Characterization of Photosensitive Composition Based on Oligo-ladder Phenylsilsesquioxane

Yuji Tashiro*, Akio Miyazato and Kohki Ebitani

School of Materials Science, Japan Advanced Institute of Science and Technology,
1-1 Asahidai, Nomi-shi, Ishikawa, 923-1292, Japan
*Grobal R&D Dielectric, Merck Performance Materials Manufacturing G.K.
3330 Chihama, Kakegawa-shi, Shizuoka 437-1412, Japan
yuji.tashiro@merckgroup.com

We have succeeded in development of alkalisoluble oligo-ladder phenylsilsesquioxane (oligo-LPSQ). Oligo-LPSQ was synthesized by the one-pot manner via silicon-pyridine adducts formation at aqueous-liquid boundary and finally product was obtained as white solid (85% yield) through re-precipitation in n-hexane. The obtained polymer is soluble in 2.38% TMAH (tetramethylammonium hydride). This polymer was characterized by MALDI-TOF/TOF-MS and 29SiNMR techniques. The properties of obtained polymer showed high thermal resistance over 400 °C and low dielectric constant under 3.2. Furthermore, the alkali soluble oligo-LPSQ can provide both positive and negative tone photosensitive LPSQ combination with diazonaphtoquinone (DNQ) and photo-acid (base) generator, respectively. Here we demonstrate features of synthesis method for alkali-soluble oligo-LPSQ, photolithographic character and the material properties.

Keywords: silanol, ladder SQ, photosensitive, diazonaphtoquinone, low-k

1. Introduction

At first, ladder-structure phenylsilsesquioxanes (LPSQ) were studied by Brown et.al. And there are many reports on synthesis of ladder SQ till date. [1-8]. Fig. 1 shows proposed ladder structure by Brown in1960 [3].

Fig.1 Ladder-structure with cis-syndiotactic configuration

Ladder type-SQ is expected to give some unique properties such as superb thermal resistance, high optical transparency and low dielectric constant compared to random structure. Recently, the silsesquioxane has been studied as an intermediate for inorganic-organic hybrid material. However, synthesis of ladder SQ was not achieved on industry stage because conventional synthesis methods were not suitable for mass-production with multi-step process and low yield. [4-6] Moreover, the film properties of ladder structure SQ had not been enough announced until today. Here we proposed new synthesis method for oligo-ladder phenyl silsesquioxane (LPSQ). It is obtained by an aqueous-organic liquid boundary reaction via silicon-pyridine interaction compound. Our synthesis method is one-pot reaction, which is simple and generates a high yield rather than previous reports [3-6]

The film derived from SQ has been studied for a long times, however they still keep our interest due to large expectation from their unique characteristic. In recent years, practical applications for semi-conductor interlayer dielectrics, photo-resist material and flat panel display industry have been proposed as LPSQ application.

On the other hand, SiNx and SiO2 deposited by plasma enhanced chemical vapor deposition (PECVD) are well established dielectric layers for TFT-LCD display. With the increasing display size, CVD equipment and its processing is becoming very costly and difficult. Thus, spin-on glass materials have been attractive for a long time due to their possibility to replace the vacuum CVD process by liquid coating process, as well as their superior properties such as high optical transparency, high thermal and good chemical durability [11]. Silsesquioxanes (SQ)
are comprised of (-Si-O-) bond, which shows inorganic properties such as high thermal resistance, high transparency and good chemical durability. By introducing organic groups, inorganic SQ can possess organic features, like solubility in organic solvent, alkali solubility, UV cross-linking, flexibility and so on. The ladder-type and cage-type SQ with high regularity structure shows promising characteristics of higher cracking threshold and thermal stability. Otherwise, more organic moiety will be necessary to achieve high cracking threshold, which usually implies low thermal and chemical durability.

Another attempt with organic SQ is an application for planarization and passivation material on TFT [12]. Organic planarization materials have been used in TFTs. Unfortunately, their performance as passivation layer is far below for practical application in oxide semiconductor. To achieve planarization layer on TFTs, high photosensitivity is necessary.

There are several reports on the photosensitivity of SQ materials, such as multi layers resists application [12-13]. Sachdev reported as two layer resist by reacting terminal silanol and DNQ [14]. These base polymers take random-structure SQ and include phenol-type ligand. Moreover, acrylics phenyl-SQ and methyl-methacrylate modified SQ are reported as base polymers of photosensitive SQ. [15-16]

In this paper, we describe the synthesis and characterization of alkali soluble oligo-LPSQ and the first report on photo-lithography system of the oligo-ladder type SQ.

2. Method

2.1. Measurement Method

**MALDI-TOF/TOFMS spectrometer:** The LPSQ samples were dissolved in a given amount of DMSO to obtain a homogeneous solution. The MALDI-TOF/TOF MS spectrum was recorded on Bluker Daltonics Ultraflextreme. DHB (2,5-Dihydroxybenzoic acid) was used as matrix and the detected mass numbers include (M + Na)+.

**Nuclear Magnetic Resonance Spectroscopy (NMR):** The solution ²⁹Si NMR measurements were carried out on a JEOL JNM ECS-400 spectrometer at 25°C. The sample was dissolved with DMSO-D₆ and the solution was measured with tetramethylsilane (TMS) as an internal reference. The 90° pulse width of 11.25 μs was employed with FID signal accumulation and the observation frequency was 79.42 MHz.

**Thermo-Gravimetric Analysis (TGA):** The RIGAKU thermo-gravimetric analyzer (Thermo-Plus) was used to investigate the thermal stability of LPSQ. The sample (about 10 mg weight) was heated under nitrogen atmosphere from ambient temperature to 400°C at a heating rate of 10°C /min in all cases.

**UV-Vis spectra:** The films on non-alkali glass were measured by Hitachi Spectrophotometer U-4000.

**C-V analysis:** Dielectric constant was measured by SSM (Solid State Instrument) 495 CV system at 1MHz. The film on n-type bare Si wafer was prepared and wafer resistance is 10 Ω.

2.2 Synthesis of alkali soluble oligo-ladder phenylsilsesquioxane (Oligo-LPSQ)

Oligo-LPSQ is synthesized with our original method that is performed using trichlorosilane as starting monomer at a liquid-liquid boundary with pyridine with \( n \)-propylacetate (pyridine/ trichlorosilane molar ratio: 2.0, reaction temperature: 0 – 5 °C, reaction time: 1hr). Re-precipitation of above reaction product is carried out in n-hexane. Synthesis scheme is shown in Fig. 2 [17].

![Schematic diagram of synthesis scheme for oligo-ladder silsesquioxane](image)

Molecular weight of obtained polymer in the typical synthesis condition was 1600 and yield was 85% (as on Si). The results of MALDI-TOF/TOF MS analysis are shown in Fig. 3. It is composed of ladder structures from mass number and the regularity in peaks path distance of m/z (138) is that for PhSiO₃H.
The structures shown in above graph are a representative structure estimated from mass number. The regularity of structure in Oligo-LPSQ can also be characterized by $^{29}$SiNMR spectrum. A literature survey suggests that the signals at around -68 ppm and around -80 ppm can be assigned to end Si atom and center Si atom respectively in the ladder structure of PPSQ [8-9].

Moreover, Fig. 4 shows $^{29}$SiNMR spectra of obtained polymer. T$^2$ and T$^3$ structure at (-68.3ppm, -70.0ppm) and (-75.5 ppm, -80.0 ppm) can be observed, respectively. Each peaks are assigned to T$^2$ (Ph-Si(OSi$^-$)$_2$OH) and T$^3$ (Ph-Si(OSi$^-$)$_3$)[10]. This further confirmed the ladder structure formation in re-precipitated polymer. Ladder structure is composed of T$^2$ and T$^3$, cage structure is only T$^1$ structure.

2.3 Film properties of Oligo-ladder phenylsilsesquioxane (Oligo-LPSQ)

The film derived from Oligo-LPSQ was prepared by the following procedure. LPSQ was spin-coated on bare silicon wafer or non-alkali glass and pre-baked at 130 °C for 90 seconds on hot-plate as pre-bake. Film properties are tested under different post cure temperature. Thermal stability, dielectric properties and optical properties were measured.

2.4 Photosensitive formulation and procedure

Alkali solubility ratio depends on the silanol contents, thus the oligo-ladder can be soluble in 2.38% TMAH (tetramethylanmoniumhydroxide) solution. Consequently, an alkali solubility ratio of the film derived obtained polymer is 600 Å /s. This value of alkali solubility is satisfactory for photosensitive formulation.

2.4.1 Positive-tone formulation (p-LPSQ)

With the Oligo-LPSQ, we prepared photosensitive LPSQ materials. Positive-tone LPSQ (p-LPSQ) is formulated with diazonaphthoquinone (DNQ), which is photo-active-compound (PAC) and sensitive to g(436nm), h(405nm), i(365nm) line UV as shown Fig. 5 [18]. And loading ratio of PAC is 12wt% for polymer.

As the LPSQ is an alkali soluble polymer, p-LPSQ can be simply applied DNQ with the oligo-LPSQ just same as DNQ/Novolak system in an aqueous-alkaline developer (2.38% TMAH). The advantage of this system is that the photolithography process has been commonly applied to produce TFTs. Photolithography condition for test in this paper is summarized in Table 1.
2.4.2 Negative-tone formulation

On the other hand, n-LPSQ is simply formulated using PAG (photo-acid-generator) such as sulfonium cation type (LW-S1B: produced by S ANAPRO Co. Ltd.), which is sensitive to i-line (365nm) and h-line (405nm) UV. Loading ratio of PAG is 2wt% for polymer content in this test. The typical lithography condition of n-LPSQ is shown in Table 2.

| Procedure                  | Positive-tone | Negative-tone |
|----------------------------|---------------|---------------|
| Pre-bake                   | 100°C C/90s   |               |
| Exposure (Canon FX-601F: g, h-line) | 190µm/cm²    | 20µm/cm²      |
| Development (2.38% TMAH)  |               | 120s          |
| Rinse (ion changed water)  |               | 60s           |
| Bleaching (g, h, i-line)   |               | 900µm/cm²     |

3. Results and Discussion

3.1 Thermal stability

High regularity ladder structure is expected to show specific material properties. Fig. 6 clearly indicates an oligo-ladder structured obtained SQ possesses quite superior heat resistance, 5% weight loss temperature is 525°C and weight loss at 800°C was 23%, respectively.

3.2 Optical Properties

Optical transmittance of oligo-LPSQ is very high (>98%@ 400 nm with 2µm film thickness) which is similar to other silicone material. Moreover, stable and independent of post-bake temperature. Even after high thermal anneal at 400°C for 60min., Oligo-LPSQ film keeps the same optical transparency as shown in Fig. 7.

The n-LPSQ shows high transparency similar to oligo-ladder SQ film. However, optical transmittance for the p-LPSQ decreases drastically at higher post-bake temperature at 400°C as shown in Table 3. This reason is simply because the Photo-Active-Compound such as DNQ starts its chemical degradation, which causes the decreasing of transparency as shown in Fig. 8.

| Samples  | Transparency(%) at 400nm (FT: 2µm) |
|----------|-----------------------------------|
|          | 250°C C cure | 400°C C cure |
| LPSQ     | >99          | >99          |
| p-LPSQ   | 96           | 75           |
| n-LPSQ   | 98           | 98           |

Fig. 6 Thermal Stability of obtained ladder SQ
(Conditions: Heating Rate: 10 °C/min, Ambient: N₂)
3.3 Electrical Properties
The dielectric constant was measured by Hg probe methods at 1MHz on MOS (Metal-Oxide-Semiconductor) structure as shown in Fig. 9. The dielectric constant value for the LPSQ, photosensitive-LPSQ formulation is very smaller than conventional acryl-based organic insulating materials ($k=3.8$ at 250º C), which gives advantage to display architecture. Even dielectric constant of oligo-ladder SQ was very small and stable at high temperature. This reason is probably due to small influence of ion polarization for ladder domain with high regularity structure.

3.4 Photolithography properties and basic lithography system
3.4.1 Positive-tone LPSQ ($p$-LPSQ)
As the Oligo-LPSQ is an alkaline soluble polymer, we can apply conventional Novolak resist system [18-20]. In an aqueous-alkaline developer (typically 2.38% TMAH), it just same as DNQ/Novolak in positive-tone system. The advantage of this system is that the photolithography process has been commonly applied to produce TFT.

Lithography system of $p$-LPSQ is estimated by conventional DNQ/Novolak resist system. However, interaction site of Novolak and LPSQ is different (phenol and silanol). Since acidity of silanol is stronger than phenol, interaction with DNQ is stronger than phenol-site. The lithographic character is intrinsically different as compared to the Novolak. However, as shown in Figs. 10 and 11, lithography character is sufficient for TFT application. Pattern resolution is 5µm and film thickness after developing is 95%.

Basic mechanism of positive-tone is composed of two-reactions as follows. In the unexposed area, interaction of silanol with PAC occurs and alkaline solubility ratio decreases. Interaction site of PAC is estimated to be -$SO_3^-$, it is a strong acceptor hydrogen as shown in Figs. 12 and 13 [19]. On the other hand, indene-carbonic acid is generated by decomposition of DNQ by photon and water addition to indenyliden keton in the exposed area. Indene-carbonic acid increases the
alkaline solubility ratio. Consequently, the alkaline solubility ratio of each area becomes much different, which is the driving force for the photo-patterning.

![Fig. 12 Interaction with silanol/PAC in the un-exposure area](image)

3.4.2 Negative-tone LPSQ

The lithography system of \( n \)-LPSQ is basically chemical amplitude system by cation of PAG. The hardening of the polymer is based on homo-condensation of silanol. In other words, a reaction of silanol is promoted by acid caused by light from PAG as shown in Fig. 14. As a result, alkali dissolution speed decreases in the irradiated area. A difference in the solubility occurs in the exposed area and the unexposed area, which is termed as pattern formation.

![Fig. 13 Indene carbonic acid generation from diazonaphthoquinone in the exposure area by water addition indenylidene keton](image)

Lithographic characteristics are sufficient for TFTs using LCD (liquid crystal display) materials. Pattern resolution is 3µm and film thickness after developing is 96% of original as shown in Figs. 15 and 16. This performance is similar to conventional photosensitive materials such as acrylic polymer which are most commonly photo-pattern-able organic polymer.

![Fig. 14 Basic reaction of negative-tone system](image)

![Fig. 15 SEM picture (L/S: 3µm) of \( n \)-LPSQ](image)

(L/S: Line & Space, film thickness: 2µm)

![Fig. 16 SEM picture (C/H: 5µm) of \( n \)-LPSQ](image)

(C/H: Contact Hole, film thickness: 2µm)

4. Conclusion

We developed oligo-ladder phenylsilsesquioxane (oligo-LPSQ) and their derivatives. The synthetic procedure oligo-LPSQ is simple and the yield is over 80%. Also it shows alkaline solubility (2.38% TMAH solution) and has high thermal stability, superior optical transparency and low \( k \). Here we also presented features of the photo-pattern-able phenylsilsesquioxane based on oligo-LPSQ. The process of \( p \)-LPSQ is basically compatible to conventional DNQ/Novolak system except for different interaction strengths of silanols as compared to the phenols. And the patterning properties were good with a resolution of 3µm for L/S patterning. On the other hand, \( n \)-LPSQ is easy to formulate using only a PAG. It also has good patterning properties and the films show high transparency even at 400 °C. This result suggests considerably sufficient properties over conventional
organic based photo-patter-able polymer such as acryl in the FPD field. This is the first reported application using LPSQ. Further study will be necessary to maximize the usage of Oligo-LPSQ performance, especially as a new positive tone system for silanol over a negative tone system.

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