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High-aspect-ratio microstructures fabricated by X-ray lithography of polymethylsilsesquioxane-based spin-on glass thick films

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Abstract In this paper, a process for 200 μm high-aspect-ratio micro-optical (HARM) structures fabricated by deep X-ray lithography (DXRL) of polymethylislesuioane-based spin-on glass (SOG) thick films is presented. The SOG material used in the whole procedures is polymethylsilsesquioxane (GR650), which is a kind of sol-gel derived material and can be cured at a reasonable low temperature (75 °C). A technique to cast thick GR650 films was established in the overall process. After consolidation, the GR650 thick films were machined to reach 200 μm uniformly. Then, as negative resists, the GR650 thick films were patterned directly by DXRL. X-ray irradiated regions can be selectively retained with high structural resolution by development in an organic solvent, such as methanol. Parameter screening was done to find minimum and maximum doses needed for patterning/cross-linking, to vary development time, and to explore different film thickness. The whole process is a novel of technique to create HARM structures based on SOG materials without using molds. This technique can be extended to considerably larger structural heights. Surface and bulk compositions of the irradiated films were measured by XPS and Fourier transform infrared spectroscopy. Surface quality by roughness testing system (WYKO RST) was investigated to fabricate the microstructure with a high-accuracy surface.

1 Introduction

Silicon dioxide (silica), like other dielectrics, functions as insulation between conducting layers, diffusion and ion implementation masks, diffusion from doped oxides, capping doped oxides to prevent the loss of dopants, getting impurities, and passivation to protect devices from impurities, moisture, and scratches [1]. In the fabrication of microelectromechanical systems (MEMS) devices, silica films can be used as etch-masks for silicon bulk micromachining. Silica also works well as a micro-optical material because of its broad transmission range, low thermal expansion, high hardness and mechanical strength and resistance to chemical attack. There are many kinds of methods to grow silicon dioxide films, such as chemical vapor deposition (CVD), physical vapor deposition (PVD), plasma-assisted deposition, and thermal growth. However, all these methods require high temperature and/or vacuum techniques and they are only applicable to thin films.

As microelectronic devices' speeds and packing densities increase, there are growing applications of sol–gel and modified sol–gel derived materials to device [2]. The increasing interest in Spin-on glass (SOG) technologies in recent years is due to the possible performance if high quality silicon dioxide films can be prepared at relative low temperature and therefore has a promising part of the VLSI technology for integrated circuit (IC) production [3].

Siloxane based SOG is a sol–gel derived material used in microelectronics fabrication. SOG derived silica films are employed in applications to require dielectric layers, planarization layers, cap layers, dopant diffusion sources, implant barrier masks, multi-layer resist patterning, and electronic packaging [2]. SOG films are normally obtained by spin coating or by dip coating, while the coating thickness of the films are limited in the range of 350–650 nm [4]. There also have been reports that the SOG thickness was limited to about 400–600 nm for the polysiloxane type and 300–400 nm for the silicate type. Thick SOG materials that are available are tending to crack and lose process integrity due to internal stress [3]. Electrophoretic sol–gel deposition is a method to obtain a thick film in a short time. Changing the electrodeposition time can control the film thickness. Moreover, the coating can be carried out at the substrates with complex forms [5].

Sol–gel processing allows the molding method for the arbitrarily shaped silica monoliths. There are reports about fabricating silica micro-lenses by hot-embossed PMMA molds [6], and also using nickel molds to realize MCP structures greater than 200 μm thick [7]. Because these two methods are limited by the use of mold structures, large, thick, and freestanding structures are confined to some degree. Obviously, the ability to dispense with mold microfabrication is of great interest.

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GR650 is a polysilsesquioxane-based SOG, which is obtained from market source. The films fabricated by GR650 have been reported by Shanmugam [8]. The regions exposed by X-ray cause cross-linking that would not dissolve in an organic solution like methanol when GR650 works as a negative resist.

There are still other methods to pattern the SOG films, like the ion beam [3, 9, 10] and E-beam [10]. Focused ion beam (FIB) has many advantages in fine pattern formation for its negligibly small proximity effect, such as for the gate electrode of metal dioxide semiconductor field effect transistor (MOSFET). SOG becomes insoluble to solvent after E-beam or FIB irradiation due to a cross-linking reaction and acts as a negative resist in E-beam/FIB lithography [10].

In contrast, with the ion irradiation, the structure of ladder silicon SOG is changed to the silicon-dioxide-like structure, thus rendering it soluble in hydrofluoric acid [11]. This is why ladder silicon SOG materials can also act as a positive resist. A similar mechanism is employed by patterned it using X-ray lithography. For example, the GR650 film, which is a kind of ladder silicon SOG, can also be as a positive resist under the deep X-ray lithography (DXRL). However, the thickness of the developed films is limited to 15 μm [8, 12].

Instead of the X-ray, FIB, and E-beam lithography, SOG materials can be patterned by UV or deep UV lithography [13, 14].

In this paper, a process to produce crack-free, smooth silica-like films with the thickness over 200 μm at reasonable low temperature will be a new technique to pattern high-aspect-ratio structures by DXRL without using molds.

2
Fabrication process and experiment

As mentioned above, we choose GR650 as the SOG material in the following processing due to its good shape stability when formed into monoliths [15]. Figure 1 shows the molecular structure of GR650.

The repeated units form the "ladder" type siloxane [8]. The GR650 film was cast on the silicon substrate with a base layer of Teflon for the consideration of the thermal expansion coefficient. The film was patterned by DXRL, synchrotron radiation. As negative resist, the areas of the SOG films not exposed to the X-ray irradiation were dissolved in methanol while the irradiated areas were kept on the base layer.

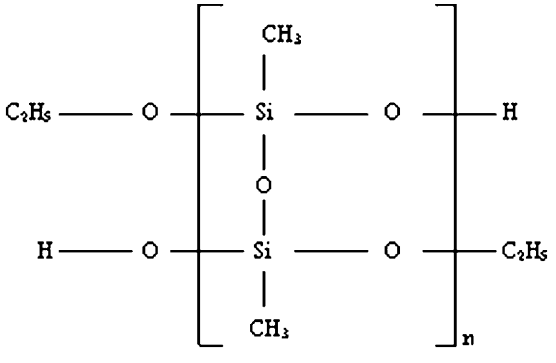

Fig. 1. The molecular structure of GR650

2.1
Thick film forming

Thick SOG film on silicon wafers is prone to fail by cracking, which results from shrinkage during drying. Cracking of the film occurs because the SOG continues to adhere to the substrate as shrinkage takes place which results in a build up of tensile stress on the film [16].

Thick GR650 film definitely cracks when consolidated directly on the silicon wafer due to the large difference of the thermal expansion coefficient between GR650 and silicon. Even when the regions of the thick film were reduced, it was easy to break the film by slightly shaking it.

Several methods are suggested for thick SOG film forming. One is a multiple coating procedure where each coated layer is annealed before the application of the next layer. Another is incorporation of a suitable additive that can change the morphology of the SOG and make it more tolerant to shrinkage. There have been reports that GR650 can be directly cast on the bare wafer by adding an acid to the solution [8]. However, this method cannot make a high-aspect-ratio structure until now. The third method is that using a substrate with the thermal expansion coefficient matching that of the SOG film can reduce SOG film stress. We employed the third method in this work to produce a firm, transparent, crack free, thick film.

A thick film up to 200 μm was obtained by casting and soft baking at a temperature around 75 °C. The sample structure was shown in Fig. 2.

In the experiment, we chose a 540–580 μm silicon wafer that provides sufficient rigidity for the processing. The PTFE film (base layer) 140 μm thick was stuck to the surface of the wafer. Above the base layer was a layer of confinement ring, which was a cycle of 140 μm thick PTFE. PTFE was chosen because its thermal expansion coefficient is very close to that of GR650. (The thermal expansion coefficient of GR650 resin is 130×10^{-6}/°C, and that of the PTFE is 124×10^{-6}/°C [8].) The inner diameter of the confinement ring was about 70 mm. Before casting GR650 solution, the sample needed to be cleaned by acetone, DI water and nitrogen, and dehydrated on a hot plate. After all the procedures were done, we used a 0.2 μm filter to cast the GR650 solution into the confinement area. Because of the shrinkage of the GR650 film during drying, the excess amount of solution was recommended. The GR650 was then evacuated at 200 mbar for 5–8 min to get rid of bubbles and remove the solvents for good quality and adhesion of the solid film on the base layer. A low viscous state of the solution was found after the vacuum process. Then, the sample was put in the Heraers Oven for soft baking.

Soft baking is an important stage for film forming. We adjusted the baking time and temperature according to the

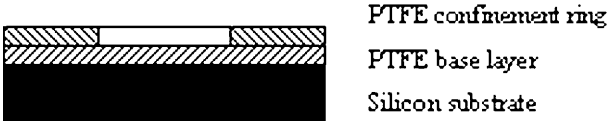

Fig. 2. The sample with the base layer and confinement ring

ratio of solvent to solution. After the soft baking, the solid GR650 film was formed, which was a kind of transparent, crack free and bubble free solid film. The hardness of the GR650 solid was related to the dwell time, dwell temperature, and the ratio of solvent to solution. Though the level of the chamber was investigated carefully, the obtained film was not smooth enough for the following processing because of its shrinkage, interior stress, and surface tension. A machining step was conducted on the film to get a 200 μm, smooth film. The sample was then ready for irradiation.

2.2 Irradiation

Using DXRL to directly pattern the spin-on glass film is a novel and promising method. DXRL is an additive fabrication technique that involves the building of a device on top of the surface of a supporting substrate. DXRL is dependent of the substrate because of the lower fabrication temperatures. It can be a room temperature process. GR650 is theoretically capable of being processed as both a positive and a negative X-ray resist. While it is applied as a negative resist, regions without irradiation should be dissolved in the developer. Areas irradiated could be developed in the HF solution when GR650 is used as a positive resist. However, the thickness of the development film was limited to 15 μm because there was about 15 μm of oxide layer after the X-ray irradiation.

The GR650 films were exposed by the facilities at the SSRL of Stanford University. The mask, with a 150 μm thick graphite sheet as the membrane and a 10 μm layer of gold as an absorber layer, has the mechanical testing structures on it. Table 1 shows the irradiation conditions for the 200 μm structures.

2.3 Development

GR650 films dissolve in most non-polar organic solvents such as alcohols and ketones [12], so we choose methanol as the developer. As negative resist, the GR650 film with a sufficient dose of X-ray irradiation can cause cross-linking and it will not be dissolved in the developer. This is the mechanism that our work is based on. The sample was held in a wafer holder with the face down in the methanol at 25 °C. A stir was set to rotate at 120 rpm. Five minutes development in methanol was sufficient to remove the unexposed region. The sample was then immersed in the DI water to get rid of the residual methanol. After that, it was dried gently by nitrogen. Longer time should be avoided because the developer may attack the exposed regions. We got very clean structures by applying 100% methanol to develop the irradiated GR650 films. The development rate was approximately 40 μm/min.

Table 1. Input parameters for X-ray exposure

First exposure dose amount (mA · min)	398
Second exposure dose amount (mA · min)	5179
First exposure scan length (cm)	1.5
Second exposure scan length (cm)	3.0

3 Results and discussion

3.1 SEM

The following pictures (Figs. 3–5) show the structures taken by SEM. The specimens were obtained from two-time exposures. The irradiation dose at the top and the bottom was 15 kJ/cm^2 and 17 kJ/cm^2, respectively. Under these conditions, the best structures have been obtained. The gage width of the specimens on the substrate is 50 μm. The length and the height are about 3.7 mm and 200 μm, respectively.

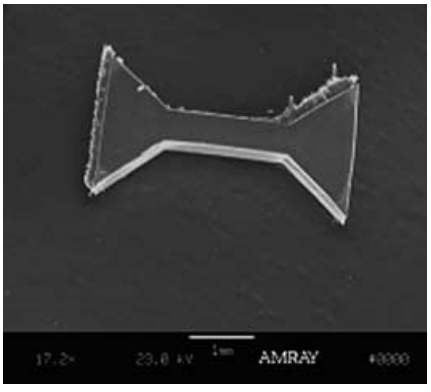

Fig. 3. SEM of micro-structure patterned by DXRL

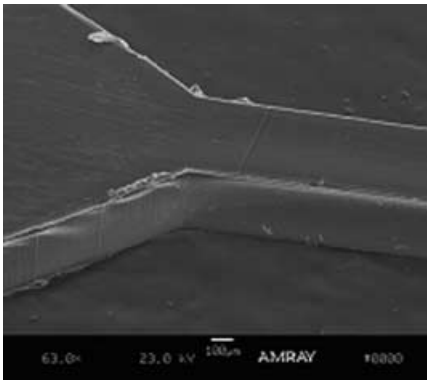

Fig. 4. Higher magnification SEM of the micro-structure, showing edge acuity

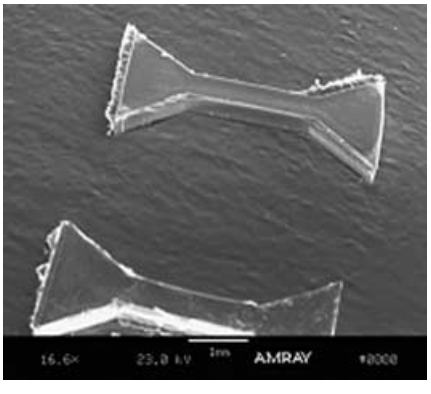

Fig. 5. SEM of two-structure array

Table 2. Surface roughness measurement of SOG

Surface roughness measurement	Roughness value	
	R_a (nm)	R_q (nm)
Top surface	4.22	5.15

From the pictures, we still see some white residuals at the top edge of the structures, which is a common occurrence. Development is a significant factor that influences the results. Longer immersion time in methanol or quicker stirring of the solvent could not solve the problem. In addition, it always causes the structures to peel off.

Resist swelling occurs in most wet development procedure involving negative resist. We found the severe swelling and unclear edges occurred in the high dose irradiation samples. It may result from a lack of contrast of the mask when using a hard source like the SSRL.

Other problems happened during the development such as fragmentation and developer attack, which may be caused by the insufficient dose of the bottom exposure that was resulted from the undercutting and cracking at the resist substrate interface, respectively.

3.2
Surface roughness (RST)

The surface roughness values obtained by a roughness step tester (RST) and the data were given in the Table 2 and Fig. 6.

The two key surface profile parameters are R_a and R_q. R_a is the roughness average, which detects general variations in overall profile height. R_q is root mean square average. The surface is a good platform for the micro-optical fabrication based on the values of R_a and R_q.

3.3
Film structure-XPS analysis

X-ray photoelectron spectroscopy (XPS) is a technique using X-ray to eject photoelectrons from the surface atoms of the material being analyzed. The kinetic energies of the photoelectrons are measured to determine the electron binding energy characteristics of the atoms in the surface. From the relative energies and intensities of the characteristic photoelectrons, the composition of the atoms on the surface can be determined. We use XPS to analyze the atomic composition of GR650 films and structures.

Based on Table 3, the components constitution of the GR650 films are similar to that of the thermally growth SiO_2.

4
Conclusions

Silica-like microstructures were fabricated by using GR650 as an X-ray resist. A technique to create HARM structures on SOG materials without the use of molds was realized. Thick, crack free films at reasonable low temperature (75 °C) were successfully fabricated. A variety of irradiation doses were employed on the resulting films. The 15 kJ/cm^2 and 17 kJ/cm^2 dose on the top and bottom give the best structures at the film thickness of about 200 μm; however, higher doses caused severe swelling. The

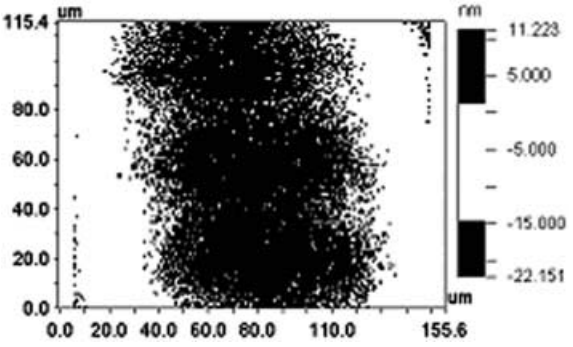

Fig. 6. RST surface testing figure

Table 3. Data of XPS analysis

	GR650 top	GR650 bottom	Thermally grown SiO_2
C	0.8	27.7	1.2
O	64.9	30.3	64.4
Si	34.4	26.7	34.4
O/Si	1.89	1.13	1.87
F	–	15.3	–

problems and analysis during the development were also given. The roughness parameters of the top surface were measured by RST. More work is needed to investigate much thicker structures with GR650 film as positive resist, with films directly on the bare silicon substrate, and with movable structures.

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