269 and 842 cm^{-1} corresponding to CH bend
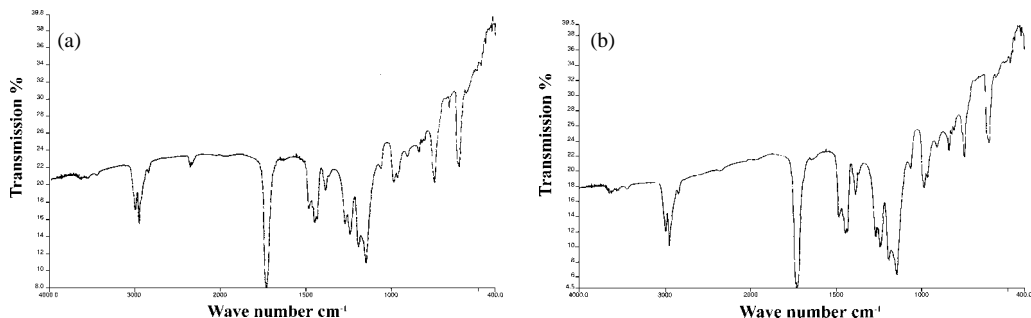

FIG. 2. IR spectra of (a) unbaked and (b) baked samples.
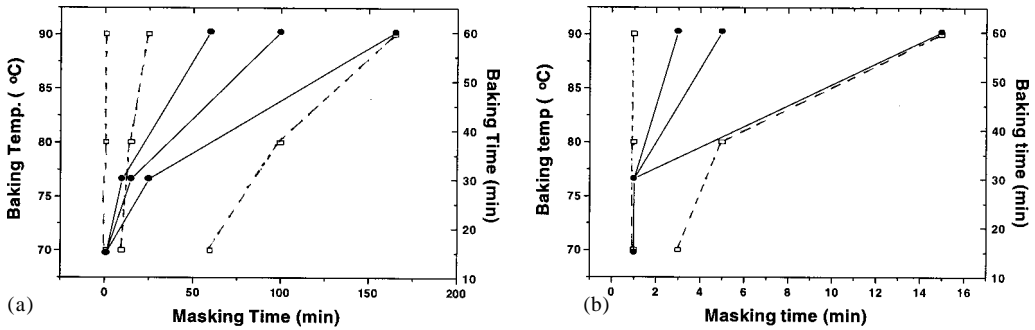
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FIG. 3. Variation of masking time of PMMA with baking temperature and baking time when dipped in KOH at (a) 60°C and (b) 80°C. □--□: Variation with banking time 15, 30 and 60 min •-•: Variation with baking temperature 70, 80 and 90°.

in CH_3, carboxyl ion and $SiOCH_3$, respectively, for baked samples (Fig. 2b). The peak of 842 cm^{-1} is reported by Mihaela Ilie *et al.*[13] to be responsible for bonding with silicon substrate. The presence of 842 cm^{-1} in baked films is an indication of improved adhesion of baked films with silicon and therefore improved masking time.

As mentioned in Introduction, a typical antireflection grating requires silicon etching till a depth of 0.3 μm, whereas a typical cantilever structure requires etching to a depth of 250 μm. Further, the etching rate of silicon at 10 wt% KOH at RT is 1.5 μm/h.[1] Therefore, etching of typical grating and cantilever requires 15 min and ~3 days, respectively. At 5 wt% KOH used in this part of experiments, the etching rate will be lower and etching time will be higher than that mentioned above. The maximum masking time of 205 min observed for PMMA in the present experiments will be sufficient to fabricate grating but not the cantilever.

Normally used temperatures of KOH for the micromachining processes are above 60°C where one achieves good etching rate of silicon. The next experiments therefore were carried out for KOH temperatures of 60°C and 80°C (Fig. 3).

Similar results on increase in masking time with increase in baking time and temperature are observed, but with reduced with masking times. The maximum masking times of KOH at 60°C and 80°C and at 90°C of baking temperature and baking time of 60 min are 165 min and 15 min, respectively.

In order to see the effect of PMMA concentration and in turn the thickness of the film on the masking time, experiments were carried out by changing the concentration of PMMA. The con-
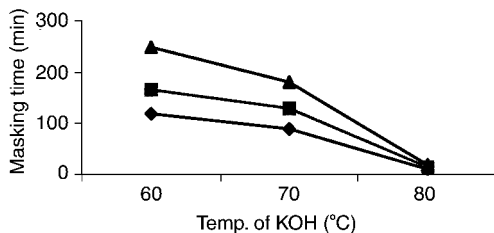

FIG. 4. Variation of masking time of PMMA with KOH temperature at different concentrations of PMMA and dipped in KOH concentration 5 wt%. ◆-0.625, ■-2.5 and 5–3.75 g/100 cc CHCl$_3$.

centration was varied by dissolving different weights of PMMA in CHCl$_3$. The temperature of KOH was varied from 60°C to 80°C. The baking temperature of 90°C and baking time of 60 min was used as it gave good results as discussed above (Fig. 4).

It is seen that the masking time improves with increase in the concentration of PMMA. Further, higher the concentration, higher is the thickness of the deposited films. The observed increase in masking time therefore can be attributed to increased thickness. But the higher thickness may pose problems in further processing of the samples for pattern transferring by lithography, especially for small feature size micromachined structures.

In the experiments so far a lower (5 wt%) concentration of KOH was used, but generally the concentration used for micromachining is 20 wt%. Experiments therefore were carried out with KOH concentration of 20 wt% (Fig. 5a).

Comparison of Figs 4 and 5a shows that at higher concentration of KOH the masking time reduces. This is as per expectation for all PMMA concentrations and KOH temperature values.

It is a well-known fact that the adhesion of film to the substrate improves if the substrate surface is made rough.[13] In the present work, the surface of silicon substrate was made rough by dipping in HF+HNO$_3$ (1:1)[14] solution for a few minutes immediately prior to coating PMMA. The results of the experiments carried out on roughened samples for the optimized baking temperature (90° C) and baking time (60 min) at 20 wt% KOH are shown in Fig. 5b. Improvement in the masking time is observed as compared to the samples where substrate was not cleaned (Fig. 5a) in HF+HNO$_3$.

These results also follow the same trend as in Fig. 5a with increase both in temperature and concentration of PMMA. The masking time obtained is more than for all the previous results for all the values of KOH temperature and PMMA concentration; for example, 325 min at 60°C for 3.73 g conc. of PMMA as compared to 180 min in the previous results. This can be attributed to increase in the adhesion of PMMA with silicon substrate due to pretreatment of the silicon substrate which was dipped in HF+HNO$_3$.

In order to use the masking material for etching specific structures in silicon it is necessary to transfer the required pattern in the masking material. The experiments for pattern transfer using photolithography technique were carried out on the films coated from PMMA concentration of 2.5 g in 100 cc CHCl$_3$ and baked at 90°C for 60 min. The process steps, which were carried out for the pattern transfer, are shown in Fig. 6. The pattern was successfully transferred in PMMA films.
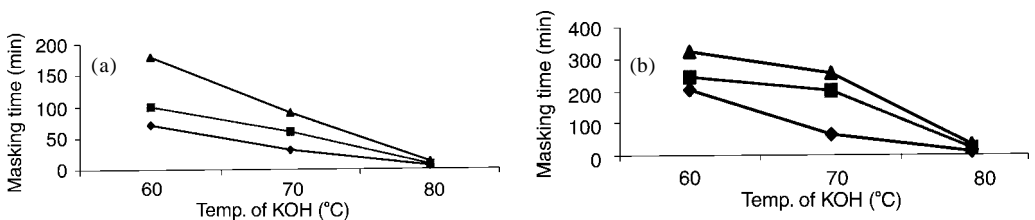

FIG. 5. (a) Variation of masking time of PMMA with KOH temperature at different concentrations of PMMA and dipped in KOH concentration 20 wt% and (b) after cleaning silicon with HF+HNO$_3$. ◆-◆ 0.625, and ■-■ 2.5 and 5–3.75 g/100 cc CHCl$_3$.
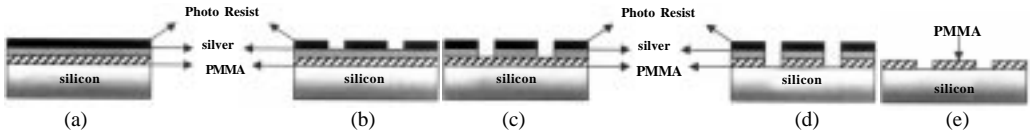
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FIG. 6. Process of transfer of pattern in spin-coated PMMA.

It is clear from the above discussion that the maximum masking time obtained is 325 min for 3.75 g PMMA concentration at 60°C KOH temperature (Fig. 5b). With this masking time one can etch out structures whose depth could be around 130 μm and 40 μm using PMMA as a mask. Thus the feasibility is demonstrated for use of PMMA as an etch mask for limited structures.

For further improvement in the adhesion of PMMA with silicon, other techniques like sputtering, plasma polymerization, plasma treatment, etc. may be tried. Work is in progress to lower the thickness obtained by these methods which will be useful in better pattern transfer by lithography.

4. Conclusion

From the experimental results obtained on the masking time of PMMA for various experimental conditions and the possibility of trasnsferring the pattern in it, it can be concluded that it is feasible to use PMMA as an etch mask for fabricating limited number of micromachined structures. Further, for better adhesion of PMMA to increase masking time and to make it durable to resist higher temperatures of KOH for higher depths of etching, different techniques like sputtering, plasma polymerization, plasma treatment for PMMA deposition need to be employed.

References

1. SEIDEL, H. *et al*.   *J. Electrochem. Soc.,* 1990, **137**, 3612.

2. BASSOUS, E.   *IEEE Trans.,* 1978, **ED-25**, 1179.

3. IRENA, ZUBEL   *Sensors Actuators A,* 2000, **84**, 116.

4. REISMAN, A. *et al*.   *J. Electrochem. Soc.,* 1979, **126**, 1406.

5. KAMINSKY, G.   *J. Vacuum Sci. Technol. B,* 1985, **3**, 1015.

6. PETERSON, K. E.   *Proc. IEEE,* 1982, **70**, 420.

7. TOFT, E. A. *et al*.   *J. Appl. Phys.,* 1991, **69**, 3733.

8. XINXIN, Li *et al*.   *Sensors Actuators A,* 1997, **63**, 1.

9. ASHRUF, C. M. A. *et al.*   *Sensors Actuators A,* 1998, **66**, 4569.

10. OSTERBROEK, R. E. *et al.*   *Sensors Actuators A,* 1999, **77**, 167.

11. SEMMACHE, B. *et al*.   *Sensors Actuators A,* 1995, **76**, 46.

12. SZE, S. M.   *VLSI Technology*, McGraw Hill, 1984.

13. MIHAELA, ILIE *et al*.   *Proc. SPIE Materials and Devices. Characterization in micromachining,* 1998, **422**, 3512.

14. RAI CHOUDHARY, P.   *Microlithography, micromachining and microfabrication II,* SPIE Press, Bellingham, Washington, USA, 1997.

15. Rai Choudhary, P. *Microlithography, micromachining and microfabrication I*, SPIE Press, Bellingham, Washington, USA, 1997.

16. Bauer, J. *et al.* *J. Vacuum Sci. Technol. B*, 1996, **14**, 2485.

17. Zambare, M. *Plasma synthesis of electron beam resists, their characterization and plasma diagnostic by Langmuir probe,* Thesis, University of Pune, India, 1996.