ELSEVIER

Sensors and Actuators B 88 (2003) 75–79

SENSORS AND ACTUATORS B CHEMICAL

www.elsevier.com/locate/sensorb

Novel approach to form and pattern sol–gel polymethylsilsesquioxane-based spin-on glass thin and thick films

Yuxin Liu[a], Tianhong Cui[a,*], Ramana K. Sunkam[a], Philip J. Coane[a], Michael J. Vasile[a], Jost Geoettert[b]

[a]*Institute for Micromanufacturing, Louisiana Tech University, 911 Hergot Avenue, Ruston, LA 71272, USA*
[b]*CAMD, Louisiana State University, Baton Rouge, LA 70803, USA*

Received 25 April 2002; accepted 22 August 2002

Abstract

In this paper, the applications of sol–gel materials and process to semiconductor industry are introduced. Based on the sol–gel technique, the spin-on glass (SOG) fabrication techniques to realize thin and thick films are presented hereby. The thin films were patterned by liquid embossing techniques. For thick films, the film thickness can reach more than 200 μm. The whole process is a novel fabrication technique for thick SOG films, which can be performed at very low temperature without using molds. It is excluded from the original thermal deposition techniques required very high temperature or vacuum facilities. Furthermore, the requirement of the sol–gel process for equipments is simple and much less expensive. The desired microstructure can be obtained directly by organic solvent development after deep X-ray lithography (DXRL). Finally, the film structures were investigated by X-ray photoelectron spectroscopy (XPS), which shows that the films have the same characteristics of the thermal silicon dioxide after DXRL.

Keywords: Spin-on glass; Liquid embossing; DXRL

1. Introduction

The sol–gel process is a series procedure involving a solution or a sol undergoing the sol–gel transition, which includes hydrolyzation, condensation (sol formation), evaporation (a viscous liquid status) and a gel transition (glass forming). The chemical reaction can be summarized in Eqs. (1) and (2).

$$\mathrm{M(OR)}_n + n\mathrm{H_2O} \rightarrow \mathrm{M(OH)}_n + n\mathrm{R(OH)}\ \text{hydrolyzation} \quad (1)$$

$$\mathrm{M(OH)}_n \rightarrow \mathrm{MO}_{n/2} + \frac{n}{2}\mathrm{H_2O}\ \text{polycondensation} \quad (2)$$

where M and $\mathrm{M(OR)}_n$ represent metal and metal alkyl radical, respectively.

The sol–gel process is currently well accepted as a simple and important technique to form thin films and coatings, which can be applied on substrates, such as metal, plastic, and ceramics by spin coating, dip coating, draining or spraying. Though it also needs to be condensed by heating, it is excluded from any deposition techniques, which make the complicated vacuum facilities necessary.

In the semiconductor industry, the sol–gel technique also refers to spin-on glass (SOG) method, due to silicon dioxide (silica/SiO_2) forming. Silica obtained from SOG can substitute thermally grown SiO_2 in some fields, such as dielectric layers, planarization layers, cap layers, dopant diffusion sources, implant barrier masks, multilayer resist patterning, and electronic packaging [1]. Compared with the fabrication methods of thermally grown SiO_2, such as chemical vapor deposition (CVD), physical vapor deposition (PVD), plasma-assisted deposition and thermal growth, the sol–gel SOG method is exclude from high temperature or vacuum facilities. Furthermore, the films can be coated inside or outside

* Corresponding author. Tel.: +1-318-257-5122; fax: +1-318-257-5104.
E-mail address: tcui@coes.latech.edu (T. Cui).

0925-4005/02/$ – see front matter
PII: S0925-4005(02)00314-3

some complex shapes over large areas simultaneously and uniformly.

2. SOG film coating and fabrication technology

2.1. Film coating

Thin SOG films are normally obtained by spin coating or dip coating, while the coating thickness is dependent on the methods and materials. There has been reported 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 films available are tending to crack and lose process integrity due to internal stress [2]. Electrophoretic sol–gel deposition is a method to obtain thick films in short time. Changing the electrodeposition time can control the film thickness. Moreover, the coating can be carried out at the substrates with complex forms [3].

Several other methods are also reported for thick SOG film formation. One is a multiple coating procedure. Another is incorporation of a suitable additive that can change the morphology of the SOG and make it more tolerant to shrinkage. There has been reported that GR650 can be directly cast on the bare wafer by adding acid in the solution [4]. But this method cannot make a high-aspect-ratio structure till now. There also has the report avoiding the film cracking by using of the chemical additives–drying control chemical additives (DCCA), which modify the surface tension of the interstitial liquid and pore size, resulting in a crack-free dried gel after heat treatment [5]. The third method is to reduce film stress by using a substrate with the thermal expansion coefficient matching that of a SOG film.

2.2. Fabrication

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 using nickel molds to realize MCP structures more than 200 μm thickness [7]. Recently, liquid embossing [8] and microcontact printing [9] are also used as the processing methods. In this work, we also applied the liquid embossing technique to pattern thin SOG film, and the results were shown in the experiment part. While these methods are limited by mold structures, large, thick and freestanding structures are confined to some degree. Obviously, the ability to dispense with mold microfabrication is of great interest.

SOG was found insoluble to solvent after energy irradiation due to a cross-linking reaction. The sources for exposure are including UV or deep UV lithography [10,11], ion beam [2,12,13], e-beam lithography [13], focused ion beam [13], and X-ray lithography.

After exposure, SOG materials can be both as positive and negative resist depending on the developer. In the exposed region, the structure of ladder silicon SOG is changed to the silicon dioxide-like structure, thus rendering it soluble in hydrofluoric acid [14]. This is why ladder silicon SOG materials can work as positive resist. Oppositely, the unexposed area dissolves in most non-polar organic solvents, which make it work as negative resist. For example, the GR650 film, which is a kind of ladder silicon SOG, can be both as positive resist and negative resist under the DXRL. However, the thickness of the developed films was limited to 15 μm as positive resist [4,15].

Here, a process to produce crack-free, smooth silica-like films up to 200 μm thick at reasonable low temperature 75 °C is a novel approach to form and pattern very thick film structures by DXRL without using molds.

3. Thin SOG film patterned by liquid embossing

Liquid embossing is a physical process to create features in functional materials. It essentially roots from basic principles of microcontact printing, which is based on molecular pattern transfer from an electrometric stamp to a solid substrate by conformal contact.

Before patterning the thin SOG films, we need the stamps for liquid embossing. The PDMS elastomer or silicon rubber is used by most researches in fabrication of stamps.

SOG layers are used to transfer patterns. A relatively thin layer of SOG was applied to Si wafer by using conventional spin coating method. The thin films obtained were very consistent for a range of liquid materials including viscosity, vapor pressure, surface wetting. By using PDMS stamp the SOG layer was embossed and was heated at 75 °C for 14 h in oven with sufficient ramp. After curing good replication of PDMS stamp's pattern was formed. Fig. 1 shows the patterns on thin SOG films. From the picture, we saw there was residual at the edges of the patterns, which may result from the demolding process.

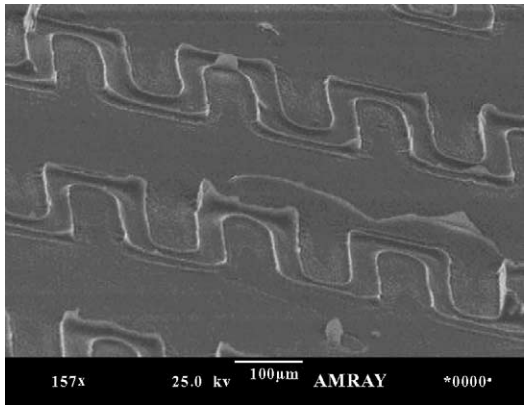

Fig. 1. SEM picture of patterns on thin SOG films.

4. Thick SOG film patterned by DXRL

4.1. Experiment

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

The third method mentioned above was employed in this work to produce a firm, transparent, crack-free, thick film. A layer of Teflon was used as a matching layer between silicon and GR650 thick film, due to the thermal expansion coefficient of Teflon matches that of GR650 very well. (The thermal expansion coefficient of GR650 resin is $130 \times 10^{-6}\ ^{\circ}C^{-1}$, and that of the Teflon (PTFE) is $124 \times 10^{-6}\ ^{\circ}C^{-1}$ [4].)

The sample with PTFE as a base layer and a confinement ring was shown in Fig. 2. We used a syringe with 0.2 μm filter to cast the GR650 solution into the confinement area. The whole sample was needed to be 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. After that, the sample was put into the Heraers oven for soft baking at the temperature 75 °C. The more detailed fabrication procedures were listed in the paper [17].

Then, the sample was ready for deep X-ray lithography (DXRL). Using DXRL to directly pattern the SOG films is a novel and promising method. GR650 is theoretically capable of being processed both as a positive and a negative X-ray resist. In this work, we are showing GR650 as negative resist after DXRL.

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. A 5 min 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.

4.2. Results

4.2.1. SEM

The following pictures Figs. 3 and 4 show the microstructures taken by SEM. The height of the microstructures is about 200 μm.

From the pictures, we see some white residuals at part top edge of the structures, which is a common occurrence. Longer immersion time in methanol or quicker stirring of the solvent could not solve the problem. Through several experiments, we found that unclear edges occurred in the high dose irradiation samples. Thus, the reason for top edge residual may be because of the higher dose on top than that in the bottom.

4.2.2. X-ray photoelectron spectroscopy (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. XPS gives the information about the elements and bonds existing on the surface of a sample. We performed XPS analysis on the microstructure before and after DXRL and compared the results.

Fig. 5 shows the results. Here, 1 is the SOG film before DXRL, 2 is the SOG film after DXRL and 3 is the SiO_2 gotten from thermal growth. From this figure, we see that the composition of the SOG film after DXRL is similar to that of the thermally grown one.

Fig. 2. Substrate with the base layer and the confinement ring.

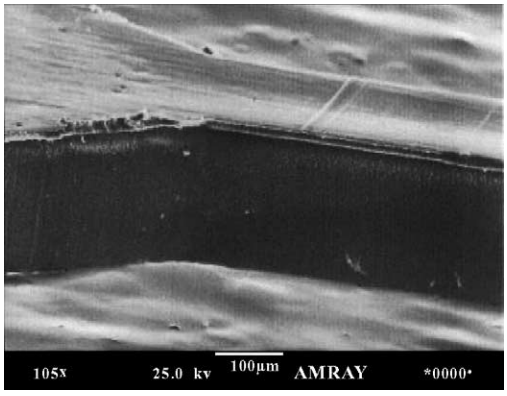

Fig. 3. SEM of microstructure patterned by DXRL showing height.

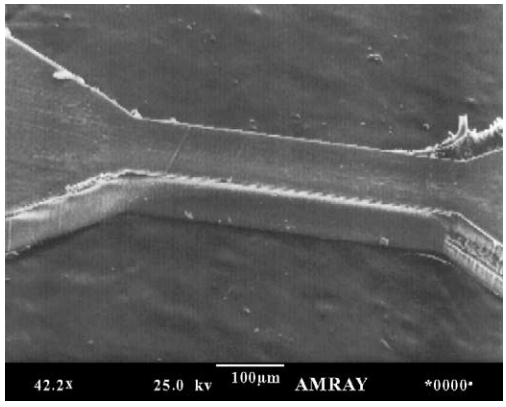

Fig. 4. SEM of showing edge residual.

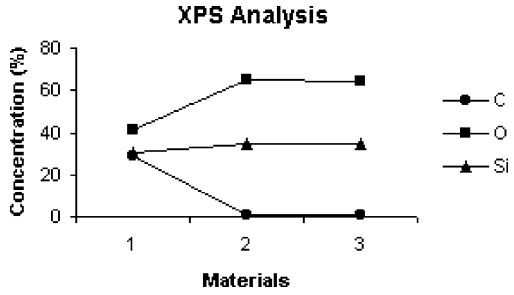

Fig. 5. XPS analysis of different elements concentration.

5. Conclusions

In this paper, the sol–gel process and their applications are reviewed. A process for fabricating 200 μm SOG micro-optical structures by deep X-ray lithography (DXRL) is presented, and showed the method is a novel approach for fabricating very thick SOG films. Through the XPS analysis, we found the constitution of the microstructures is similar to that of the thermally grown SiO_2. The SOG films gotten from this procedure can replace the thermally grown SiO_2 in some fields. Moreover, we showed some results of thin SOG films patterned by liquid embossing method, which is also a novel method for pattern transferring. There are many potential applications and promising directions for both thin and thick SOG films, such as higher microstructures resulted from positive and negative resist, three-dimensional structures, integrity with the other materials like conducting polymer, etc.

Acknowledgements

This work was partially supported by NSF/LEQSF (2001-04)-RII-02 grant ''Micro/Nanodevices for Physical, Chemical and Biological Sensors''.

References

[1] B.G. Bagley, W.E. Quinn, S.A. Khan, P. Barboux, J.M. Tarascon, Dielectric and high T_c superconductor applications of sol–gel and modified sol–gel processing to microelectronics technology, J. Non-Cryst. Solids 121 (1990) 454–462.
[2] N. Mariya, Modification effects in ion-implanted SiO_2 spin-on glass, J. Electrochem. Soc. 140 (1993) 1442–1450.
[3] K. Hasegawa, et al., Preparation of thick inorganic composite films by electrophoretic sol–gel deposition using organically modified silica particles and polyethylene maleate, Chem. Lett. (1997) 1115–1116.
[4] V.-A. Shanmugam, Fabrication of Silica-Like Structures by Deep X-Ray Lithography, Master's Thesis, Louisiana Tech University, 2000.
[5] D. Levy, L. Esquivias, Sol–gel processing of optical and electro-optical materials, Adv. Mater. 7 (1995) 120–129.
[6] Y. Han, Investigation of Microlens Fabrication Processes, Master's Thesis, Louisiana Tech University, 1998.
[7] R.H. Liu, The fabrication of non-planar spin-on glass microstructures, J. Microelectromech. Syst. 8 (1999) 146–151.
[8] C.A. Bulthaup, E. Wilhelm, B. Hubert, B. Ridley, J. Jacobson, All additive fabrication of inorganic logic elements by liquid embossing, Appl. Phys. Lett. 79 (2001) 1525.
[9] C. Marzolin, A. Terfort, J. Tien, G.M. Whitesides, Pattering of a polysiloxane precursor to silicate glasses by microcontact printing, Thin Solid films 315 (1998) 9–12.
[10] M.P. Andrews, Spinnable and UV-patternable hybrid sol–gel silica glass for direct semiconductor dielectric layer manufacturing, Proc. SPIE 3678 (1999) 1252–1262.
[11] P. Coudray, J. Chisham, S. Iraj Najafl, Ultraviolet light imprinted sol–gel silica glass low-loss waveguides for use at 1.55 μm, Opt. Eng. 36 (1997) 1234–1240.
[12] A. Milgram, J. Puretz, A bilevel resist for ion beam lithography, J. Vac. Sci. Tech. B3 (3) (1985) 879–883.
[13] K. Suzuki, Focused ion beam lithography using ladder silicon spin-on glass, J. Appl. Phys. 33 (1994) 7033–7036.
[14] K. Suzuki, Focused ion beam lithography using ladder silicon spin-on glass as a positive resist, J. Appl. Phys. 35 (1996) 6517–6520.
[15] V.-A. Shanmugam, Silica-Like Micro-Structures Fabricated by X-Ray Irradiation of Polymethylsilsesquioxane-Based Spin-on Glass Films, in: SPIE's 2000 Symposium and Education Program on Micromachining and Microfabrication, 2000, p. 14179.
[16] R. Osredkar, Spin-on glass material curing and etching, Microelectron. Reliab. 34 (1994) 1265–1267.
[17] Y. Liu, T. Cui, P. Coane, M.J. Vasile, J. Goettert, High-aspect-ratio microstructures fabricated by X-ray lithography of polymethylsilsesquioxane-based spin-on glass thick films, Microsyst. Technol., in press.

Biographies

Yuxin Liu is currently a PhD student at Institute for Micromanufacturing of Louisiana Tech University. She received the BS from Beijing Institute of Technology and received the MS from Changchun Institute of Optics and Fine Mechanics in 1996 and 2000, respectively. Now she is currently working under the instruction of Dr. Tianhong Cui, and her research interests include microstructure fabrication and polymer microelectronics devices.

Tianhong Cui received the BS from Nanjing University of Aeronautics and Astronautics in 1991, and PhD from Chinese Academy of Sciences in 1995. He has also served as a postdoc at Tsinghua University from 1995 to 1997, and at Department of Electrical and Computer Engineering at University of Minnesota from 1997 to 1998. He joined National Laboratory of Metrology in Japan as a research fellow under STA fellowship from 1998 to 1999. In 1999, he joined the faculty as an assistant professor at Institute for Micromanufacturing of Louisiana Tech University. His present research interests include polymer micro/nanoelectronics, MEMS new fabrication technologies, novel micro devices and microsystems, and nanotechnology.

Philip J. Coane received an AS degree in electronic engineering from Los Angeles Pierce College and a BS degree in physics from California State University. In 1978, Mr. Coane joined the IBM T.J. Watson Research Center as Research Project Manager with responsibility for the fabrication of advanced sub micrometer CMOS and bipolar semiconductor devices. In 1993, Mr. Coane joined the Louisiana Tech University, Institute for Micromanufacturing and is currently the Associate Director of operations at this facility. His research interests include the application of electron beam, optical and deep X-ray lithography processes to fabricate prototype microstructures and devices. Mr. Coane has authored/co-authored over 60 publications and holds five patents on microfabrication concepts.

Michael J. Vasile received BS in chemistry at Rutgers University, PhD in physical chemistry from Princeton University, and postdoctorate studies at

the National Research Council of Canada. Twenty-five years of research in plasma chemistry, molecular beam/mass spectrometry and focused ion beams at Bell Labs, Murray Hill, ended with early retirement as a distinguished member of technical staff in 1993. He then became the Tolbert Pipes professor at the Institute for Micromanufacturing, Louisiana Tech University, working in focused ion beam applications and X-ray lithography, as applied to microstructure formation. Dr. Vasile is now an independent consultant on contract to Sandia National Laboratories.