# Further Investigation of Hydrogen Silsesquioxane E-Beam Resist as Etching Mask for Cryogenic Silicon

C. K. Yang, G. Pandraud, K. Babaei Gavan, E. van der Drift and P. J. French

***Abstract*— Hydrogen silsesquioxane (HSQ) is a silicon rich polymer, it was first developed as a silicon-oxide based floatable insulating layer for CMOS technologies. However, since it was also sensitive to extreme ultra-violet lights and electron-beam energies, more and more technologies start to use the material as negative lithography resist for submicron and nanometer device pattering. In most of applications, HSQ is used in combination with a thicker polymer underlayer in which this thick underlayer will be the etching mask. In this work, we investigate the possibility of using HSQ without an underlayer and we hardened the material to improve its etching resistivity.**

**One particular plasma etching we are interested is the cryogenic SF6 silicon etching; such etching are commonly used for very high aspect ratio etching of silicon and important for nanostructures requiring vertical side walls and no undercuts. In cryogenic etching, $SiO_2$ is used as masking layer providing very high etching selectivity to silicon; since HSQ is a silicon-oxide rich material, it is also selectively etched in cryogenic systems. We present our results on the effect of HSQ baking temperature and baking time, and test the etching properties under cryogenic etching process.**

**Using this technique, we were able to pattern and etch lateral silicon cantilevers with feature size less than 500 nm and aspect ratio more than 1:4.**

***Index Terms*— Nanotechnology, electron beam lithography, plasma materials – processing applications**

## I. INTRODUCTION

Decades after the demonstration of micro-electro-mechanical systems (MEMS), silicon wafer processes have advanced in big leaps and in fast pace. The MEMS concept and its supporting technologies not only combined the electro and mechanical domains in a miniaturized way, but also created possibilities of making devices not imaginable before. Although MEMS processing is still mainly based on silicon wafer processes, it is different to its CMOS process counterparts; one of the variations is to fabricate free standing, movable three dimensional devices on the surface of wafer. In recent years, part of the MEMS community has started to gain interests in scaling the MEMS further down, creating nano-electro-mechanical systems (NEMS). The result is devices that are more responsive, more sensitive and less energy consuming. Scaling of sub-micron and nanometer devices can be achieved either by top-down or bottom-up approaches; while the majority of nanotechnology community emphasize on the bottom-up approach, the silicon based NEMS fabrications are still dominated by the top-down technologies used by its MEMS predecessor. More controllable process, vast knowledge accumulated and easier integration to electronics, are the reasons that NEMS continues the top-down approach used in MEMS. Nevertheless, transferring processes optimized for micron structures to sub-microns is not a simple matter of shrinking; when the device dimension hits the diffraction limit of lights, many key steps in MEMS fabrication have to be replaced by different technology and materials.

In this paper, we used electron beam (e-beam) lithography to fabricate lateral silicon cantilevers. The cantilevers have submicron thickness which is defined by the e-beam lithography, and width in microns defined by the etching depth; free standing structures of these dimensions requires a high anisotropic dry etching with a strong masking layer to endure the etching and the bombardments of plasma species. Here we investigate the possibility of using a single thin photoresist layer for high resolution e-beam lithography and use the layer directly as the masking material for the following deep silicon etching process. We use a commercialized hydrogen silsesquioxane (HSQ), Fox12® from Dow Corning, as our e-beam sensitive masking layer, and cryogenic silicon etching to achieve a high anisotropic profile with smooth sidewall surfaces.

In the following sections, material background of the HSQ will be introduced, followed by the experiment procedure, and finally the results and conclusion.

## II. HSQ AS NEGATIVE E-BEAM RESIST

HSQ is originally developed for low temperature dielectric layer purpose in integrated surface, furthermore because it can be spin coated on wafers, it is also used for gap filling and

---

Manuscript received October 1, 2008. This work was supported in part by the Dutch NanoNed Project Code TQVB46.

C. K. Yang and P. J. French are with the Technical University of Delft, Faculty of Electrical Engineering, Mathematics and Computer Science, Department of Microelectronics, Electronic Instrumentation Labs. (phone: +31-(0)15-2786518; fax: +31-(0)15-2785755; e-mail: c.k.yang@tudelft.nl).

G. Pandraud, K. Babaei Gavan and E. van der Drift are with the Technical University of Delft, Faculty of Applied Physics, Kavli Institute of Nanotechnology.

planarization. However it was discovered later that the material is also sensitive to extreme ultraviolet light and electrons [1], [2] this made it possible to use the HSQ as photoresist. HSQ is an inorganic three-dimensional polymer material, when it is exposed to high energy radiation, the three dimensional Si-H cage structures crosslink into a network structure of Si-O-Si bonds, which is less soluble to alkaline developers. It has been also noted by Namatsu *et al.* [3] that HSQ's compact cage structure allows it to aggregates less after cross-linking exposures; this means the bulk molecules form less at the edge of the patterns, giving less linewidth fluctuations and hence achieving higher linewidth resolution comparing to other negative e-beam resists.

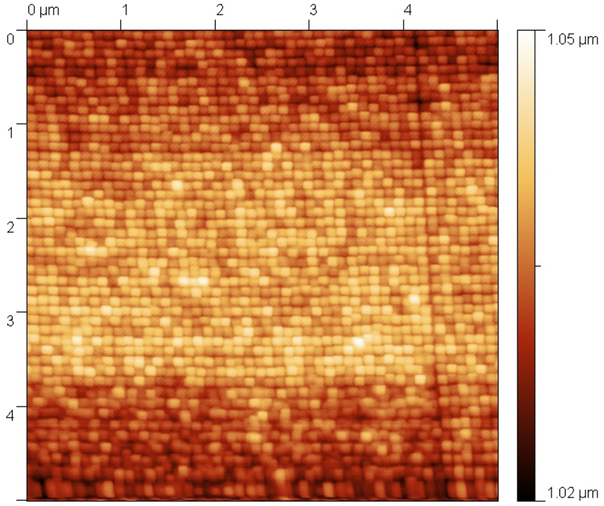


Fig. 1. High dosed HSQ surface after development, the pattern of dots are the writing pattern of the Ebeam, the dot size are 100 nm x 100 nm, which is the spot size used.

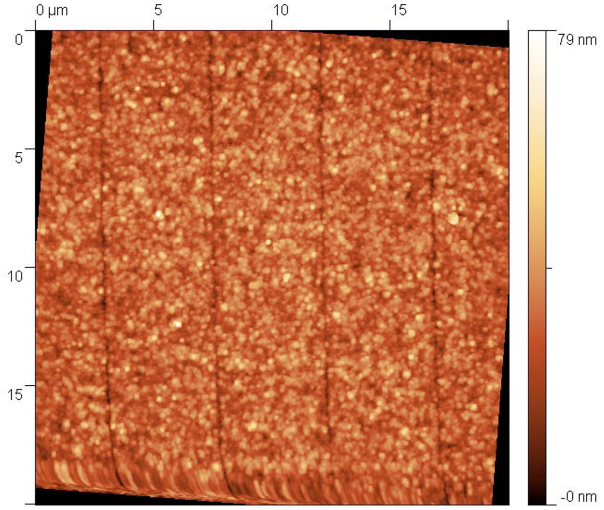
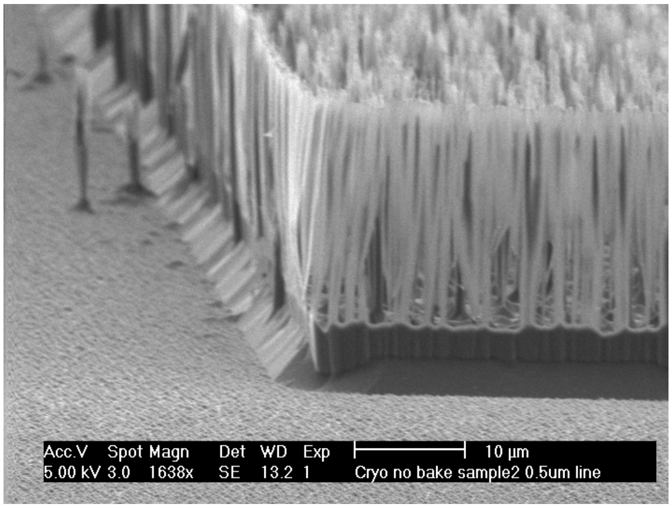


Fig. 2. Low dosed HSQ surface after development. The randomly distributed dot may be caused by the partially stripping of top layer.

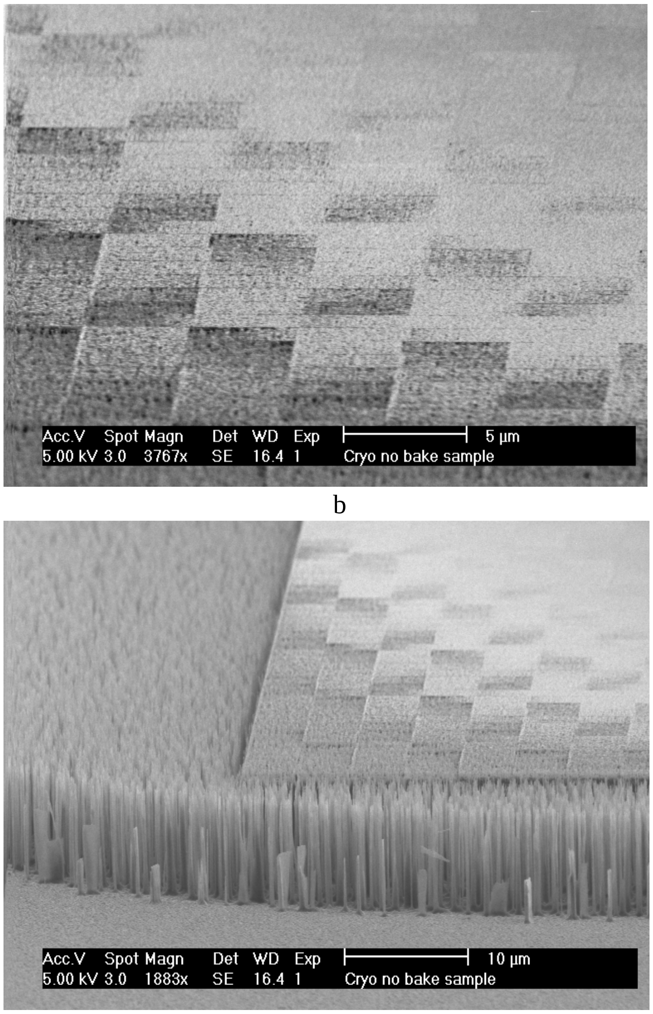
Henschel *et al.* [4] have studied in details the use of HSQ as negative e-beam resist. They discovered that strong developer concentrations increase the contrast but lower the sensitivity of the exposure; whilst a prebake of the resist improves the sensitivity, but deteriorate the contract and reproducibility. Therefore an optimization of the recipe will be needed by selecting right baking temperature and time, and right developer concentration. In our experiment, we observed beam spot size and dose dependency of HSQ. Figure 1 shows an AFM scan of a highly dosed (450 µC/cm2), HSQ resist; dots of well aligned 100 x 100 nm2 are clearly visible, these dots corresponds to the spot size and writing pattern of the e-beam. Shown in figure 2 is a lightly dosed (75 µC/cm2) HSQ surface, the dot size are still the same, but randomly ordered and are different in height. We believe the difference of the two is in the development phase. The light dose beams was only able to cross-link the HSQ partially, therefore allowing the developer to strip part of the surface away, leaving a rough and randomly distributed 100 nm dots; the developer also thinned down the layer thickness 100 nm less compared to the high dosed parts.

In our experiment, we first used the bilayer HSQ/Novolak technique developed by van Delft et al. [5] The technique uses HSQ as e-beam sensitive mask to pattern the hardbaked Novolak layer, then use the Novolak as the etch mask of the silicon. The bilayer technique works well, but it requires two times pattern transfer and affects the resolution. Therefore on our later experiments we patterned the HSQ directly on device substrate. The Novolak underlayer is not needed to our process because the cryogenic anisotropic etching has a slow etch rate on silicon-oxides. However, this does require post-expose treatment to the HSQ for an optimized etching resistance. The details of the process and result of the treatment is discussed in the next section.

Figure 3a, b and c show examples of using FOx-12 as direct masking. In subfigure 3a, the resists is over-etched and the silicon grass formation is caused by the e-beam spot seen in the AFM image. Subfigure 3b shows the writing pattern of the e-beam and subfigure 3c shows the over-dosed case.



a



b

c

Fig. 3. Examples of using FOx-12 as direct masking for silicon etching. 3a shows overetching and formation of silicon grass. 3b and 3c shows the ebeam patterns and example of overdose.

## III. PROCESS AND EXPERIMENTS

To test the etching properties of HSQ in cryogenic silicon etching, we spin coated FOx-12 at speed of 1000 rpm, further performed a 2 stage pre-baking on hotplates, one at 150ºC and one at 200ºC, both for 2 minutes. The layers was then patterned by e-beam at 450 µC/cm2 and developed. We first developed the samples in pure MF322 for 1 minute, followed by a diluted MF322 (90% H2O) for 30 secs finally in H2O for 30secs. The result is pattern layer of about 200nm thick, measured by a Dektak profilometer with nanometer resolution.

The etching rate of FOx-12 is highly recipe dependent; in our experiment, we used a relatively slow but high anisotropic etching recipe in an Adixen ICP etcher, the recipe used is shown in table 1. An interferometer is added to the etcher to monitor the etching progress in real-time; Silicon, thermal $SiO_2$ and FOx-12 (baked at 500ºC for 1 hr 30 min) etch rate are measured and compared in figure 4. The interferometer signal gave us a very similar etching signature between the thermal SiO2 and the baked FOx-12 resist. The signal drop in the Si measurement after 32 sec is due to the switching-off of the etching process, and same for the SiO2 etch after 200 sec. In the FOx-12 measurement, the HSQ is consumed after 170 sec reaching the Si underneath. In order to understand the physical meaning of the interferometry signals, we loaded samples and stop its etching at different stage of the signal (figure 5); in this way we were able to confirm the etch stop.

TABLE 1.
ANISOTROPIC CRYOGENIC SILICON ETCHING RECIPE USED FOR THE TEST.

| Si Cryogenic etch | |
|---|---|
| SF6 flow | 130sccm |
| O2 flow | 16sccm |
| RF Power | 800W |
| Chuck Bias | 90V |
| Temperature | -130C |

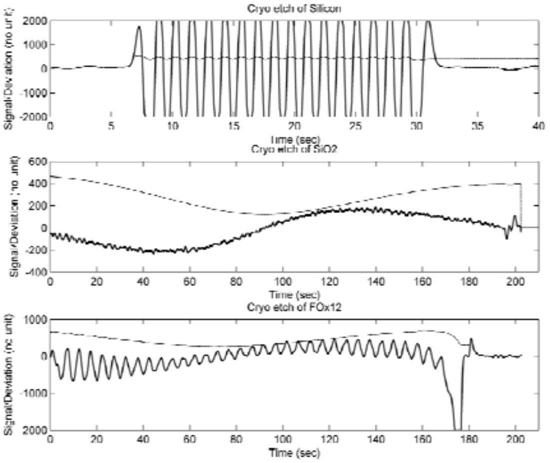


Fig. 4. Interferometer etching signal of silicon, thermal SiO2 and FOx-12 in cryogenic etch. The dotted lines replresents the laser intensity signal and the thicker solid lines are the derivative of the signal.

HSQ is usually cured at high temperature to form insulating silica layer. The transformation of the HSQ at curing can be determined by measuring its Si-H/Si-O ratio6; higher Si-O content signifies transformation into silica, and therefore advantageous as masking material in the cryogenic silicon etching.

We baked the HSQ at different temperature ranging from 300°C up to 500°C on a hot plate in open air; the etching rate is measured by loading patterned HSQ on silicon sample into the cryogenic etcher. Etch time is determined by the interferometer measurement. Shown in figure 6 is the etch rate measurement of FOx-12 at different temperature for 30 min. Tests were also conducted for the same temperature, but at 30 min, 60 min, 90 min and 120 min baking time; the baking time didn’t affect the etching rate.

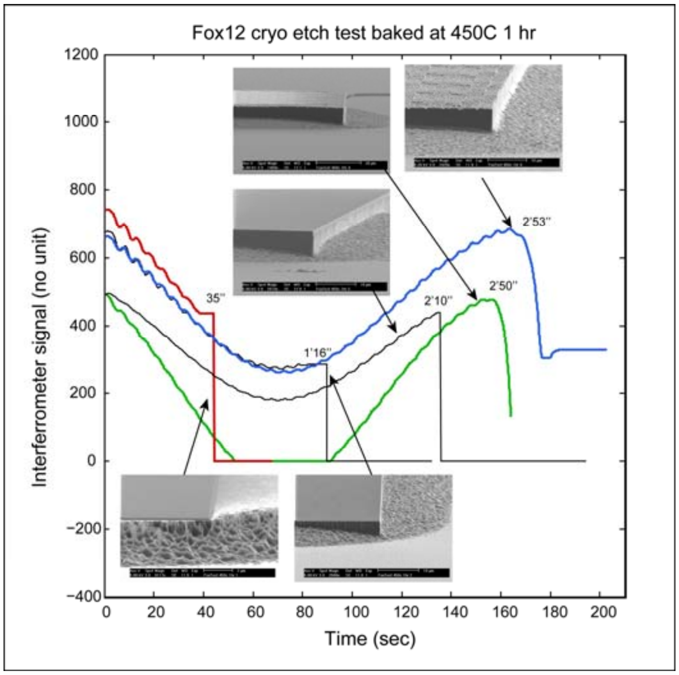


Fig. 5. Interferometer etching signal and its corresponding SEM image. The FOx-12 stayed smooth and flat throughout the etching until 2’10’’, by 2’50’’ and 2’53’’ it starts to get consumed, at the same time the laser signal drops.

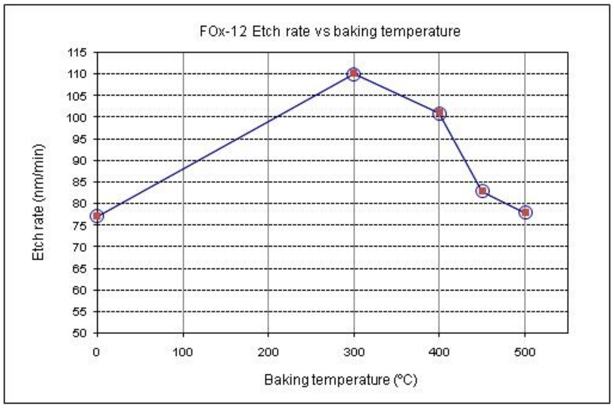


Fig. 6. Etching rate of FOx-12 under cryogenic etching process; samples are pre-baked, exposed, developed under the same recipes, and finally baked at different temperatures for 30 min.

## IV. RESULTS CONCLUSION

The etching rate characteristic we obtained has a similar trend to what O’Faolain et al. found in their work on GaAs and InP etching [6], however they still used PMMA as e-beam resist to pre-pattern the HSQ instead of direct exposing it. As suggested by the study of Yang and Chen [7], at 250-350ºC the cage-network redistributes, and at 350-435ºC the Si-H bond dissociates and network redistribution occurs, while above 435ºC Si-O-Si bonds increase and collapse of the pore structure occurs, forming a more dense silica-like material. Although the change in HSQ properties during the curing step is dependent on the curing environment, such as in open air, in dry N2 or in vacuum, the transformation from Si-H to Si-O bond is known. It is however left unclear to why the etch rate peaked at 300ºC. From our data we conclude that it is beneficial to ensure the formation of Si-O-Si network framework for a better silicon-HSQ etching selectivity. Although the etch rate of HSQ is still higher than a thermal SiO2, it should still withstand to most of requirements for typical NEMS structures. Shown in figure 7 are fabrication results of 1µm and 500nm lateral cantilevers using Fox-12 as direct mask.

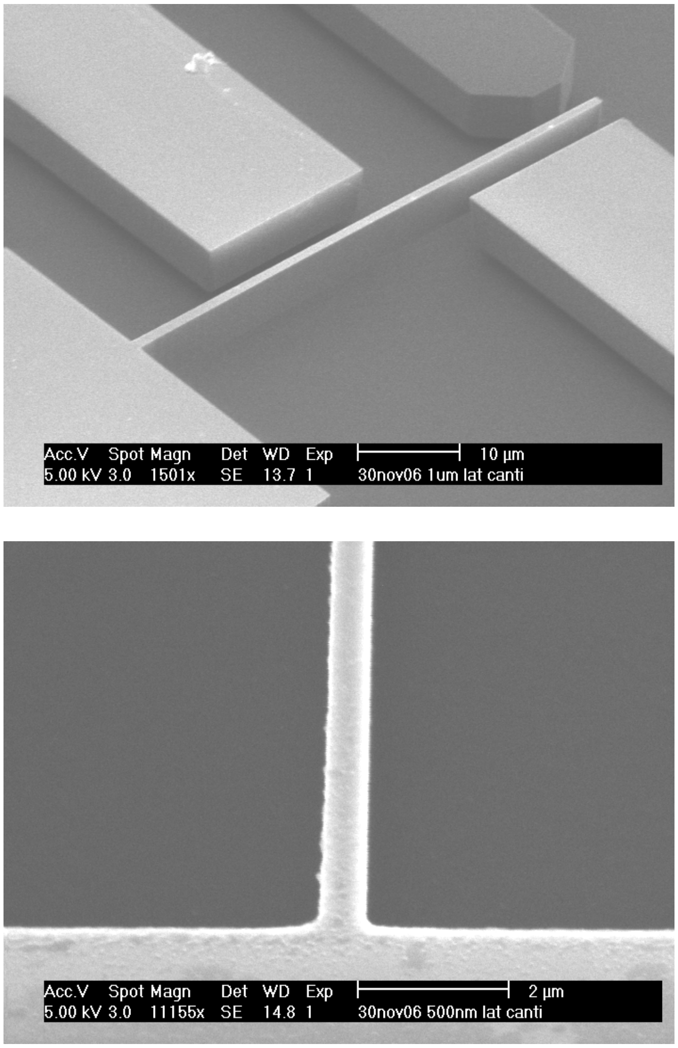


Fig. 7. Fabrication of submicron structures with FOx-12.

## REFERENCES

[1] H. Namatsu, T. Yamaguchi, M. Nagase, K. Yamazaki and K. Kurihara, Microelect. Eng. 41/42, 331-4, 1998.

[2] I. Junarsa, M.P. Stoykovich, P.F. Nealey, Y. Ma, F. Cerrina and H.H. Solak, J. Vac. Sci. Technol. B, 23, 1, 138-43, 2005.

[3] H. Namatsu, M. Nagase, K. Kurihara, K. Iwadate, T. Furuta and K. Murase. J. Vac. Sci. Technol. B, 13(4), 1473-6, 1995.

[4] W. Henschel, Y.M. Georgiev and H. Kurz. J. Vac. Sci. Technol. B 21(5), 2018-25, 2003.

[5] F.C.M.J.M van Delft, J.P. Weterings, A.K. van Lagen-Suurling and H. Romijn. J. Vac. Sci. Technol. B, 18(6), 3419-23, 2000.

[6] L. O’Faolain, M.V. Kotlar, N. Tripathi, R. Wilson and T.F. Krauss. J. Vac. Sci. Technol. B 24(1), 336-9, 2006.

[7] C.C. Yang and W.C Chen. J. Mater. Chem. 12 1138-41, 2002.