Spin-on-Glass (SOG) for the Trilayer Imaging Process

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ABSTRACT: Maleic acid catalyzed hydrolysis and condensation of tetramethoxysilane was carried out in 1-propoxy-2-propanol to prepare a spin-on-glass (SOG) material for the trilayer imaging process. The material was found to be stable enough for industry use. Minor amounts of methylsilsesquioxane and photoacid generators were introduced into the material. Thin resist (top layer) patterns were imaged on the SOG film (intermediate layer), which was coated on a hard-baked i-line resist (bottom layer). The SOG film showed sufficient adhesion to the resist patterns, and superior resist profiles were imaged on the film. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 636–640, 2003

Key words: spin-on-glass; sol–gel; trilayer imaging process; lithography

INTRODUCTION

A spin-on-glass (SOG) material has been developed for the trilayer imaging process that can be applied to sub-180 nm device fabrication. The continual shrinkage of the critical dimension in integrated circuits makes it difficult to get an adequate resolution and a process window in a lithography process. Thinner resists will be able to offer the process requirement since the aspect ratio of their patterns can be reduced.[1,2] When the resists are applied to a conventional single layer process, however, the potential of the resist mask will be insufficient due to the lack of remaining resist after substrate etch. The trilayer imaging process can provide the solution to the etching disadvantage.[3–6]

In the trilayer imaging process, thin resist (top layer) patterns are imaged on a silicon oxide layer that is coated on a thick bottom layer composed of the organic antireflective material. The patterns are precisely transferred down to the lower layer through an anisotrope reactive ion etching with high etch selectivity (Fig. 1).

From the viewpoint of process simplification, it is usually desirable to apply SOG rather than chemically vapor-deposited (CVD) SiO_2 film to the middle layer.[2,6] However, SOG precursors in general have been handled with considerable care because they are made up of labile polysiloxane sol. The polysiloxanes are prepared by sol–gel polymerization of alkoxysilanes.[7–16] These polymers tend to grow until they reach a size where three-dimensional gel networks are formed unless stored at a lower temperature. The rapid evolution of the sol–gel structure interferes seriously with uniforming the quality of the resulting film. When the evolution influences the viscosity of the sol, for instance, it will be very difficult to adjust the thickness of the resulting film. It is believed that the sol has to be controlled by an appropriate choice of reaction catalysts and solvents for practical use.[17–23] The optimum catalysts not only control the hydrolysis and condensation of alkoxysilanes, but also the charge on the surface of the resulting particle. At the point of zero charge, electrostatic repulsion between particles is created to prevent aggregation. It is also possible to prevent coagulation by using organic solvents as the adsorbed layer on the sol, which constitute a steric barrier.[17]

The application of SOG to the trilayer imaging process has an additional disadvantage that the SOG tends to lose its adhesion to the organic resist patterns. The hydrophilic surface of the SOG containing Si–OH groups should account for the matter. An organic SOG can be expected to improve the adhesion to the resist patterns without any tedious hydrophobic surface treatment.

This paper deals with the SOG material for the trilayer imaging process. The characteristic features of the material are as follows.

The SOG precursor consists of polysiloxane and is stable enough for industry use. The polymer is prepared mainly by maleic acid catalyzed hydrolysis and condensation of tetramethoxysilane (TMOS) in 1-propoxy-2-propanol (PGPE). The material also contains a small amount of methylsilsesquioxane (MSQ = $MeSiO_{1.5}$) and photoacid generators (PAGs). The SOG film shows sufficient adhesion to the resist pat-

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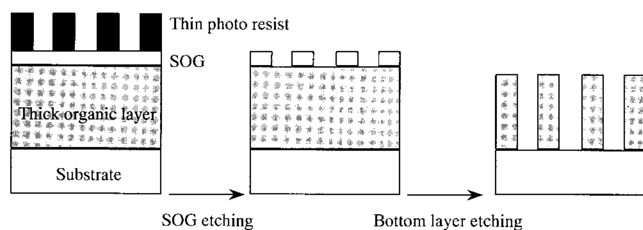


Figure 1 Process flow of the trilayer imaging process.

terns. This feature is generated by the hydrophobic surface of the film containing MSQ.[24]

The photogenerated acid in the SOG film makes it possible to obtain superior resist profiles on the film. In the absence of the acid, a significant amount of residue remains at the foot.

EXPERIMENTAL

Solvents and materials

All the solvents, acids, and PAGs were used without further purification. TMOS and MTMS were distilled before use. A chemically amplified positive photoresist (KRF M60G), an i-line photoresist (IX795G), and tetramethylammonium hydroxide (TMAH) solution (PD523AD) were purchased from JSR Co. Ltd.

Preparation of SOG precursor (1)

To a solution of TMOS (28.94 g, 190 mmol) in 81.14 g of PGPE was added dropwise at 60°C a solution of maleic acid (0.57 g, 4.89 mmol) in distilled water (13.80 g, 767 mmol). After 4 h of stirring at 60°C, the resulting mixture was concentrated under reduced pressure to afford a colorless SiO_2 sol (100 g).

A solution of maleic acid (1.10 g, 9.48 mmol) in distilled water (18.69 g, 1.04 mol) was added dropwise at 60°C to a solution of MTMS (42.42 g, 311 mmol) in 37.97 g of PGPE.

The solution was diluted with PGPE (59.86 g) after 2 h of stirring at 60°C. The resulting mixture was concentrated under reduced pressure to afford a MSQ sol (100 g).

To a mixture of a SiO_2 sol (21.88 g) and MSQ sol (4.40 g) was dissolved 0.12 g of triphenylsulfonium trifluoromethanesulfonate (TPST). Dilution of the resulting mixture with PGPE (51.80 g) and distilled water (1.91 g) afforded **1** (80 g).

Preparation of SOG precursor (2)

A solution of maleic acid (0.79 g) in distilled water (33.63 g) was added dropwise at 60°C to a mixture of TMOS (40.59 g) and MTMS (8.13 g) in 116.865 g of 1-ethoxy-2-propanol (PGEE). After 4 h of stirring at 60°C, the resulting mixture was concentrated under reduced pressure to afford a SiO_2/MSQ sol (100 g).

Dilution of the sol (12.88 g) containing 0.05 g of TPST with PGPE (52.6 g), PGEE (12.6 g), and distilled water (1.93 g) afforded **2** (80 g).

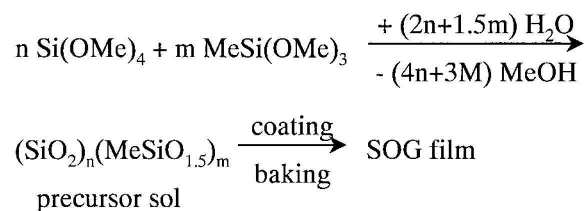
Apparatus

A Tokyo Electron Clean Track ACT8 was used for coating of intermediate and bottom layers (SOG and i-line photo resist) on silicon wafers. Coating and development of a chemically amplified positive photoresist were conducted with a Tokyo Electron Clean Track MARK-8. Film thickness was measured using a KLA Tencor thin film measurement system Prometrix UV-1280SE, a Dainippon Screen Lambda A VL-M6000-LS, and a Sloan Technology Division surface texture analysis system Dektak3030ST. Optical constants of films were measured using a KLA Tencor thin film measurement system Prometrix UV-1280SE. DUV exposure (248 nm) was carried out on an Nikon NSR2205EX12B excimer laser stepper (NA = 0.55, σ = 0.80) with annular illumination. Scanning electron microscopy (SEM) photographs were taken on a Hitachi scanning electron microscope S-4100. A thin layer of platinum–palladium was coated on all SEM samples to avoid charging. A Kyowa Interface Science automatic contact angle meter CA-V was used for measuring a contact angle on a film.

RESULTS AND DISCUSSION

Preparation of SOG precursors

An aqueous solution of maleic acid was added dropwise at 60°C to a mixture of TMOS and MTMS (TMOS/MTMS = 2/8) in PGPE.[25] After stirring for 4 h, the resulting mixture was concentrated under reduced pressure to give the polyorganosiloxane sol. Unpatterned silicon wafers were coated with the sol and baked on a hot plate at 200°C for 60 s.



The 1110 nm thick film was obtained at a fixed revolution. The stability of the sol was estimated by monitoring the change in thickness of the film formed from the solution, which was allowed to stand at 40°C. When the solution was allowed to stand for 1 week, the 1200 nm thick film was obtained under the same treatment as described above; thus it was found that

the degree of an increased thickness was about 8%. Under the conditions, PGPE solution of the polysiloxane was found more stable than the other solutions such as *n*-butyl-acetate (BA), propylene glycol methyl ether acetate (PGMEA), 2-heptanone (MAK), and ethyl-3-ethoxypropionate (EEP). When the BA solution was left for 1 week, the resulting film increased by 30%. Precipitation or gelation was observed after allowing the solutions of PGMEA, MAK, and EEP to stand. The sol prepared in 1-ethoxy-2-propanol (PGEE) marked nearly the same stability as the PGPE solution marked. The investigated solvents are familiar in the electronics industry. This results occur because the electrosteric stabilization of the polysiloxane prevents coagulation effectively with an assistance of PGPE.[17] It is apparent that there should be an appreciable interaction between hydroxyl groups in PGPE and silanols in the polymer.

It has been reported that the gelation rate for TEOS hydrolyzed with aqueous acid solution is minimized at about pH1.5.[17,18] The authors investigated the effects of catalysts by reference to the acidity. Dichloroacetic acid catalyzed hydrolysis and condensation of a mixture of the alkoxysilanes (TMOS/MTMS = 2/8) in PGPE also provided the stable siloxane sol. The film result from the solution, which was kept standing for 1 week, was found to be a 8% increase in thickness compared with that result from the fresh solution. Under the conditions, the sol using acetic acid (pKa 4.76) was found to be a 17% increase in film thickness. The stability of the solution was thus inferior to those using maleic acid (pKa 1.91) and dichloroacetic acid (pKa 1.26). These results suggest that acids such as maleic acid and dichloroacetic acid successfully controlled the surface potential of the colloids and provided effective electrostatic repulsion between the colloids to prevent their aggregation. The colloids in the solutions should be the most stable at the isoelectric point.

The conditions thus determined (PGPE, maleic acid) have been applied to the preparation of the SOG precursors for the trilayer imaging process. To a solution of TMOS in PGPE was added dropwise at 60°C an aqueous solution of maleic acid. After 4 h of stirring at 60°C, the resulting mixture was concentrated under reduced pressure to afford a colorless SiO_2 precursor sol. The film of uniform thickness was given by the removal of methanol, which was generated as a result of the hydrolysis of TMOS. Under similar conditions, maleic acid catalyzed hydrolysis and condensation of MTMS provided the MSQ sol. The SOG precursor (**1**) was prepared by mixing those sols and an appropriate PAG. The added proportion of the MSQ sol and PAG to the SiO_2 sol was adjusted to give the best lithographic performance.

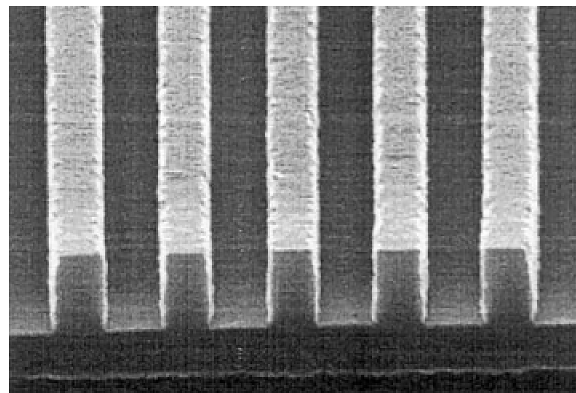


Figure 2 Top resist profile (180 nm line/space) on the optimum SOG.

Lithographic evaluation

In order to evaluate the lithographic performance on the trilayer process, three materials were stacked on a silicon wafer as follows. An i-line photoresist (JSR IX795G) was spin-coated on unpatterned silicon wafers and cured at 300°C for 60 s to give the 700 nm thick-bottomed organic layer. The refractive index (n) and extinction coefficient (k) of the film was 1.88 and 0.21 at a 248 nm imaging wavelength, respectively. The resulting wafers were coated and cured on a hot plate at 300°C for 60 s to form the 70 nm thick SOG intermediate layer. The optical properties of the film was $n = 1.53$ and $k = 0.00$ at the imaging wavelength. The SOG film consisted mainly of SiO_2 and $MeSiO_{1.5}$. The major features of the infrared (IR) spectrum were at the 3400, 1277, 1065, 941, and 798 cm^{-1} bands. The 1065 cm^{-1} band is attributed to the Si–O–Si structure. The 3400 and 941 cm^{-1} bands are assigned to the SiOH structure. The 1277 and 798 cm^{-1} are associated with the $SiCH_3$ structure. Finally, a chemically amplified positive photoresist (JSR M60G) was coated on the SOG layer and baked at 140°C for 60 s. The top layer was adjusted to be 280 nm thick after curing.

DUV exposure (248 nm) was carried out on an excimer laser stepper with annular illumination. The resulting film was postexposure baked at 140°C for 90 s and developed with 2.38 wt % TMAH solution for 30 s.

Figure 2 shows the 180 nm line/space feature of the top photo resist on the SOG, which is coated on the bottom layer. The superior profile, which was free from residue at the foot of the top layer, has been achieved. It has been found that the antireflective bottom organic layer quenched a standing wave effectively and contributed to the clean images. A wide variety of PAGs was applicable to the SOG. Good results were obtained by using photoactive sulfonium compounds. On the SOG not containing PAGs, patterning the top resist resulted in a significant amount of residue at the foot (Fig. 3). It is concluded that

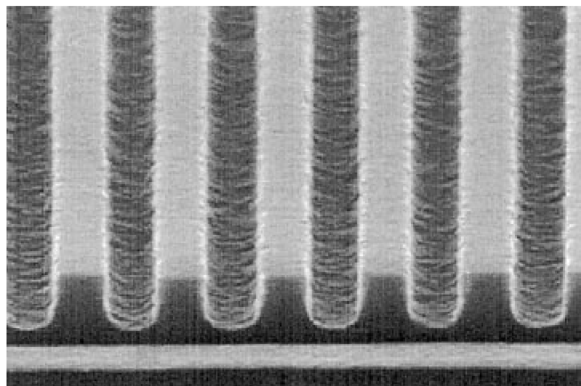


Figure 3 Cross-section of 180 nm dense line on the SOG not containing PAGs.

insufficient deprotection of the photoresist was catalyzed by photogenerated acid at the foot not as concentrated as that at the head. Extensive study of the residue is now under investigation.

Adhesion to the resist patterns

The hydrophobic surface of the SOG layer was found to be very useful for good adhesion to the top resist patterns. No patterns were remained on the SOG not containing MSQ, whose surface is considerably hydrophilic. The hydrophobicity on the SOG surface was estimated simply by measuring the contact angle of water on the surface of the film (Fig. 4). The contact angle was increased remarkably with increasing the amount of MSQ by weight, particularly when the content was less than 2 wt %, to the total weight of the SOG. At 5 wt % and above, the contact angle was kept approximately constant. In practice, satisfactory adhesion to the top resist images was demonstrated on the SOG film that contains 5 wt % of MSQ. When SOG precursor (**2**) was prepared by hydrolysis and condensation of the *mixture* of TMOS and MTMS, the hydrophobicity on the surface of the copolymer film was not very sensitive to the MSQ content (Fig. 4). Good adhesion to the resist patterns required a large amount of MSQ in precursor **2** than was employed as an ingredient of precursor **1**. The results demonstrated that MSQ bearing hydrophobic methyl group was concentrated at the surface of the film given from precursor **1**.

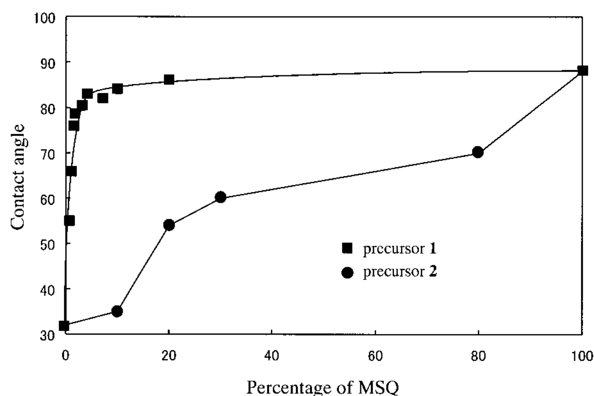


Figure 4 Variation of the contact angle of water on the SOG film as a function of the percentage of MSQ.

TABLE I
Atomic Ratio and C/Si Value of the SOG Film

Precursor	Atomic ratio[a] (%) C	O	Si	C/Si Ratio
1	29	46	25	1.2
2	15	60	25	0.6

[a] The values are calculated from the peak intensities of C_{1s}, O_{1s}, and Si_{2p}.

The electron spectroscopy for chemical analysis (ESCA) technique also made the concentration clear. C_{1s}, O_{1s}, and Si_{2p} signals of the SOG films containing 20 wt % of MSQ were recorded at the photoelectron take-off angle (TOA) of 45°. Table I shows the atomic ratios calculated from the signal intensities and the C/Si values. The C/Si values were indicative of the carbon uptake on the surface of the film that was formed from precursor **1**. The theoretical atomic ratio of 7(carbon):61(oxygen):32(silicon) leads the C/Si value to 0.2 on the presumption that the films are completely uniform and no concentration.

In the image transfer process, the photoresist pattern is first transferred into the SOG middle layer. The imaged SOG layer functions as an etch mask for transferring images down to the bottom organic layer. From the viewpoint of etch selectivity, the much less abundant organic component in the SOG should be desirable for a precise image transfer. Precursor **1** thus offers a distinct advantage over precursor **2**, which contains the considerably large amounts of methyl group to obtain good adhesion to the resist patterns.

Stability of the SOG precursor

The SOG precursor was found quite stable even at room temperature. Even if the solution was kept for 28 days at 23°C, the resulting film showed no appreciable change in thickness (Fig. 5). The superior resist profile on the film was intact.

CONCLUSION

A SOG material for the trilayer imaging process has been developed. The SOG precursor was prepared by acid catalyzed hydrolysis and condensation of TMOS and MTMS. Various combinations of acids and solvents were examined for the reaction. The choice of the solvent strongly influenced the stability of the precursor. Fairly stable precursors were obtained by

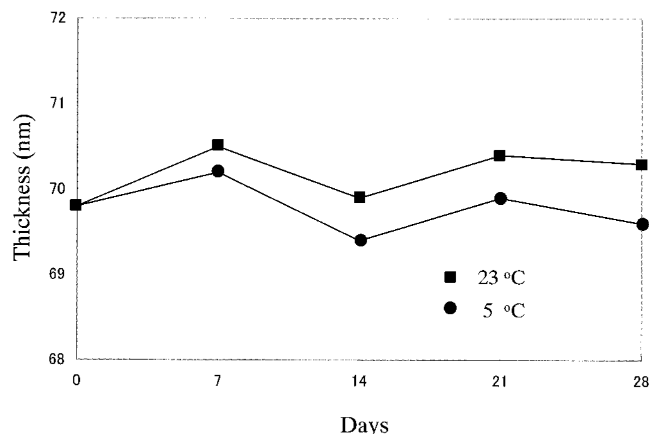


Figure 5 Storage time dependence of the SOG film thickness.

using maleic acid in PGPE. The optimized conditions have been applied to the preparation of SOG precursor. Lithographic evaluation of a photoresist was carried out on the SOG film, which was coated on the bottom organic layer. When adding small amounts of MSQ and PAGs to the SOG, the photoresist was able to resolve 180 nm line/space features on a 248 nm stepper. Photoacid in the SOG film served to improve the quality of the top resist patterns. Imaging the top resist resulted in a significant amount of residue at the foot on the SOG not containing PAGs. MSQ plays a role to join the SOG to the resist patterns. No patterns remained on the SOG free from MSQ. Even if the material was allowed to stand for 4 weeks at room temperature, owing to its high stability, a variation in thickness of the resulting SOG film was not detected. In addition, good lithographic performance of the photoresist on the SOG film remained unchanged.

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