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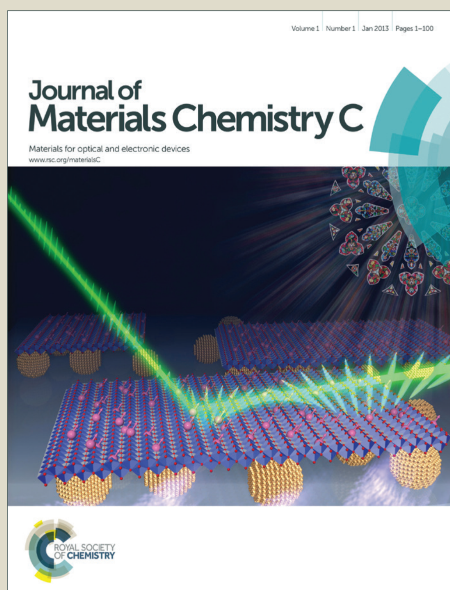

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COMMUNICATION

Soluble Polycyclosilane-polysiloxane Hybrid Material and Silicon Thin Film Having Optical Properties at 193 nm and Etch Selectivity

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In order to develop soluble silicon materials and silicon thin film having optical properties at 193 nm, high silicon content and etch selectivity for O_2 and CF_x plasmas, a polycyclosilane precursor was synthesized. A new class of polycyclosilane-polysiloxane hybrid materials and its thin films exhibited good optical properties at 193 nm without organic absorbant and proper etch selectivity.

In the process of semiconductor manufacturing, there are essential silicon materials, such as silicon substrates, silicon oxide and silicon nitride.[1-4] The lithography process, which specifically includes light exposure, etching, and developing processes, requires silicon materials having photosensitivity to a light source and etch selectivity to plasmas. Because chips are currently manufactured using a deep UV light source (193 nm, ArF), silicon materials that absorb light at 193 nm with etch selectivity are necessary. For example, the spin-on hardmask (SOH) process requires a silicon material with specific optical and etch properties.[5,6] The SOH process has attracted growing interest from semiconductor manufacturers as it allows for the control of desirable pattern depth after an etch step with lower cost and higher throughput.

To illustrate the basic concept of lithographic SOH materials, Figure 1 depicts photoresist (PR) patterning and consecutive etch steps in a silicon-HM (hardmask), a carbon-HM, and a substrate using trilayer. The trilayer resist stack consists of PR, Si-HM, C-HM and substrate (a). In (b), the PR is patterned using a deep UV light source, and in (c), Si-HM is rapidly etched by CF_x plasma due to etch selectivity with organic PR. (d) The patterned Si-HM serving as a mask for oxygen plasma etching of C-HM allows for deep patterns of C-HM, (e) and after an etch step using the deep patterned C-HM, a substrate with a desirable pattern depth is finally obtained. In the SOH process, Si-HM plays a dual role: an anti-reflective role for proper PR patterning in the exposure step, which requires optical properties at 193 nm of Si-HM, and a hardmask role for pattern transfer to C-HM during the etch step, which is ensured by the high etch resistance against oxygen plasma.

Currently, commercially available silicon materials adopt a phenyl group to achieve an optical absorbance at 193 nm, but their Si (or SiO) contents deteriorate due to carbon atoms from the phenyl group resulting in the reduction of etch selectivity. In general, a high etch selectivity is achieved by a high Si (or SiO) content, which suggests that a silicon material with high Si content is strong resistant to oxygen plasma and is rapidly removed by CF_x plasma.[7-11] The need for advanced silicon materials without aryl groups prompted us to develop a new optical absorbant at 193 nm.

Thus, we have pursued the development of a new class of non-phenyl polycyclosilane-polysiloxane hybrids as unprecedented liquid precursors that have optical absorbance in the deep UV range and etch selectivity. Because the Si-Si-Si bond of polysilane exhibits absorptive properties in the deep UV region due to the σ-σ^* transition, and increases Si (or SiO) content as opposed to an aryl group, polysilane is a promising candidate for use as a new optical absorbance material at 193 nm.[12-14] In order to make thin film with nanometer thick through spin coating, the materials should be soluble in organic solvents and thermally and oxidatively stable in the air. We decided to choose cyclosilanes[15-20] as a chromophores, and synthesized a new condensation-polymer precursor, ethoxycyclosilane. The general properties of cyclosilanes are known to be similar to those of aromatic compounds, which come from the delocalization of σ(Si-Si) electrons.[21-24] In this report, we describe the synthesis and structure of a hexaethoxyhexamethylcyclohexane (**3**) as a novel polymer precursor, its copolymerization with methyltrimethoxysilane, and the optical and etch properties of the

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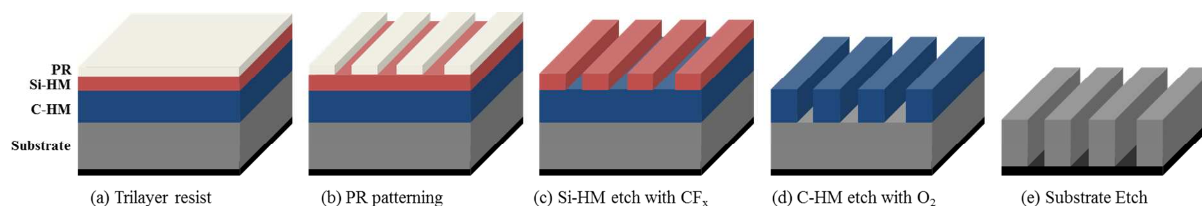
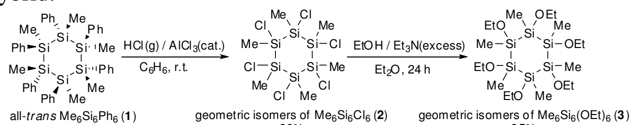


Figure 1. Lithographic SOH process of the trilayer.

film prepared from a new class of polycyclosilane-polysiloxane hybrid.



Scheme 1. Synthesis of $Me_6Si_6(OEt)_6$ (**3**)

Hexachlorohexamethylcyclohexasilane (**2**) was synthesized in 96% yield from $Me_6Si_6Ph_6$ (**1**) using the method developed by Hengge and coworkers.[25-28] White solid of pure **2** was obtained as geometric isomers through sublimation of a reaction mixture at 130 ^{o}C under 0.02 torr (Scheme 1). Recrystallization of the solid in *n*-hexane at -20 ^{o}C afforded colorless crystal in 58% yield. An X-ray diffraction study on single crystals of **2** confirmed the two geometric isomers. Interestingly, two structures are all-trans configurations with opposite positioning (axial in **2a** and equatorial in **2b**) of the chlorine atoms (Figure 2). Two geometric isomers **2a** and **2b** were included in 49.4% and 50.6%, respectively in the lattice.

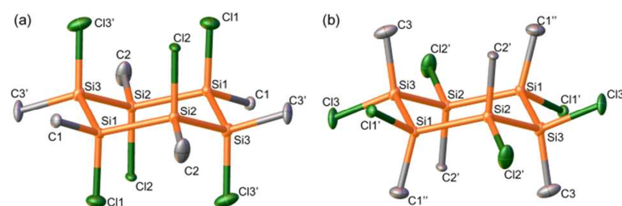


Figure 2. Molecular structure (30% thermal probability ellipsoids) of all-*trans* **2**. (a) All-*trans* **2a** (Cl atoms occupy axial positions) and (b) all-*trans* **2b** (Cl atoms occupy equatorial positions). Hydrogen atoms have been omitted for clarity. The inversion center is located in the center of the 6-membered ring. Selected bond lengths (Å) and angles (deg): Si1-Si2 = 2.335(9), Si1-Si3 = 2.335(6), Si2-Si3 = 2.339(0), Si1-Si2-Si3 = 110.8(1), Si2-Si1-Si3 = 112.9(1), Si2-Si3-Si1 = 111.9(2). See the Supporting Information for details.

The average bond lengths of Si-Si (2.33 Å) and Si-Cl (axial: 2.036 Å, equatorial: 2.037 Å) in **2** are similar with those of Si_6Cl_{12} (Si-Si: 2.34 Å, Si-Cl: 2.03 Å) and the average Si-Si-Si bond angle (111.8^{o}) in **2** are slightly smaller than that of Si_6Cl_{12} (112-114°).[29]

A new condensation-polymer precursor **3** was synthesized by alcoholysis of geometric isomers **2** with EtOH in the presence of excess Et_3N in Et_2O at -78 ^{o}C. When ethanol was added to **2**, white salt ($Et_3N^+Cl^-$) was immediately formed. After 6 h stirring at -78 ^{o}C, the reaction mixture was slowly warmed to room temperature. The white salt was removed by a series of three filtrations and washes with *n*-hexane, without contacting air and moisture. Geometric isomers of **3** were separately obtained as a white solid in 26% yield and pale green oil in 74% yield. The white solid of **3** was determined to be an all-*cis* isomer by X-ray structure analysis (Figure 3). All-*cis* **3** was crystallized in the cubic space group I43d and the 6-membered ring has a chair conformation. The ethoxy groups are alternatively oriented to axial and equatorial positions. The average Si-Si bond length (2.36 Å) in all-*cis* **3** is similar to that in **2**. To our knowledge, only one publication has described bond lengths (1.67-1.68 Å) of Si-OR in cyclic silane,[30] which is relatively longer than those in our results (average 1.63 Å).

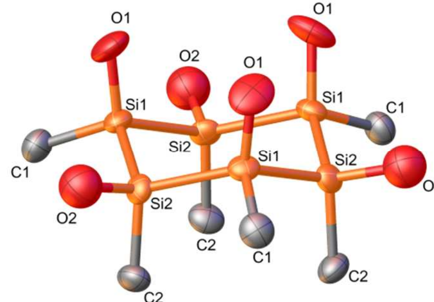


Figure 3. Molecular structure of all-*cis* **3** in the crystal (30% thermal probability ellipsoids). The C_3 axis is located in the center of the 6-membered ring. Hydrogen atoms and ethyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1-Si2 = 2.368(5), Si2-Si1 = 2.360(5), Si1-C1 = 1.898(1), Si1-O1 = 1.619(1), O1-C3 = 1.366(1), C3-C4 = 1.463(1), Si2-C2 = 1.879(1), Si2-O2 = 1.644(1), O2-C5 = 1.402(1), C5-C6 = 1.38(3); Si2-Si1-Si2 = 109.6(9), Si1-Si2-Si1 = 112.9(2), C2-Si2-O2 = 101.5(6), C1-Si1-O1 = 109.0(6), Si2-O2-C5 = 137.3(1), Si1-O1-C3 = 133.8(1). See the Supporting Information for details.

The ^{29}Si NMR of the all-*cis* **3** resonated at 4.22 ppm and geometric isomeric mixture of **3** resonated from 2.89 to 9.79 ppm. The ^{1}H NMR of all-*cis* **3** showed three resonances SiCH_3 (*s*, δ 0.50), SiOCH$_2$$CH_3$ (*t*, δ 1.27) and SiOCH_2CH$_3$ (*q*, δ 3.94).

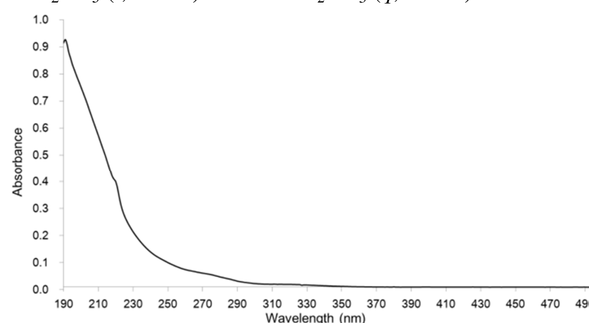


Figure 4. UV/Vis spectrum of mixture **3** in *n*-pentane.

The deep UV absorption property of **3** was higly important in order to apply it to a new optical absorbant at 193 nm. As wished, the λ_{max} of **3** was 191 nm (ε: 9700) in *n*-pentane (Figure 4), making it highly suitable for anti-reflective materials in the ArF lithography process. Long wavelength absorption properties were also identifed at 270 nm (ε: 550) and 320 nm (ε: 105), which is unique to cyclopolysilane derivatives.[31] It is noteworthy that absorption at 193 nm was successfully achieved using the cyclosilane derivative without the presence of a phenyl group.

We synthesized a polycyclosilane-polysiloxane hybrid material from the co-condensation polymerization of MTMS (methyltrimethoxysilane) with the new condensation-polymer precursor **3** (Scheme 2) to prepare an organic solvent-soluble polymer material. The hydrolysis of only compound **3** gave insoluble products. To prevent the formation of sol or gel of the copolymers, optimal reaction conditions were investigated. First,

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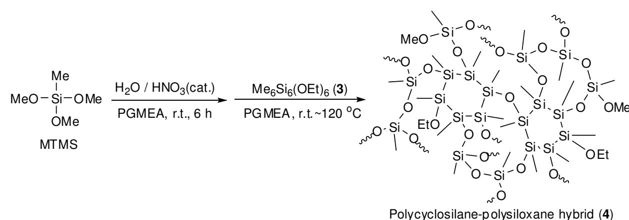
hydrolysis and condensation of MTMS were carried out in aqueous acid conditions at r.t. for 6 h in PGMEA solvent (propylene glycol monomethyl ether acetate). After water and MeOH were partially removed by vacuum pump to reduce the condensation reaction rate, the mixture of **3** diluted in PGMEA was added to the reaction mixture to prepare a hybrid material of polycyclosilane-polysiloxane (**4**). The hydrolysis and condensation reaction of **3** with the MTMS mixture were carefully carried out with variable temperatures (r.t.-120 °C) for 1-2 weeks to avoid formation of sol and gel. The reaction was monitored by GPC.



Scheme 2. Synthesis of polycyclosilane-polysiloxane hybrid (**4**).

The n and k values of films were measured using an ellipsometer depended on the molar ratio of **3**. The results indicate that the consecutive silicon bonds responsible for absorption of 193 nm light were thermally and oxidatively stable under the baking conditions and that it is possible to control the n and k values. In preliminary research, a polymer containing decaalkoxycyclopentasilanes was prepared,[32-33] however the polymer was not stable under baking conditions and therefore resulted in an inappreciable k value. Etch resistances against O_2 and CF_x plasmas were examined showing that etch rates were also dependent on the molar ratio of **3**. Etch selectivity was calculated as 4.73:1, 4.67:1 and 4.23:1, respectively, using etch rates for O_2 and CF_x plasmas. As silicon contents (molar ratio of **3**) increased, the etch selectivity also increased. Film densities, as determined by X-ray reflectivity (XRR), were approximately 1.20 g/cm^3.

^{29}Si CP/MAS NMR spectra of each Si-HM film show an M (R_3SiO) unit (δ from -3 to -22 ppm) with a T ($RSiO_3$) unit (δ from -61 to -65 ppm) but no D (R_2SiO_2) or Q (SiO_4) units (See the Supporting Information). This means that cyclohexasilane did not decompose during condensation polymerization or during baking at 200 °C.

The chemical compositions of films **4** were also examined with high resolution XPS, as shown in Figure 5. Full XPS survey spectra of the three films showed that the dominant signals came from Si, C and O. The amount of silicon and oxygen decreased and the amount of carbon increased from films **4a** to **4c**. Each atomic percentage was correlated with the molar ratios of MTMS and **3**. Figure 5 b-d shows the high-resolution XPS spectra of the Si 2p of films **4**. Three components were fitted with three peaks and a Shirley background.[34] Three components, Si-O, Si-C and Si-Si were assigned at 102.67, 101.55 and 100.64 eV, respectively.[35-37]

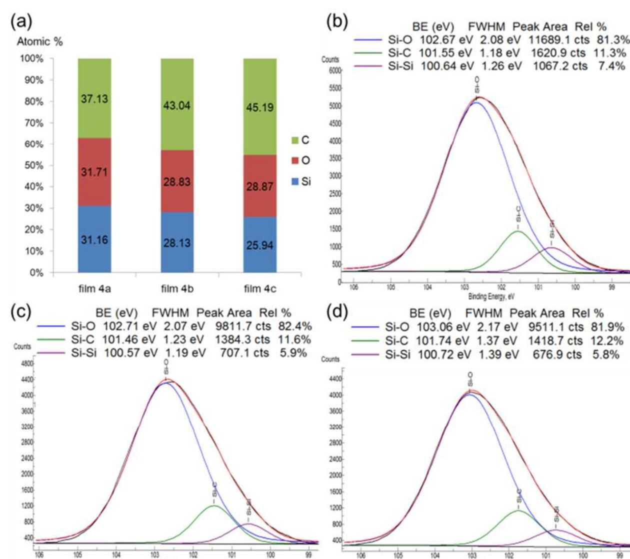


Figure 5. Chemical compositions of the films **4** (a). High resolution Si 2p XPS spectra of the film **4a** (b), film **4b** (c) and film **4c** (d). The peaks were fitted (red) with Gaussians of three components shown respectively (blue, green, and purple curves).

Conclusions

In summary, the new precursor, hexaethoxyhexamethyl-cyclohexansilane (**3**) was used for the polycyclosilane-polysiloxane hybrid materials. The molecular structure of geometric isomers **2** and all-*cis* **3** were elucidated by X-ray crystallography. We successfully demonstrated that the silicon hybrid materials containing polycyclosilane without organic chromophores, and its thin films showed good optical properties at 193 nm and etch selectivity, which could be controlled by changing the molar ratio of **3**.

Acknowledgements

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Notes and references

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Table 1. Refractive index (n), extinction coefficient (k), etch resistance [CF_x, (O_2/N_2)] and density of films **4**.

Films	MTMS [molar ratio]	$Me_6Si_6(OEt)_6$ (3) [molar ratio]	Mw	ρ [g/cm^3]$^{a)}$	193 nm n	193 nm k	Etch rate [Å/s] O_2/N_2	Etch rate [Å/s] CF_x	Etch selectivity$^{b)}$
film **4a**	4	6	7000	1.21	1.703	0.271	14.02	66.35	4.73 : 1
film **4b**	5	5	3900	1.20	1.676	0.212	17.20	80.40	4.67 : 1
film **4c**	6	4	2800	1.18	1.661	0.166	18.06	76.57	4.23 : 1

a) Density of films were measured by XRR; b) $CF_x/(O_2/N_2)$

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† Electronic Supplementary Information (ESI) available: Experimental procedures, products characterization data, NMR (^{1}H, ^{13}C, ^{29}Si) spectra, extinction coefficient (k), and details of X-ray crystallographic data included in the supporting information. See DOI: 10.1039/c000000x/

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Graphical abstract

Silicon thin films prepared from a new class of polycyclosilane-polysiloxane hybrid materials by sol-gel reaction. The films showed good optical properties (refractive index and extinction coefficient) at 193 nm and their etch selectivity for O_2 and CF_x plasmas, which meets the need of current semiconductor lithography process (193 nm light source).