Bilayer Resists for 193 nm Lithography: SSQ and POSS

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Positive 193 nm bilayer resists based on polysilsesquioxanes (SSQ) and polyhedral oligomeric silsesquioxanes (POSS) are described. Fluoroalcohol is employed as an acid group. Our POSS materials are prepared by condensation of functional trialkoxysilane rather than by the commonly employed hydrosilylation on POSS and consist of T\textsubscript{3} while the hydrosilylation method produces Q\textsubscript{3} POSS. The condensation method is more suitable for scale-up, producing POSS materials with higher glass transition temperatures. The materials were analyzed by \textsuperscript{19}F, \textsuperscript{13}C, and \textsuperscript{29}Si NMR to determine composition and to quantify Q/T. The SSQ and POSS materials with the same compositions were compared in terms of the degree of hydrogen bonding by IR and the dissolution behavior by quartz crystal microbalance (QCM). Densities of the SSQ polymers were determined by X-ray reflectivity measurements and Rutherford back-scattering. Positive resists formulated with ternary SSQ and POSS were evaluated for contact hole and line/space applications, respectively. Characterization and lithographic performance of SSQ and POSS resists are described in detail.

Keywords: polysilsesquioxane, POSS, condensation, 193 nm lithography, bilayer resists, fluoroalcohol, chemical amplification, molecular glass resists, hydrogen bonding, deprotection

1. Introduction

Efforts to extend ArF (193 nm) lithography to 65, 45, and even 32 nm nodes continue. In addition to immersion lithography at 193 nm, we have been pursuing a bilayer imaging scheme employing silicon-containing resists for its potential for better process latitudes than single layer resists. A large number of bilayer resists have been investigated [1] since the first report in 1985 [2]. For the chemically amplified bilayer resists to function, the resist polymer must contain an acid-labile group, an acidic (polar) group, and Si in sufficient concentration, for imaging performance in aqueous base and dry etch resistance in oxygen reactive ion etching (RIE). It is, however, often difficult to balance the three requisite functionalities in organic polymers containing Si in the side chain. Therefore, we have selected polysilsesquioxanes (SSQ) as our 193 nm bilayer resist platform [3] because of high Si contents, good transparency, high etch resistance, minimal outgassing, minimal line slimming during SEM inspection, and ease of functionalization [3]. Furthermore, our SSQ systems employ fluoroalcohol instead of carboxylic acid as an acid group because it provides a much better dissolution behavior than carboxylic acid [4].

In addition to linear silicon-containing polymers, polyhedral oligomeric silsesquioxane (POSS) compounds have drawn a great deal of attention as a new architecture of resist materials (Figure 1). Its use as a molecular glass resist [5] has been recently described as a potential means to improve resolution and reduce line edge roughness (LER) [6]. We have synthesized POSS compounds for use in chemical amplification resists by condensation instead of the commonly employed functionalization through hydrosilylation.

In this paper are described characterization and lithographic performance of SSQ and POSS materials containing fluoroalcohol (Figure 1).
2. Experimental

2.1. Materials

The synthesis of SSQ polymers was previously described [3]. Bicyclo[2.2.1]-hept-5-ene-2-(1,1,1-trifluoro-2,2-trifluoromethyl-propane-2-ol) [7], and norbornene ethylenecyclopentyl ester were employed in hydrolysis with trialkoxy silane and the hydroxylated products were hydrolyzed with acid or base and then subjected to a condensation reaction under basic conditions, by varying the ratio of the monomers.

POSS compounds were prepared as follows. Hydroisilylation was carried out with trialkoxy silane on functionalized norbornenes, the products were purified and then subjected to condensation (Figure 2).

In a similar fashion lactone was introduced in SSQ and POSS.

Triphenylsulfonium nonaflate (TPSONf) was employed as our primary photochemical acid generator (PAG) and the casting solvent was propylene glycol methyl ether acetate (PGMEA) or a mixture of PGMEA and cyclohexanone.

2.2. Measurements

$^1$H, $^19$F, $^{29}$Si, and $^{13}$C NMR spectra were obtained at room temperature on a Bruker Avance 400 spectrometer. Quantitative $^{13}$C and $^{29}$Si NMR was run at room temperature in acetone-d$_6$ in an inverse-gated $^1$H-decoupled mode using Cr(acac)$_3$ as a relaxation agent on a Bruker Avance 400 spectrometer. $^{29}$Si NMR spectra were also acquired on a JEOL JNM-ECP300 spectrometer in CDCl$_3$ using a Teflon tube.

Molecular weights of the polymers were measured in tetrahydrofuran (THF) on a Tosoh HLC-8220 gel permeation chromatograph (GPC) relative to polystyrene standards. IR spectra were recorded on a Thermo Nicolet 670 FT-IR spectrometer on a film cast on a NaCl plate. Film thickness was measured on a Tencor alpha-step 2000. A quartz crystal microbalance (QCM) was used to study the dissolution kinetics of the polymer films in an aqueous tetramethylammonium hydroxide (TMAH) solution (CD-26 or AD-10), by measuring frequency and resistance using 5 MHz crystals. Contact angles were measured on an AST Products VCA 2500XE video contact angle system using 2 µL of filtered deionized water.

Specular x-ray reflectivity measurements were performed using a diffractometer (X’Pert Pro MRD, Panalytical) with ceramic x-ray tube (wavelength=0.154 nm) and high resolution horizontal Goniometer (reproducibility +/- 0.0001 degrees). The x-ray beam was line focused by a multi-layer crystal and a four bounced Ge (220) crystal was used as a monochromator. The reflected beam was received into a proportional gas filled detector after bancing Prefix triple axis optics module. The critical angles from the reflectivity data were obtained from the peak
position of $Iq^4$ vs. $q$ plots ($q = (4\pi/\lambda) \sin \theta$, where $\lambda$ is wavelength, $\theta$ is the grazing incident angle of the x-ray beam).

SSQ samples were analyzed by Rutherford Backscattering Spectrometry (RBS) using an NEC 3UH Pelletron running He$^+$ at 2.3 MeV in the standard IBM geometry. Two measurements conditions were used. For measuring H, the incident angle was 75°, with the detector set at 30°. A 7 micron Al foil was used to adsorb the forward scattered He beam. For measuring non-H elements the incident angle was 7° and the detector was set at 100°. Accumulated charge was 40 µC with a 20 nA beam current. The samples were rastered 50 mm² during analysis to prevent beam damage.

2.3. Lithographic Characterization

Contrast curves of our bilayer resists were generated by exposing the resist films coated on an AR19 antireflective coating on an ISI 193 nm stepper with a numerical aperture (NA) of 0.60. Postapply and postexposure bake (PAB and PEB) temperatures were varied by using a thermal gradient plate (TGP) [8]. Imaging was performed on 193 nm full field scanners with NA of 0.75 and 0.85, using commercial underlayers. Development was carried out for 60 sec in AD-10 (0.26 N TMAH).

3. Results and Discussion

3.1. POSS Synthesis and Characterization

Functionalization of POSS is typically accomplished by hydroxylation of octasilane POSS having R in Figure 1 of $-\text{OSi(CH}_3\text{)}_2\text{-H}$ with olefin bearing a desired functionality using a Pt catalyst [6,9]. This procedure provides flexibility in selection of a functional group and a high Si concentration. However, the pot yield tends to be low, the glass transition temperature ($T_g$) tends to be low, and contamination with a metal catalyst is an issue. Therefore, we have decided to prepare our POSS compounds by condensation of functionalized trialkoxysilane, which is more suited for scale-up and provides higher $T_g$.

Figure 3 presents a GPC curve of a typical condensation POSS product. The POSS fraction (lower molecular weight peak) is typically 70% and we call this material “POSS-70.” Fractionation by GPC provides “quasi POSS” with 97% POSS concentration. Since the economy of synthesis and purification is an important consideration, we have employed POSS-70 as our resist material.

Figure 4 shows a 39.7 MHz $^{29}$Si NMR spectrum of POSS-70 consisting of NBEC/BNHFA/lactone B in CDCl$_3$. It is clear that the compound consists exclusively of $T_1$ (-70 ppm, 98%); the silicon atoms on the ring is connected to three O-Si linkages and one carbon atom. For comparison, a $^{29}$Si NMR spectrum of a POSS compound prepared by conventional hydroxylation [6] is presented in the inset. The sharp peak at -110 ppm is ascribed to $Q_2$ (Si is connected to four O-Si linkages and a peak at 10 ppm to the Si atoms in the pendant O-Si(CH$_3$)$_2$-C group. The hydroxylation POSS synthesis is generally carried out on tetracyclododecene structures in an attempt to increase $T_g$. Detailed NMR analysis of SSQ polymers has been previously reported [3].

Figure 4. $^{29}$Si NMR spectra of POSS compounds prepared by condensation and hydroxylation (inset) in CDCl$_3$ and acetone-d$_6$, respectively.
The NBHFA-substituted trialkoxysilane readily formed POSS by condensation, providing a high POSS concentration of 91% without fractionation, as the GPC curve in Figure 4 indicates. The weight-average molecular weight and $T_m$% of the NBHFA-POSS were 2,550 and 92.3, respectively, and its $T_c$ was 29°C.

![Fig. 5. GPC curve of NBHFA-POSS prepared by condensation (no fractionation)](image)

and polytetrafluoroethylene is characterized with a very high density of 2.00-2.30 g/cm³[10].

3.2. Comparison of SSQ and POSS

IR spectra of a NBHFA SSQ “homo” polymer and a POSS bearing NBHFA connected to the eight ring silicon atoms are compared in Figure 6. As reported previously [3], the NBHFA SSQ “homo” polymer contains as much as 45% of silanol end groups. However, the degree of hydrogen bonding of the hydroxyl group is very much similar in SSQ and POSS.

Dissolution kinetics curves in CD-26 of the NBHFA-SSQ and -POSS are compared in Figure 7. While the SSQ “homo” polymer dissolves at 4,000 A/sec in a linear fashion, the NBHFA-SSQ dissolves initially at 2,400 A/sec and slows down to ca. 400 A/sec near the substrate.

As the SSQ polymers were suspected to have low densities, which could contribute to acid diffusion, our SSQ polymers were subjected to X-ray reflectivity measurements and their atomic compositions determined by RBS. The results are summarized in Figure 8. The density of our F-containing SSQ polymers ranged from 1.3 to 1.5 g/cm³ and increased as the Si and/or F concentration was increased. For reference, a conventional POSS without fluorine had a density of 1.35 g/cm³ and a polymethacrylate bearing hexafluoroalcohol 1.47 g/cm³. Poly(methyl methacrylate) and amorphous polystyrene have a density of 1.19 and 1.04-1.065 g/cm³, respectively.

![Fig. 6 IR spectra of NBHFA-based SSQ and POSS](image)

![Fig. 7. Dissolution kinetics curves of NBHFA-based SSQ and POSS in CD-26](image)

![Fig. 8. Density of fluorinated SSQ polymers as a function of Si and F concentration](image)
3.3. Lithographic Comparison of SSQ and POSS

Resists were formulated with SSQ and POSS consisting of NBECF/NBHFA/lactone. As IR spectra in Figure 9 indicate, the degrees of hydrogen bonding of OH and ester carbonyl groups in NBECF/NBHFA/lactone A are very similar in the SSQ and POSS resists. Contrast curves were generated for a SSQ and POSS resist formulated with a composition of NBECF/NBHFA/lactone B by exposing the resists on our ISI 193 nm stepper (NA=0.60) followed by postexposure bake (PEB) at various temperatures for 60 sec. The PEB temperature was varied from 92 to 122 °C on a single wafer, using our thermal gradient hot plate (TGP) while the postapply bake (PAB) temperature was kept constant at 120 °C (60 sec). Development was carried out in AD-10 for 60 sec. The film thickness was measured after PEB (before development) and after development to produce chemical and development contrast curves, respectively, which are presented in Figure 10. In both cases, the thicknesses in the lightly exposed films before and after development were essentially the same, indicating that swelling in the partially exposed regions is insignificant. The POSS-based resist exhibited only a small PEB temperature sensitivity. We evaluated the SSQ and POSS-based resists for contact hole and line/space patterning, respectively.

Fig. 9. IR spectra of SSQ and POSS consisting of NBECF/NBHFA/lactone A

Fig. 10. Contrast curves of SSQ- (left) and POSS-based (right) resists showing PEB temperature effects

Fig. 11. DOF of SSQ resist in comparison with a contact hole POR resist for various hole and pitch sizes

Fig. 12. DOF of POSS resist in comparison with a line/space POR resist for various space, line, and pitch sizes
The depth of focus (DOF) at 5% exposure latitude (EL) of the SSQ-based resist is compared with that of our process of record (POR) single layer resist for contact hole imaging (Figure 11). The two resists had overall similar process latitudes in printing 110-120 nm holes in different pitches. In line/space patterning, the POSS-based resist was superior to the SSQ-based resist and compared with our single layer POR resist. As Figure 12 demonstrates, the POSS-based bilayer resist exhibited more than 2x DOF (0.40 vs. 0.17 µm) in patterning of isolated spaces (P1000S111) and a slightly shallower DOF in patterning of isolated lines (P1000L152). The process latitudes for dense 80 nm line/space patterns were similar in the two resists.

In Figure 13 are presented scanning electron micrographs (SEM) of contact hole patterns (115 nm) printed in the SSQ bilayer resist (top) and those etched in a commercial underlayer with no etch bias. The etch selectivity was >4:1 and the etch profiles were good.

Figure 14 presents SEMs of dense line/space patterns (70, 80, and 90 nm) printed in the POSS bilayer resist (top) and etched in an underlayer (bottom). The selectivity of etch was >4:1 and the etched profiles were excellent.

4. Summary

- Functional POSS compounds were prepared by hydrolysis-condensation of functionalized trialkoxysilane instead of functionalization by hydrosilylation for ease of scale-up.
- The condensation products containing about 70% POSS were employed in resist formulation without fractionation. GPC fractionation produced almost pure POSS (97%).
- NBHFA condensed to POSS readily, providing POSS concentration of 91% without fractionation. The NBHFA-POSS dissolved in a nonlinear fashion at 2,400-400 A/sec in CD-26 while the NBHFA SSQ homopolymer (containing 45% silanol ends) at 4,000 A/sec. Hydrogen-bonding in the NBHFA POSS and SSQ was very much similar.
- Densities of SSQ polymers were determined by combining x-ray reflectivity and RBS data and ranged from 1.3 to 1.5. Introduction of Si and/or F increases the density.
- Bilayer resists were formulated using POSS and SSQ made from the NBEC/P/NBHFA lactone. The degrees of hydrogen bonding of OH and also of ester C=O were very similar for the POSS and SSQ resists.
- The SSQ and POSS resists exhibited superb performance in contact hole and line/space imaging, respectively. Chemical and development contrast curves were generated for varying PEB temperatures using our TGP. No swelling was observed in the partially exposed areas.
- The SSQ and POSS resist performances were compared with respective single layer POR resists. The process latitude of the SSQ resist was as good as that of a POR single layer resist in contact hole printing. The POSS-based bilayer resist had a huge DOF (>2x of the POR resist) in isolated space imaging while it was a little weaker than the POR resist in isolated line imaging.
- The SSQ and POSS resists provided >4:1 etch selectivity and good profiles with no bias after etch.

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References