Synthesis of alkali-soluble silicone resin suitable for resist material in microlithography

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(*Received 13 February 1989; revised 21 April 1989; accepted 11 May 1989*)

An alkali-soluble silicone resin, acetylated phenylsilsesquioxane oligomer (APSQ), was synthesized from phenylsilsesquioxane oligomer by Friedel Crafts acetylation. Silanol groups are simultaneously formed in APSQ through this acetylation. The presence of silanol groups makes APSQ soluble in alkaline aqueous solutions. Silicone-based results composed of APSQ and sensitizers were prepared for ultraviolet (u.v.), deep u.v., electron beam and X-ray lithographies. These resists based on APSQ can be developed with alkaline aqueous solutions and have high resistance to oxygen reactive ion etching.

(Keywords: silicone; phenylsilsesquioxane; oligomer; acetylated phenylsilsesquioxane; Friedel Crafts acetylation; lithography; resist; two-layer resist)

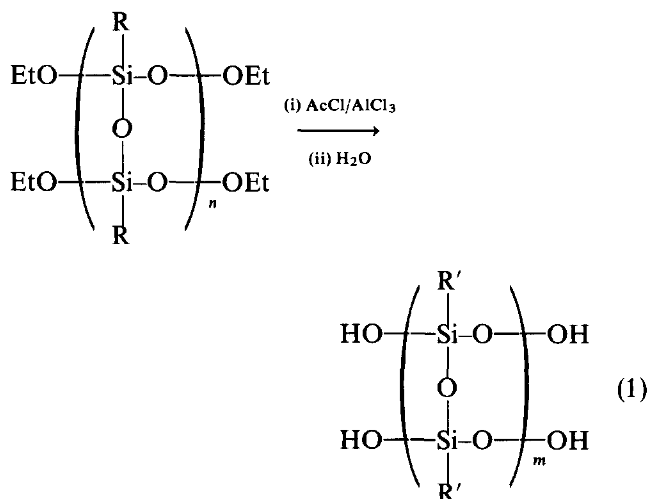
INTRODUCTION

Resist materials play a crucial role in defining pattern features in large scale integrated circuits (LSI). LSI pattern rules have shrunk to the submicrometre range to achieve high integration densities. This trend requires high resolution resist materials. Silicone-based resists coupled with a two-layer resist process[1–3] are promising candidates for submicrometre lithography. Silicone-based resists which can be developed with alkaline aqueous solutions have the further advantages of compatibility with the current novolac-type photoresists and less pollution from organic solvents[4,5].

Silicone-based resists must satisfy several requirements, including sensitivity, resolution, high glass transition temperature (T_g) and resistance to oxygen reactive ion etching (O_2 RIE). Resistance to O_2 RIE is an important factor, especially for the two-layer resist process, and allows transfer of top silicone-based resist images into bottom organic resists. Among many silicone resins, polyphenylsilsesquioxane seems to have the most suitable molecular structure for silicone-based resists from the viewpoints of resistance to O_2 RIE and high T_g. We used low molecular weight phenylsilsesquioxane (PSQ) oligomer to improve resolution characteristics and modified it to be an alkali-soluble resin, acetylated phenylsilsesquioxane oligomer (APSQ), by Friedel Crafts acetylation with acetylchloride (AcCl) and $AlCl_3$. In this report, we describe the synthesis and characterization of APSQ and comment on its application in microlithography.

SYNTHESIS

APSQ was synthesized as follows. A solution of 33 g of anhydrous $AlCl_3$ in 100 ml of AcCl was cooled at 19°C in a three-necked flask equipped with a thermometer, a dropping funnel, and a desiccant column. Another solution of 13 g of PSQ oligomer (glass resin GR950, Owen-Illinois Co.) in 100 ml of AcCl was dropped into the $AlCl_3$ solution from the funnel. Care was taken to prevent the reaction temperature from rising above 21°C. After stirring for 90 min, the solution was poured into 4.5 l of iced water and stirred for 30 min. White sticky precipitate of APSQ was washed with 3 l of water. A colourless APSQ solid was obtained after drying in vacuum. APSQ was precipitated twice with a tetrahydrofuran–water system. The yield was 8 g. The total reactions are described as follows:



where $R = C_6H_5$ and $R' = C_6H_5$ or $C_6H_4COCH_3$ or OH. For GR950 $M_w \approx 900$ and for APSQ $M_w \approx 1300$. Note that end groups of GR950 are capped with ethoxy groups and that the main chains of GR950 and APSQ may be disordered from the silsesquioxane ladder structure as described below.

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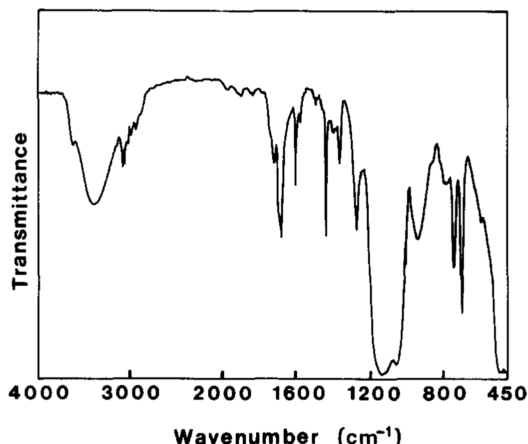


Figure 1 I.r. spectrum of acetylated phenylsilsesquioxane oligomer (APSQ) film

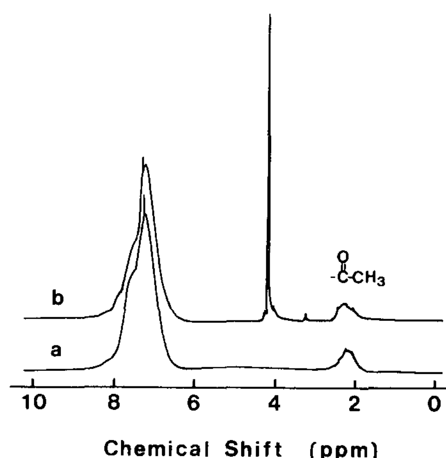


Figure 2 ^{1}H n.m.r. spectra of APSQ: (a) in $CDCl_3$; (b) in $CDCl_3/CD_3OD$ mixture

CHARACTERIZATION

The weight averaged molecular weight of APSQ determined by gel permeation chromatography was ≈1300 on the basis of polystyrene standards, which was slightly higher than that of GR950, ≈900. An attempt at conventional elemental analysis for APSQ failed because silicon carbide was irregularly produced during the measurement. Therefore, we identified the molecular structure of APSQ using infrared (i.r.) and nuclear magnetic resonance (n.m.r.).

Figure 1 shows the i.r. spectrum of APSQ film. Major absorption peaks of C–H stretching (3080–2940 cm^{-1}), Si-phenyl (1435 cm^{-1}), Si–O–Si (1200–1000 cm^{-1}) and phenyl groups (750 and 700 cm^{-1}) agreed with those of GR950. Peaks at 1680 and 3400 cm^{-1} correspond to acetyl and OH groups. The i.r. data indicates that APSQ molecular structure is fundamentally similar to GR950 except for the addition of acetyl and OH groups. Brown reported that high molecular weight polyphenylsilsesquioxane has *cis*-syndiotactic ladder structure and exhibits two characteristic i.r. peaks at 1045 and 1155 cm^{-1} for Si–O–Si asymmetrical stretching[6]. Both APSQ and GR950 showed the mixed spectrum of these two characteristic peaks and a broad band, suggesting that the APSQ main chain has incomplete *cis*-syndiotactic silsesquioxane ladder structure.

Figure 2 shows ^{1}H n.m.r. spectra of APSQ in $CDCl_3$ and in a mixture of $CDCl_3$ and CD_3OD. APSQ exhibits two peaks in $CDCl_3$, but three peaks in the $CDCl_3$ and CD_3OD mixture. Peaks at 1.7–2.6 ppm and at 6.4–8.4 ppm are assigned to acetyl groups and phenyl groups (involving acetylated phenyl groups), respectively. Introduction of acetyl groups to phenyl groups was confirmed by ^{13}C n.m.r. A sharp peak at 4.0 ppm in *Figure 2b* was assigned to CD_3OH produced as the result of H–D exchange between OH groups in APSQ and CD_3OD. Motion of OH groups in APSQ is restricted by the rigid main chain so that its spectrum in $CDCl_3$ is broadened and not observable in *Figure 2a*.

Figure 3 shows ^{29}Si n.m.r. spectra of GR950 and APSQ. GR950 has low molecular weight and showed two peaks at −70 and −77 ppm. The former peak is attributed to siloxane units with phenyl and ethoxy side chain groups, which may be the chain ends. The latter peak is attributed to framework phenylsilsesquioxane units since PSQ prepolymer (Petrarch Systems Inc., $M_w = 9500$) showed a single peak at the same chemical shift, as shown in *Figure 4*. On the other hand, APSQ showed four peaks at −69, −78, −89 and −100 ppm. The peaks at −69 ppm and −78 ppm were attributed to siloxane and framework phenylsilsesquioxane units, respectively. (In this paragraph, we use the term 'phenyl' not only for phenyl groups but also for acetylphenyl groups because these substituents could not be distinguished in the ^{29}Si n.m.r. spectra.) When APSQ was treated with trimethylsilylchloride to kill hydroxy groups, the peaks at −69, −89 and −100 ppm became weak and a new peak at −109 ppm assigned to silicon atoms binding to four siloxane groups appeared. This observation indicates that silicon atoms corresponding to the peaks at −69, −89 and −100 ppm have silanol structure. These peaks are probably assigned to siloxane units with phenyl and hydroxy groups, siloxane units with dihydroxy groups and framework silanol groups, respectively.

According to these analyses, we conclude that APSQ

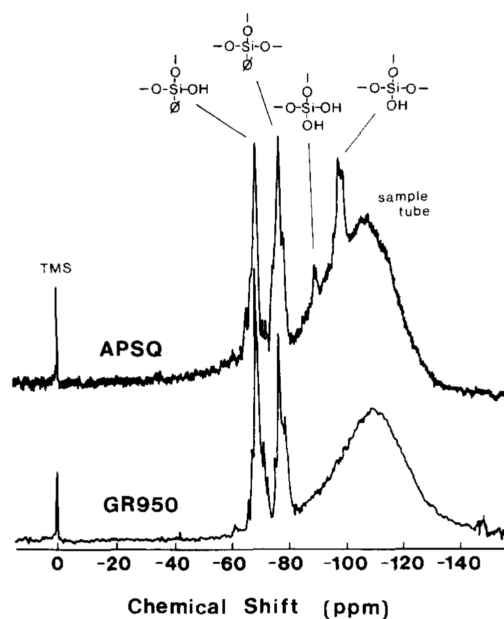


Figure 3 ^{29}Si n.m.r. spectra of GR950 and the resulting APSQ in acetone-d_6. Chromium acetylacetonate was used as a relaxation reagent

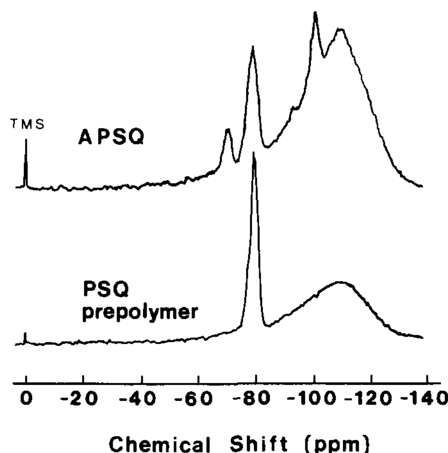


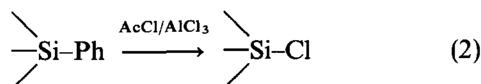
Figure 4 ^{29}Si n.m.r. spectra of PSQ prepolymer and the resulting APSQ in acetone-d_6. Chromium acetylacetonate was used as a relaxation reagent

has three kinds of pendant groups, phenyl, acetylphenyl and hydroxy (silanol). The composition of these three groups changes due to the synthetic conditions. However, typical molar ratios of these groups were 0.55:0.07:0.38, on the basis of ^{1}H n.m.r. signal intensities.

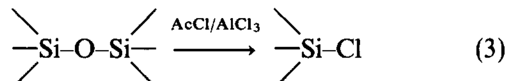
DISCUSSION

N.m.r. studies indicate that the formation of silanol groups is the major reaction, rather than the acetylation of phenyl groups. One possible reaction to form silanol groups is the exchange of ethoxy groups for hydroxy groups, since APSQ involves no ethoxy groups, as shown in *Figure 2*. However, the reaction route may be complicated. N.m.r. and gel permeation chromatography (g.p.c) studies suggest that condensation and esterification of GR950 occur along with the elimination of ethoxy groups when GR950 is dissolved in AcCl. The acetoxy silyl structure formed by the esterification is hydroxylated during sedimentation in water, although this route contributes only $\approx 3\%$ to the total silanol amount in APSQ, estimated by ^{1}H n.m.r.

The more important reactions pass through the scission of Si–phenyl and Si–O–Si bonds. An experiment on the PSQ prepolymer, which has no ethoxy groups, proved the possibility of these reactions since the resulting APSQ has a similar molecular structure to the APSQ made from GR950, as shown in *Figure 4*, although signal intensities in *Figure 4* are slightly different from those in *Figure 3*. Si–C bonds have low resistance to electrophilic attack compared to C–C bonds. In alkylsilanes and arylsilanes, Si–C bonds can be substituted for Si–Cl bonds under Lewis acids[7]. Si–phenyl bonds in PSQ oligomer and prepolymer seem to suffer similar chlorination under our synthesis conditions (equation 2). Si–O–Si structure is relatively strong and stable, but it may also suffer chlorination under Lewis acids (equation 3). The Si–Cl groups produced are hydroxylated to Si–OH groups during sedimentation in water (equation 4).



(2)



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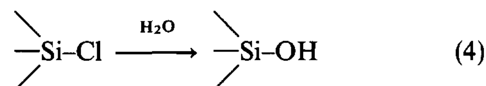

(4)

Because of the presence of silanol groups, APSQ is soluble in alkaline aqueous solutions. Thin APSQ film spin-coated on a silicon wafer was dipped in a tetramethylammonium hydroxide (TMAH) aqueous solution for 1 min to estimate its solubility in alkaline aqueous solutions. The APSQ film dissolved in a TMAH solution over a critical TMAH concentration (C_{crit})[8], which we used as a solubility index. *Figure 5* shows the dependence of C_{crit} on the silanol content in APSQ. C_{crit} increased as silanol groups were terminated with trimethylsilyl groups. The C_{crit} value also changed due to synthetic conditions. The C_{crit} dependence for both cases lay on the same curve, indicating that the solubility of APSQ depends only on the silanol content and not on the preparation methods, either trimethylsilylation or synthetic condition control.

Solubility in alkaline aqueous solutions is a promising characteristic for the matrix resin in multi-component resist materials because it allows development with alkaline aqueous solutions. Conventional novolac-diazonaphthoquinone positive photoresists, which are currently very widely used in LSI fabrication, use this alkali development system. Resists which are developed with organic solvents usually swell in the developer. Swelling reduces pattern resolution. However, alkali-developable resists scarcely swell in the developer and therefore show superior performance in terms of resolution characteristics.

APPLICATIONS FOR MICROLITHOGRAPHY

We prepared various two-component resists using APSQ as a matrix resin. An APSQ–diazonaphthoquinone resist called SPP (silicone-based positive photoresist)[9,10] exhibits high resolution with ultraviolet (u.v.) exposure. SPP seems to be the most suitable silicone-based photoresists for the two-layer resist system. An APSQ-polysulphone resist called SPR (silicone-based

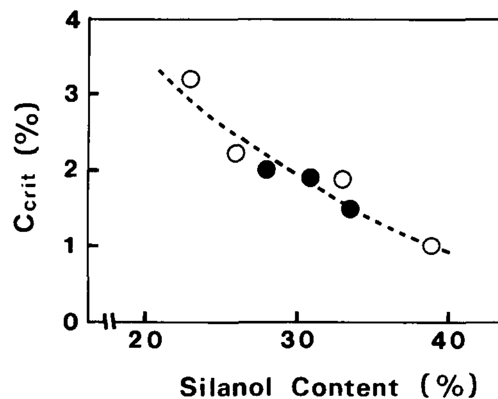

Figure 5 Relationship between silanol content in APSQ and critical tetramethylammonium hydroxide concentration (C_{crit}), where APSQ begins to dissolve in a 1 min dipping test. Species with different silanol content were prepared by synthesis condition control (○) and by appropriate trimethylsilylation (●)

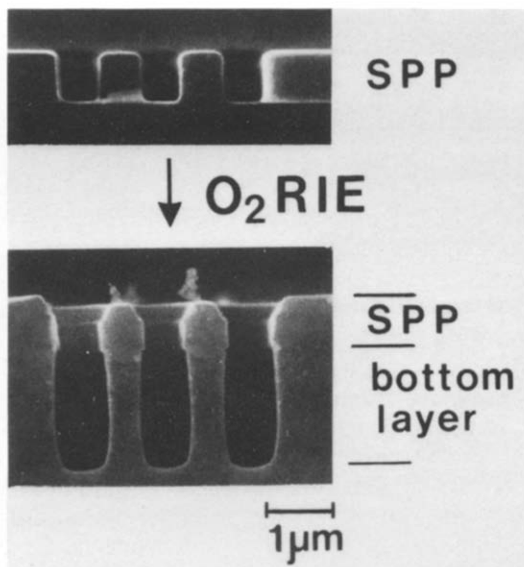

Figure 6 0.6 μm line and space patterns of SPP/novolac two-layer resist fabricated by u.v. lithography and after oxygen reactive ion etching (O_2 RIE). Resist thickness: SPP, 0.6 μm, novolac (MP2400), 2.0 μm

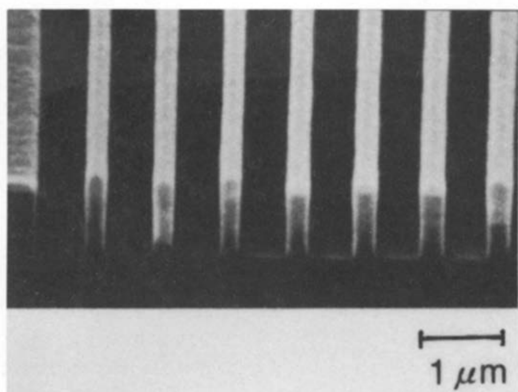

Figure 7 0.8 μm pitch line and space pattern of SPR/novolac two-layer resist fabricated by electron beam lithography after O_2 RIE

positive resist)[8] is sensitive to electron beams and X-rays. An APSQ-azide resist called SNP (silicone-based negative photoresist)[11] is sensitive to deep u.v., electron beams and X-rays. SNP scarcely swells in developers so that its resolution is very high for a negative resist.

Figure 6 shows SEM images of SPP/novolac two-layer resist patterns fabricated by u.v. lithography. The upper micrograph shows the cross section of SPP 0.6 μm line and space pattern and the lower micrograph shows the replicated pattern by O_2 RIE. O_2 RIE rapidly etches normal organic polymers, but makes a thin barrier layer like SiO_2 on the surface of top silicone-based resists[2]. Thus the top layer remains with a slight deformation of pattern shape while the bottom layer is completely fabricated by O_2 RIE. *Figures 7* and *8* show SEM images of SPR/novolac two-layer resist patterns fabricated by electron beam and X-ray lithographies, respectively. SPR of 0.3 μm initial thickness acted as a sufficient barrier layer against O_2 RIE. *Figure 9* shows an SEM image of 0.48 μm wide SNP pattern fabricated by deep u.v. (KrF excimer laser) lithography. Both SNP and SPP can provide a rectangular cross-sectional pattern, which is important for fabricating the bottom layer with precise pattern size control.

The silicon atoms in APSQ are so abundant that both APSQ-based resists and APSQ are very durable to O_2 RIE. Etching rates were measured with a parallel plate RIE instrument at an oxygen pressure of 10 mTorr ($\approx$1.3 Pa), r.f. power of 0.1 W cm^{-2} and bias of 350–400 V. The etching rates of APSQ, SPP, SNP and SPR were 3, 4, 3 and 6 nm min^{-1}, respectively, whereas that of a novolac resist (Microposit MP2400, Shipley) was 90 nm min^{-1}. The ratios of these etching rates are in the range 15–30. This high resistance to O_2 RIE enables excellent performance as the top barrier layer.

CONCLUSION

We synthesized an alkali-soluble silicone resin called APSQ through Friedel Crafts acetylation of phenylsilsesquioxane oligomer with acetylchloride and $AlCl_3$. N.m.r. and i.r. studies indicate that silanol groups are simultaneously formed in APSQ, probably via the scission of Si–phenyl and Si–O–Si bonds. Silanol content reaches $\approx$40 mol% among all substituents in APSQ. The presence of silanol groups makes APSQ soluble in alkaline aqueous solutions. Silicone-based resists com-

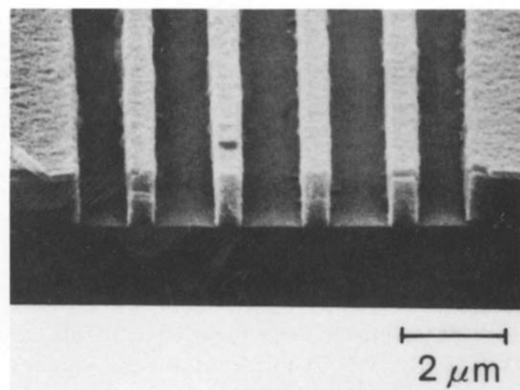

Figure 8 1.7 μm pitch line and space pattern of SPR/novolac two-layer resist fabricated by X-ray lithography after O_2 RIE

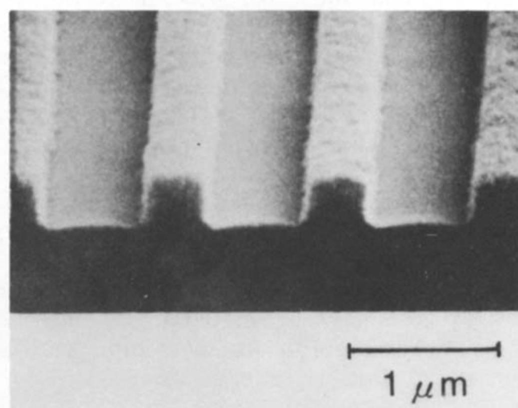

Figure 9 0.48 μm wide pattern of SNP fabricated by excimer laser lithography

posed of APSQ and sensitizers were prepared for u.v., deep u.v., electron beam and X-ray lithographies. These resists based on APSQ can be developed with alkaline aqueous solutions and have high resistance to O_2 RIE. APSQ is a useful matrix resin for alkali-developable silicone-based resists which enable submicrometre lithography using a two-layer resist process.

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