



Polyhedral oligomeric silsesquioxane (POSS) acrylate copolymers for microfabrication: properties and formulation of resist materials

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Abstract

Novel polymers containing polyhedral oligomeric silsesquioxane (POSS) pendant groups have been synthesized and evaluated as components of resist formulations. Random copolymers of polymerizable ethyl-POSS containing monomers with various acrylate type monomers including tert-butyl methacrylate and 2-(trifluoromethyl) acrylic acid, were used in positive, aqueous base-developable resist formulations and evaluated at thicknesses in the range of 100 nm. Copolymers with optimized monomer composition provide materials with good film forming properties, and high sensitivity at 157 nm (1–10 mJ/cm² under open field exposure). High resolution patterning under these conditions has shown potential for sub 100 nm lithography upon further material optimization. Moreover, pattern transfer studies have shown that 100 nm thick films of POSS containing materials, having ~9% silicon content provide the necessary oxygen plasma resistance for use as bilayer resists.

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1. Introduction

Silicon-containing polymers have been used extensively for various applications such as nanolithography [1], nanoimprint lithography [2], fabrication of microfluidic devices [3]. Nanostructuring is used to control the physical and biological function of materials and to improve radically

the physical properties of traditional materials. We are currently investigating polyhedral oligomeric silsesquioxanes (POSS) as silicon-containing components of photoresists suitable for nanofabrication. Each POSS unit contains non-reactive organic functionalities that make the POSS based nanostructured materials compatible with polymers, biological systems, and surfaces. In addition, POSS-bearing chemicals can contain one or more covalently bonded reactive functionalities suitable for polymerization, grafting, surface bonding, or other transformations (Fig. 1(a)) [4].

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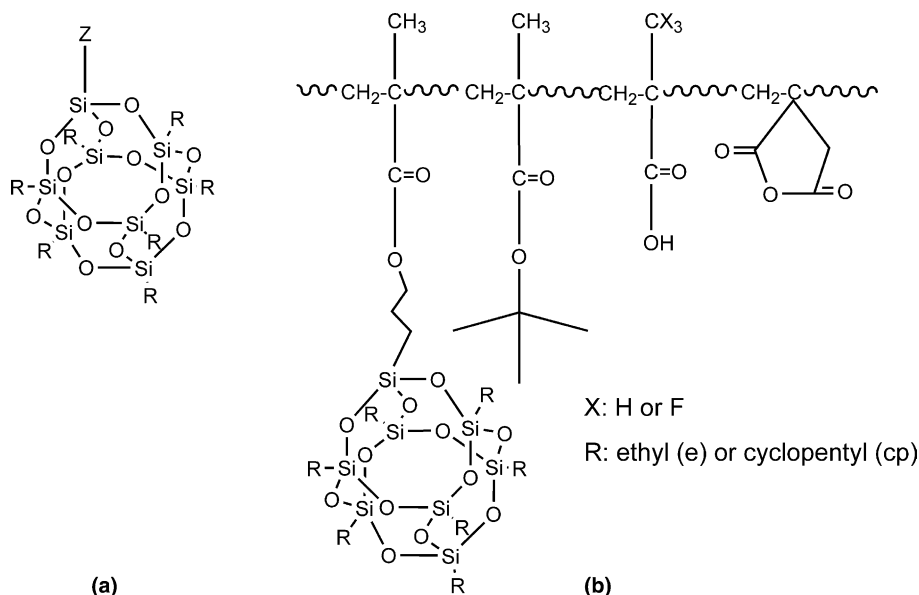


Fig. 1. (a) Anatomy of a POSS nanostructured chemical. R represents non-reactive organic groups for solubilization of the molecule and compatibility with other organic species. X represents reactive groups for grafting or co-polymerization. (b) A POSS copolymer containing POSS, TBMA, MA or triFMA, IA (R: ethyl or cyclopentyl).

In the field of microlithography, POSS polymers can find applications as components of bilayer resists, due to their high etch resistance to oxygen plasma [5]. Comparing to siloxanes, ladder-type silsesquioxanes or other silicon-containing polymers, POSS-based resists additionally present the advantages of positive-tone behavior, high glass transition temperature (T_g) values and well defined structures. Especially in the case of 157 nm or EUV lithography, where thin or ultra-thin films are a prerequisite, the inherent etch resistance property of POSS resists becomes highly desirable. However, due to absorbance restrictions at 157 nm, partial or full fluorination of the comonomers is needed to improve high-resolution performance.

In the present work, POSS monomers were copolymerised with fluorinated and non-fluorinated monomers of the acrylate type in various compositions [6]. The physical properties as well as the etching behavior of this new class of materials are examined. For the materials with optimized composition, high resolution evaluation has been performed under 157 nm exposure, showing potential for sub 100 nm lithography. First pattern

transfer efforts prove the feasibility of POSS-based copolymers as bilayer resists.

2. Experimental

2.1. Physicochemical characterization

Absorption spectra in the VUV were recorded with a J.A. Woollam VUV variable angle spectroscopic ellipsometer (VASE) VU301 and/or a SOPRA GES5-PUV spectroscopic ellipsometers. Modulated differential scanning calorimetry (MDSC) measurements were carried out with a DSC 2920 (TA Instruments) at a heating rate of 10 °C/min. The surface hydrophobicity was estimated by the contact angle formed by a deionised water (Millipore Milli-Qplus) droplet placed on the film surface, using Digidrop DGW-EWS equipment. A Perkin–Elmer Paragon Identity Check FT-NIR spectrophotometer equipped with a deuterated diglycerine sulphate detector was used to collect FT-IR spectra with resolution 4 cm^{-1} at 64 scans. Samples were prepared on single-polished silicon substrates. The FT-IR measurements were made

in transmittance mode for thin films (typical thickness: 150 nm).

2.2. Oxygen plasma etching studies

Thin films of POSS copolymers were spin cast on top of 350 nm thick hard baked novolac. Etch resistance studies of the films were performed in an inductively coupled plasma (ICP) etcher (MET) from Alcatel (composed of a cylindrical alumina source and a diffusion chamber). The temperature of the sample was controlled at 15 °C by mechanical clamping and helium backside cooling. The etching conditions were: oxygen plasma (100 sccm, 10 mTorr), source power: 600 W and bias voltage: –100 V. Etching rate was monitored with laser interferometry. Surface roughness was measured before and after etching in contact mode, with a Topometrics TMX 2000 atomic force microscope (AFM). The total etching time for the surface roughness measurements was equal to the etch time for the novolac end-point plus 20% overetching. The total time of etching for etch-rate and selectivity measurements (novolac underlayer/resist) was as high as 900% overetching.

3. Results and discussion

POSS monomers were copolymerized with other monomers, such as methacrylic acid (MA), methyl methacrylate (MMA), tert-butyl methacrylate (TBMA), itaconic anhydride (IA) and 2-(trifluoromethyl) acrylic acid (TFMA), in various compositions following a procedure described elsewhere [6,7]. An example of such a copolymer is shown in Fig. 1(b). Each monomer employed in

the acrylate platform serves a specific reason: methacryloxy propyl POSS is used as the etch barrier imparting the required etch resistance, TBMA plays the role of the protecting group which, upon exposure and subsequent heating, undergoes the acid catalysed deprotection reaction while hydrophilic groups such as MA or IA may be added in order to provide good adhesion and increase the aqueous base solubility (dissolution promoters).

Table 1 shows some typical physical properties of the synthesized POSS copolymers. For comparison purposes PTBMA is included in the table. The T_g of the resist formulations containing polyhedral silsesquioxanes ranges from 110 to 150 °C for the materials tested. Increase of the polyhedral silsesquioxane component increases the material's T_g . Furthermore, all synthesized POSS copolymers are hydrophobic independently of the POSS content. The water contact angle was measured to be in the range of $100^\circ \pm 10^\circ$ for POSS contents 20–100% w/w. The presence of such bulky hydrophobic alkyl-POSS groups in resist formulations often results in micro phase separation degrading the lithographic performance. Especially for the copolymer consisting of cyclopentyl-POSS (cp-POSS) and TBMA (row 1 in Table 1), severe development problems were encountered. High segregation of the POSS cages near the surface, as was determined by XPS studies, may be a factor that has affected the development process [7].

At 193 nm the absorbance coefficient values are lower than the corresponding ones at 157 nm. For the lithographically useful materials, i.e., the ethyl-POSS (e-POSS) ter- or quarter polymers (rows 2 and 3), the lowest absorbance value is achieved for the fluorinated terpolymer consisting of e-POSS,

Table 1
Physical properties of synthesized POSS copolymers (e: ethyl, cp: cyclopentyl)

Copolymer composition (% w/w)	T_g (°C)	Contact angle (°)	Surface segregation	a (μm^{-1}) at 157 nm	a (μm^{-1}) at 193 nm	$R_{\text{novolac}}/R_{\text{copolymer}}$
20 cp-POSS/80 TBMA	114	92	High	–	–	5:1
30 e-POSS/40 TBMA/20MA/10 IA	142	96	Low	5.2	0.67	20:1
30 e-POSS/40 TBMA/30 TFMA	130	94	Low	4.0	–	9:1
100 e-POSS	251	101	No	3.1	0.17	>50:1
100 cp-POSS	350	116	No	7.6	4.55	40:1
100 TBMA	100	86	–	6.5	–	–

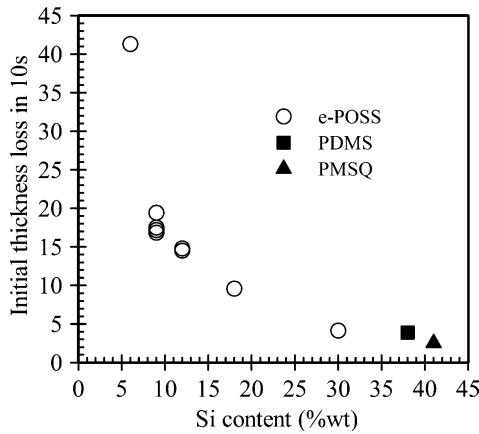


Fig. 2. Thickness loss versus silicon content, after 10 s of etching in ICP oxygen plasma with 100 V bias. Comparison with poly dimethyl siloxane (PDMS) and poly methyl silsesquioxane (PMSQ).

TBMA and TFMA. However, the value of $4.0 \mu\text{m}^{-1}$ is still high for single layer applications at 157 nm. Nevertheless, both etch resistance en-

hancement and low surface segregation, allow possible use of e-POSS based materials for bilayer applications.

Cyclopentyl-substituted POSS copolymers show less etch resistance and higher surface roughness compared to ethyl-substituted polymers. At only 20% overetching the surface roughness of the cp-POSS was ~ 15 nm (rms value) while, on the contrary, e-POSS films showed only ~ 0.3 nm surface roughness. This signifies that e-POSS films are appropriate for high resolution imaging where small roughness is necessary. The reason for this difference might lie in the inherent POSS morphology: it is possible that during etching cp-POSS is stripped by the surrounding organic cyclopentyl groups and the larger distance between the cp-POSS units compared to the e-POSS units prevents the formation of a smooth oxide surface.

On the other hand, polymers containing 30% or higher w/w (i.e. 9% Si content) ethyl-substituted

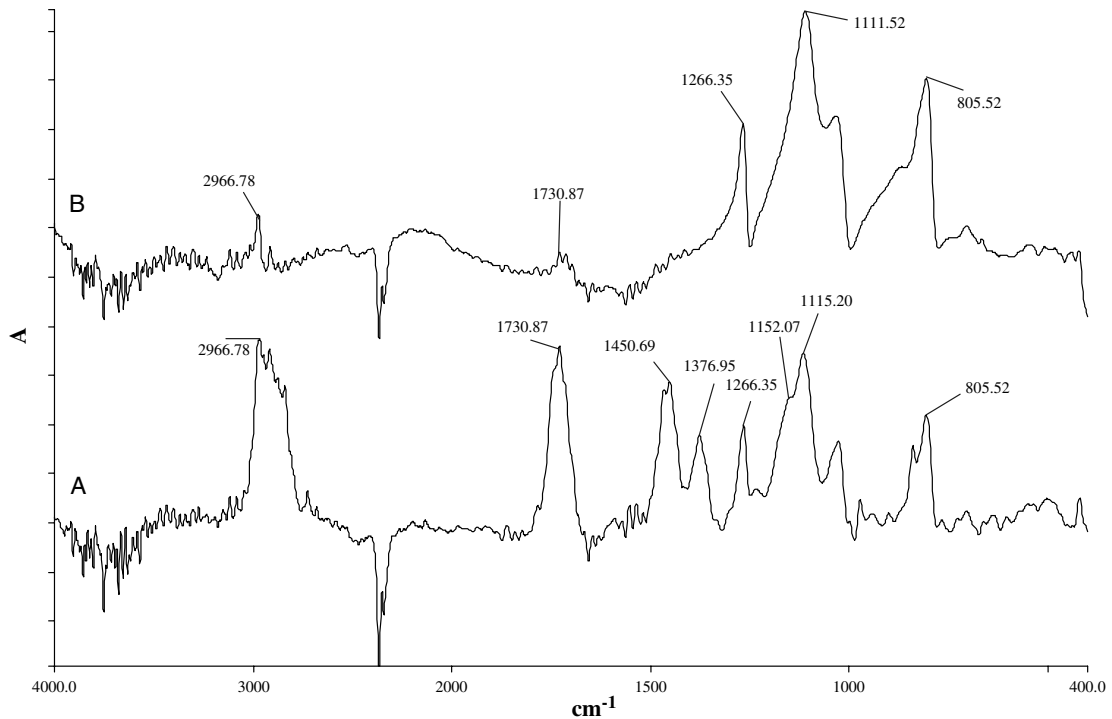


Fig. 3. (A) copolymer consisting of ethyl POSS–TBMA–MA–IA before plasma etching (film thickness: 147 nm on 350 nm hard baked novolac). (B) copolymer consisting of ethyl POSS–TBMA–MA–IA after 150 s oxygen plasma etching (film thickness:70 nm). In both spectra the novolac spectrum has been subtracted.

POSS cages provide the necessary etch resistance as well as low surface roughness to oxygen plasma etching at 100 nm film thickness. In addition, the etch resistance of the fluorinated polymer (30% POSS) is adequate and similar to the etch resistance of the non-fluorinated polymer (25% POSS) [7].

Moreover, the thickness loss is a strong function of the POSS content and decreases as the POSS content increases as shown in Fig. 2. The first fast thickness loss is attributed to etching of the organic groups from the surface of the film, while the subsequent etching rate reduction is attributed to oxide formation. A similar mechanism has been proposed for PDMS, however more studies are necessary to determine the surface oxide layer thickness for POSS materials [8].

FT-IR spectroscopy has been used for detecting the formation of the SiO_x layer during the oxygen plasma etching. Fig. 3 shows the normalized FT-IR spectra of a POSS quarter polymer (components: e-POSS, TBMA, MA, IA) before etching (spectrum A) and after 150 s etching (spectrum B). 150 s etching corresponds to 15% of the total etching time of the copolymer. The following peaks exist in spectrum A and become significantly weak after oxygen-plasma treatment (spectrum B): 2967 cm^{-1} , attributed to C–H stretch, 1450 , 1377 cm^{-1} : C–H bend, 1731 cm^{-1} : C=O stretch, 1152 cm^{-1} : C–O stretch. On the other hand, peaks that become predominant in spectrum B are the peaks corresponding to the silicon containing part of the

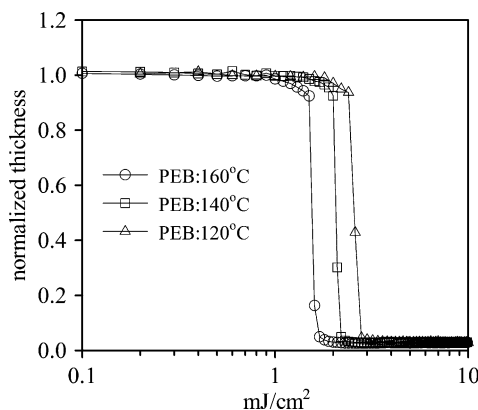


Fig. 4. Contrast curves of POSS copolymer containing ethyl POSS, TBMA, TFMA for various post-exposure bake temperatures.

copolymer, i.e., the peak at 1266 cm^{-1} attributed to Si–C stretch and at 1112 cm^{-1} corresponding to Si–O–Si stretch (cage structure). These data point to a strong oxidation of the POSS layer and formation of an oxide-like surface while the peak at 1266 cm^{-1} indicates that the surface layer contains not only Si–O bonds but also Si–C bonds. This is in agreement with results obtained for ladder-type silsesquioxanes with XPS analysis [9].

Solutions (4–6% w/w) of the candidate resist materials were prepared in either methyl isobutyl ketone (MIBK), or propylene glycol methyl ether (PGME). The photoacid generator (PAG) used in resist formulations, was perfluorooctylsulfonate based. High resolution 157 nm exposures were performed at International Sematech (Austin, TX) on an Exitech microstepper (0.6 NA) using alternating phase-shift masks (σ 0.3). In Fig. 4 the contrast curves of a fluorinated POSS copolymer show high sensitivity and contrast for various post exposure bake temperatures. Lithographic evalu-

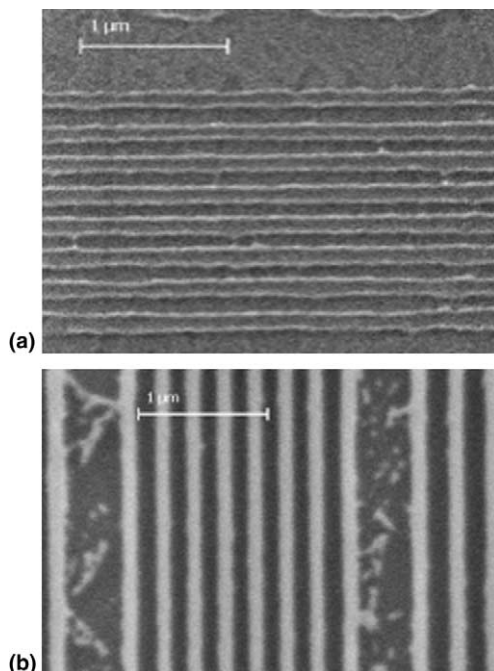


Fig. 5. SEM pictures of POSS copolymer containing ethyl POSS, TBMA, TFMA: (a) after wet development 100 nm s^{-1} 1:1 are resolved (dose: 25.0 mJ/cm^2); (b) after partial dry development of the underlayer with two-step plasma etching: 100 nm s^{-1} 1:1.5 (dose: 20.5 mJ/cm^2).

ation for the same material is shown in Fig. 5(a). 100 nm s^{-1} are resolved. Additionally, in Fig. 5(b) first pattern transfer attempts are presented proving the feasibility of POSS-based copolymers as bilayer resists.

4. Conclusions

Ethyl-POSS unit containing polymerizable monomers can be used in the synthesis of copolymers useful as resist components for nanofabrication. Resist formulations suitable for 157 nm lithography can be obtained by copolymerizing POSS containing monomers with partially fluorinated acrylates. Sub 100 nm resolution potential and effective pattern transfer using oxygen plasmas have been demonstrated. These results show the potential of this resist platform although further optimization is necessary.

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