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Styryl Silsesquioxane Photoresist

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ABSTRACT: There is a substantial need for photopattern-able, heat resistant, and transparent materials that are applicable to electronic devices, such as imaging or display elements. Styryl silsesquioxane based photoresist forms thin micro patterns after i-line exposure and alkaline development, and the resulting transparent film shows remarkable heat resistance. Radicals generated from a photoinitiator induce polymerization of styryl functionality in the photoresist film to form the micropatterns. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41459.

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INTRODUCTION

Silicon oxide (SiO_2) is well known to have high heat resistance, high transparency, and good chemical durability. Thin SiO_2 film is created after thermal oxidation of silicon or chemical vapor deposition in general, and it offers many industrial applications mainly as a protection film. Because of its extreme process, however, alternative ways to obtain the film are still continuously expected from the aspects of process simplicity.

Spin-on glass is one alternative that can be applied to a variety of substrates. Among vast amounts of research and development regarding spin-on glass materials,[1–8] much attention has been specifically focused on silsesquioxane (SSQ) sol. The sol is usually synthesized by hydrolytic condensation of substituted trichrolosilanes or trialkoxysilanes.[9–22] Substituents on the silicon atom play a very important roll in gaining feasible stability of the sols. For example, sol synthesized from tetraalkoxysilanes is quite susceptible to gel transformation. Conversely, methyl trialkoxysilane-derived sol keeps its original fluidity for a prolonged period because of the inert methyl substituent in the sol.[8]

Another benefit that can be gained from an easily coatable SSQ sol is that extra functions can be introduced into the material. One of the most attractive functions is photosensitivity.[23–32] Photo exposure to a thin film that consists of properly formulated SSQs and photoactive compounds yields silicon-containing small patterns after development. Both positive- and negative-tone SSQ photoresists have been studied.[27–31] Loading of Diazonaphthoquinone (DNQ) derivatives give a positive-tone photoresist.[26] Negative-tones can be created by loading SSQs with photo acid generators (PAGs)[27] or photo radical initiators.[28–32]

DNQs are well known as photoactive compounds that have a strong dissolution inhibition, and are widely used for conventional i-line photoresist formulations. Through this effect, alkaline soluble SSQs can remain in unexposed area. While considerably high resolution will be an advantage of this material, it does also seem to have one disadvantage. Extra photo exposure onto formed patterns is required to consume excess DNQs in the patterns to obtain the desired high transparency. PAGs generate acid on photo exposure, and the acid catalyzes hydrolytic condensation of SSQs to create insoluble silicon-containing patterns. Control of acid diffusion will be a key to creating a reproducible of the pattern size. Narrower patterns will be formed by slower condensation, wider patterns by faster reactions. Therefore, a post exposure bake (PEB) step is usually applied to handle this material well. Photo radical initiator induced pattern forming seems to be more attractive than other previous described systems in terms of process simplicity because this system does not need extra exposure or PEB in principle. However, it should be noted that radically cross-linkable substituents on the silicon atom are indispensable to obtaining photo exposed patterns after development. Acryl and methacryl structures are most commonly loaded for this purpose, but can be disadvantageous as they will cause degradation under elevated temperature.

Thus, it is obvious that there is still a strong need for very practical SSQ photoresist in view of the developmental status described above. We recently found that micro patterns are obtainable from a photo resist formulation that consists of styryl SSQ and specific photo radical initiators. It was unexpected that a styryl group would work well in a film to form small patterns.

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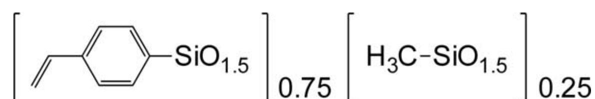

Figure 1. Structure of the styryl SSQ in this report.

Preparation, photolithography, chemistry, and film properties of the photoresist are discussed in this report. Synthetic procedure and formulation are mentioned in the preparation section. The lithographic process description and pictures of resulting patterns can be found in the photolithography section. It will be found in the chemistry section that the choice of photoinitiators is quite important for the photoresist formulation. Polymerization of styryl functionality in a film is also discussed in this section. Thermal, optical, and electric properties are discussed specifically in the film properties section.

EXPERIMENTAL

Chemicals

p-Styryl trimethoxysilane (StTMS) was purchased from Shin-Etsu Chemical Co. 2, 2′-Bis (2-chlorophenyl)−4, 4′, 5, 5′-tetraphenyl-1, 2′-biimidazole was obtained from Tokyo Chemical Industry Co. The other photoactive compounds were purchased from BASF. XHRi, antireflective coating (ARC) was purchased from Nissan Chemical Industries. Tetramethyl ammonium hydroxide (TMAH) solution was provided by JSR Corporation. Commercially available methyl trimethoxysilane (MTMS) and 1-methoxy-2-propanol (PGME) for the electronics industry were used. All chemicals were used without further purification.

Preparation of SSQ Photoresist

A solution of maleic anhydride (0.069 g) in 4.6 g of PGME was added to a solution of StTMS (45.09 g, 201 mmol), MTMS (9.13 g, 67 mmol), and ultrapure water (14.59 g, 810 mmol) in 46.0 g of PGME was added at room temperature. After stirring for 3 h at 60°C, the reaction mixture was concentrated under reduced pressure to remove both excess water and methanol that was produced by hydrolytic condensation of the starting materials. The resulting product shown, in Figure 1, was diluted with PGME to create a colorless SSQ solution (103 g). The molecular weight of the polymer was 600 and the total solid content of the solution was 40.1%. To the solution (2.75 g) were added [1-(4-phenylsulfanylbenzoyl) heptylideneamino] benzoate (**1**) (0.11 g) and a minor amount of surfactant in PGME (3.09 g) to yield a photoresist (5.95 g).

Apparatus

Tokyo Electron Clean Track Mark Vz or Mark 8 was used to coat, bake, and develop the SSQ photoresist. I-line exposure of the photoresist was carried out using Nikon NSR i10D. X-section images of the micro patterns were taken using a Hitachi scanning electron microscope S-4200. Spectrometric film thickness measurement was carried out using DNS Lambda Ace VM-2010. Optical index was measured using J. A. Woollam M-2000 Ellipsometer. JASCO spectrophotometer V-7300 was used to measure the transmittance of the photoresist film on a glass wafer. Dielectric constant was collected on a Hewlett Packard HP4284A precision LCR meter. Raman spectra were measured on a Ranishaw's inVia Reflex Raman Microscope and Spectrometer. Thermo Scientific FT-IR Nicolet 6700 was used to measure IR spectra. TGA measurement was carried out on a Hitachi High-Tech Science TG/DTA 7300.

RESULTS AND DISCUSSION

Photolithography

A 1.42 um thick film of the photoresist was applied on a 160 nm thick layer of ARC. The thickness of the ARC was carefully calculated on PROLITH, KLA-Tencor's lithography simulation software to minimize reflectivity to the photoresist. The photoresist film was exposed to 365 nm light through a

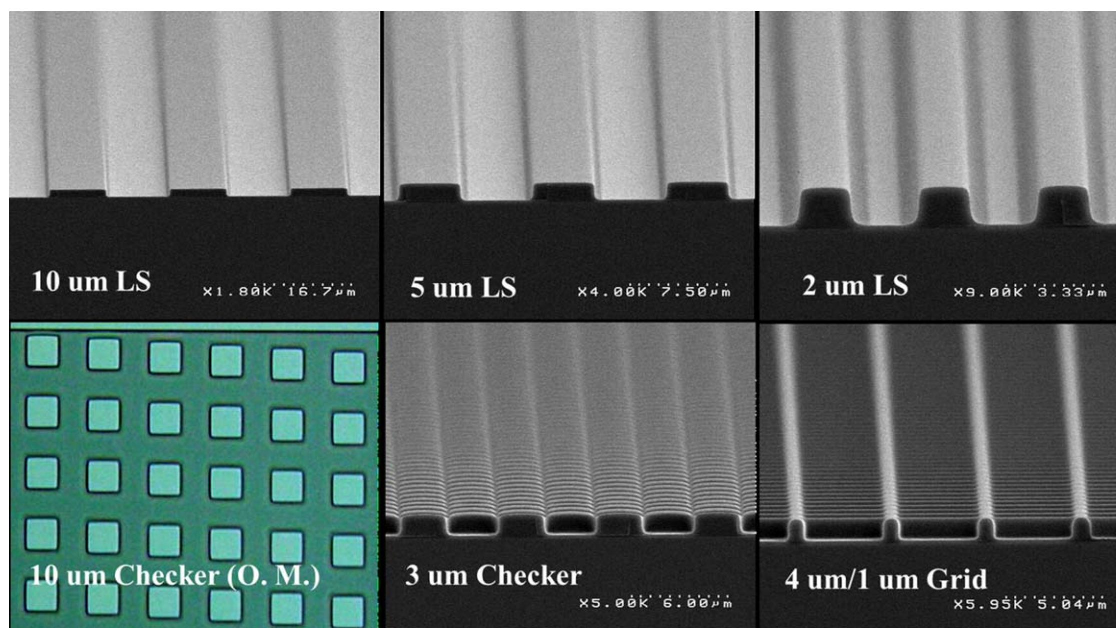

Figure 2. Patterns obtained from the styryl SSQ photoresist. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

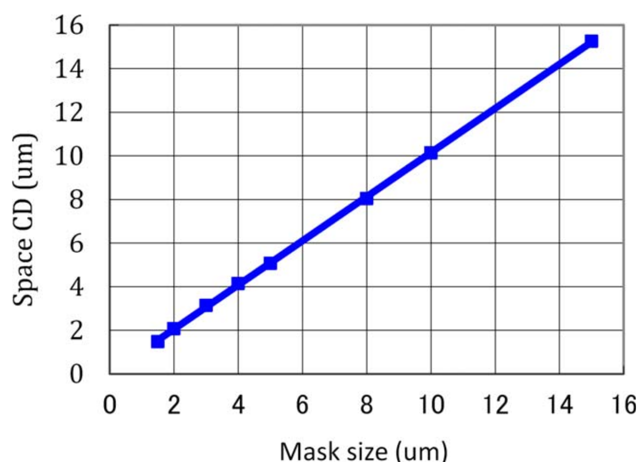

Figure 3. Mask linearity plot of the styryl SSQ photoresist. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

patterned mask on a Nikon i-line stepper, followed by a development using 2.38 weight percent TMAH. The resulting wafer was baked at 230°C and 1.26 um thick micro patterns were obtained (Figure 2). Various patterns, such as lines and spaces, checkers, and grid patterns, were formed using the photoresist.

A mask linearity plot of the resist suggests that the resist can resolve approximately a 2 um space under these conditions (Figure 3). Residue at the line foot interrupts the resolution under 2 um.

Chemistry

Photoinitiators. Radical polymerization of the styryl functionality in the SSQ provides its negative-tone contrast after alkaline development. Initiator **1** was found to be the best photoinitiator we tested for our formulation. Figure 4 shows the structures of the tested photoinitiators,[33] and the photo patterning results are summarized in Table I.

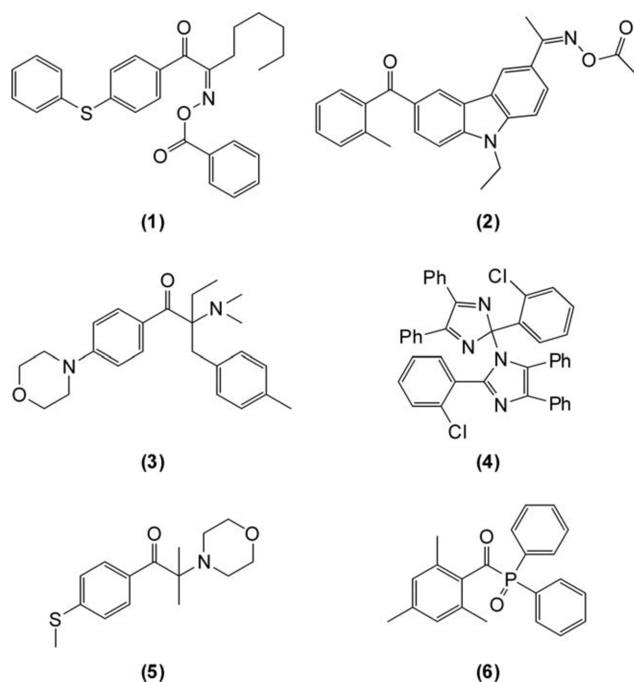

Figure 4. Photoinitiators tested for the SSQ photoresist formulations.

Table I. Photo Patterning Result of Various Photoinitiator Formulations

Photoinitiator	Pattern printing	Remarks
1	Good	
2	Good	Residue on unexposed area
3	Good	Residue on unexposed area
4	No pattern	Insolubilization
5	Trace	Mostly dissolution
6	No pattern	Complete dissolution

Two factors are key in selecting a proper photoinitiator for the styryl SSQ photoresist. One is the effective generation of active radical species,[33–35] and the other is an absence of structures[33] that can interact with SSQs. 1-[9-Ethyl-6-(2- methylbenzoyl)-9H-carbazol-3-yl] ethanone-1-(O-acetyloxime) (**2**) is said to generate a reactive methyl radical. It worked as well with initiator **1** to form micropatterns, however, severe residue was observed on unexposed areas (Figure 5).

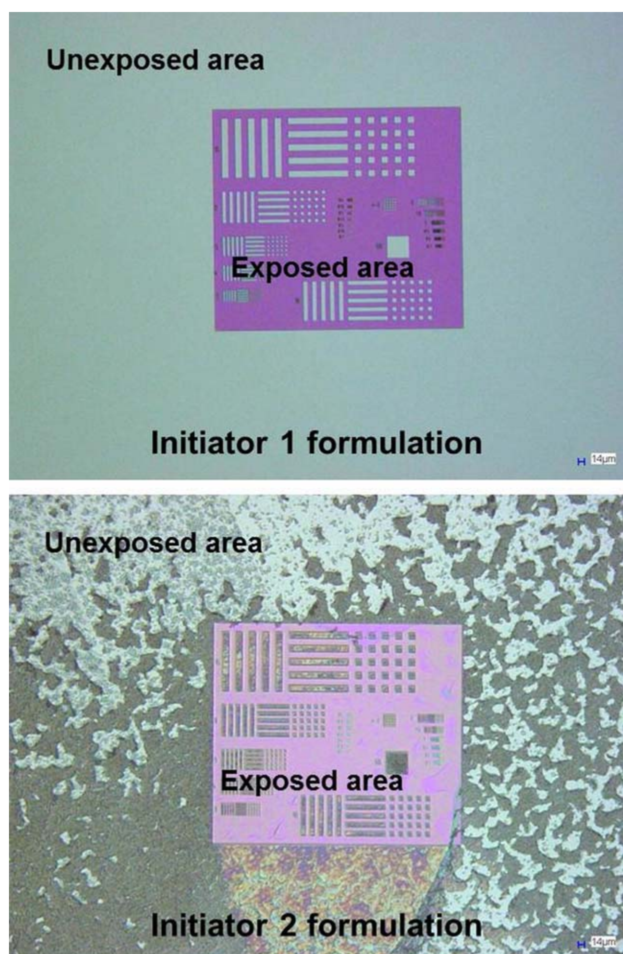

Figure 5. Optical microscopic image of the SSQ photoresist patterns. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

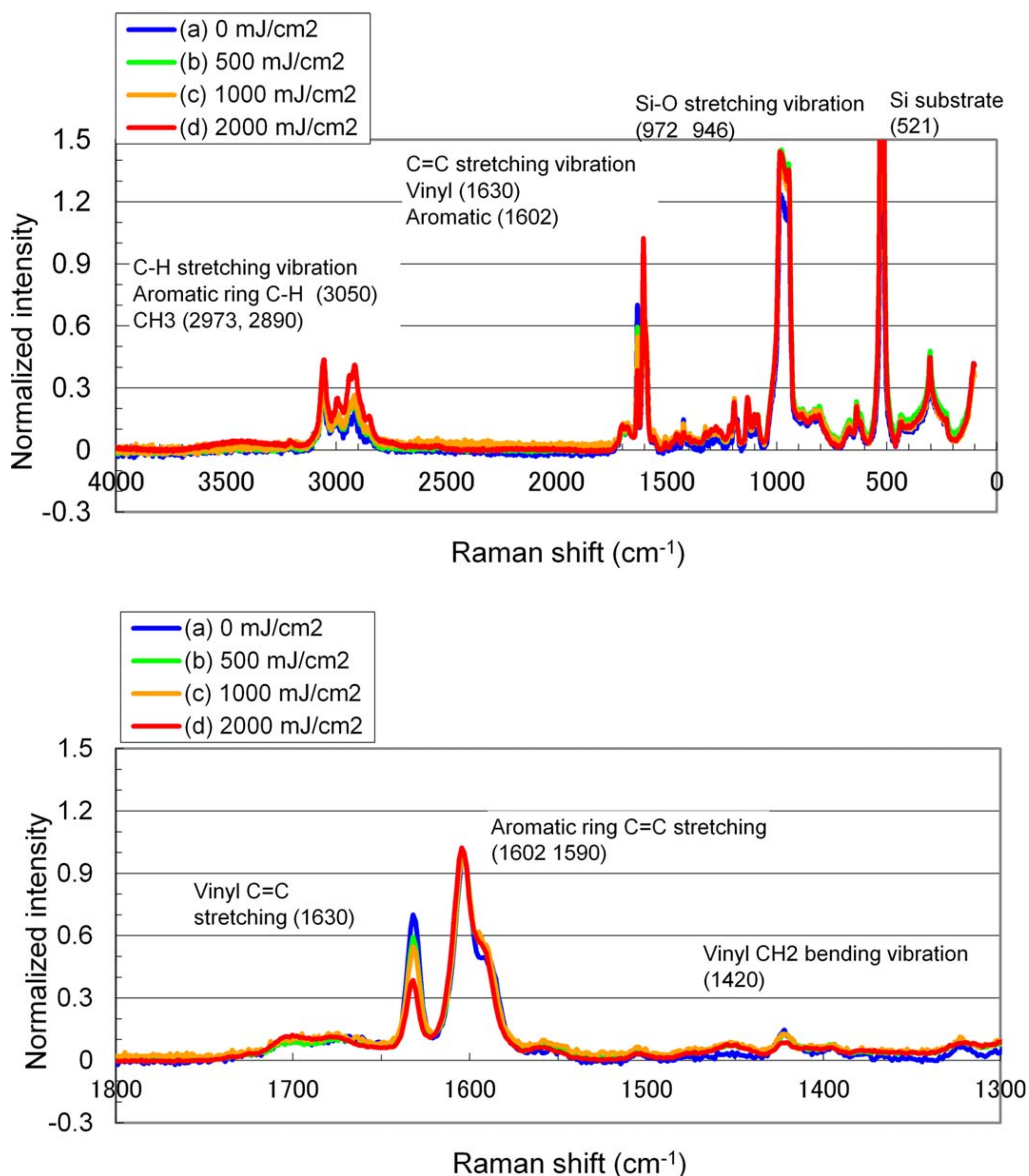

Figure 6. Raman spectra of the styryl SSQ films exposed to (a) 0 mJ/cm^2 (blue lines), (b) 500 mJ/cm^2 (green lines), (c) 1000 mJ/cm^2 (orange lines), and (d) 2000 mJ/cm^2 (red lines). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2-Dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl) butan-1-one (**3**) also generated severe residue. The residue can be interpreted as a hydrolytic condensation of SSQs that is catalyzed by tertiary amine structures in initiators **2** and **3**. The tertiary amine structure is supposed to interact with the silicon atoms to generate reactive silicate species. Substituent exchange reactions of the species can cause the condensation reaction without photo irradiation. The dark condensation reaction was prominent when 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole (**4**) was loaded into the photoresist formulation. The whole film turned insoluble in alkaline developer, thus no pattern was obtained. 2-Methyl-4′-(methylthio)-2-morpholinopropiophenone (**5**) had limited ability to forward the photopolymerization, and only traces of patterns were obtained. Polymerization did not proceed when 2, 4, 6-trimethylbenzoyl-diphenyl-phosphine oxide (**6**) was loaded. Alkaline developer developed both exposed and unexposed regions completely. The absorptions of initiator 5 and 6 are relatively lower than initiator 1–3 at 365 nm.[33] This may be one of the reasons for low photo reactivity of initiator 5 and 6.

Polymerization in a Film. Confocal Raman Microspectroscopy proved the polymerization of styryl functionality in the photoresist film. Figure 6 shows the Raman spectra of unexposed and exposed films on bare Si wafers. A peak at 1630 cm^{-1} was assigned to a carbon–carbon (C═C) double bond stretching vibration of the vinyl structure. The signal intensity of the vinyl structure decreased in accordance with an increased exposure dose. This means the polymerization of styryl functionality after

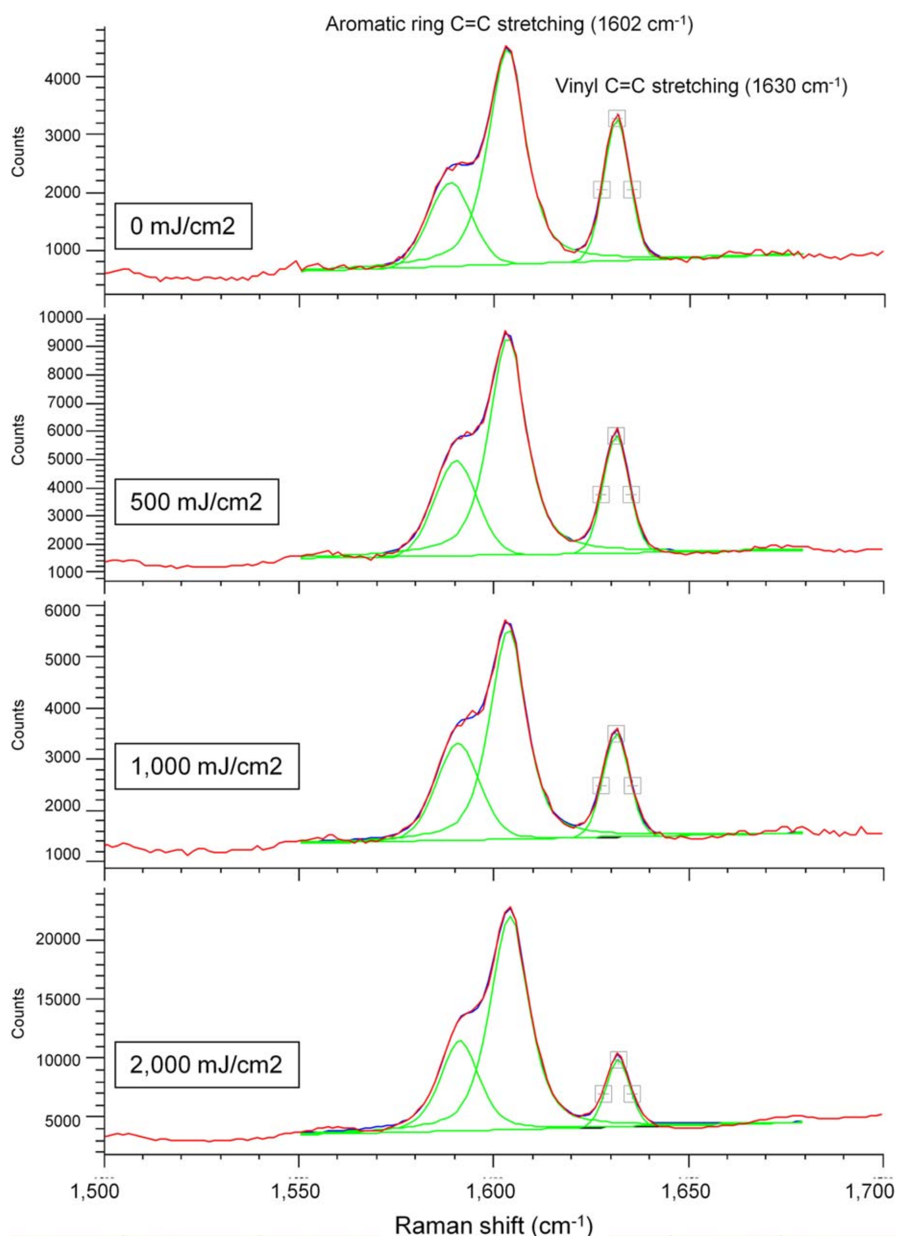

Figure 7. Peak separated Raman spectra of the styryl SSQ films (green lines) exposed to increasing *i*-line doses from 0 to 2000 mJ/cm^2 (red lines are originals). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

photo exposure, and the reaction itself, forms developer-insoluble patterns in the photoresist.

Consumption of the functionality was estimated using the area ratio method. First, an aromatic signal was extracted from a C═C stretching region (1500–1700 cm^{-1}) on WiRe2.0, Renishaw's software for Raman spectroscopy (Figure 7). The region was successfully separated and the peak at 1602 cm^{-1} was assigned to an aromatic signal that does not itself undergo changes in intensity. An area comparison between a vinyl signal at 1630 cm^{-1} and aromatic signal at 1602 cm^{-1} was carried out (Figure 8), and it was calculated that less than 20 percent consumption of styryl functionality is enough to form patterns because the exposure energy for the lithography in Figure 2 was in the range of 250–500 mJ/cm^2. Forty-four percentage of the functional group was still left in a film even after exposure at 2,000 mJ/cm^2.

The consumption of the styryl functionality was also observed for the formulation loaded with N-hydroxynaphthalimide triflate that is well known as an i-line active PAG. Unlike the radical polymerization in the SSQ loaded with initiator 1, cationic polymerization is proper to explain this result. As for the SSQ without any photoactive compounds, the functionality in the SSQ remained intact in the film because the film is transparent at 365 nm light.

The SSQ loaded with initiator 1 works only with the polymerization of its styryl functionality, whereas both the styryl

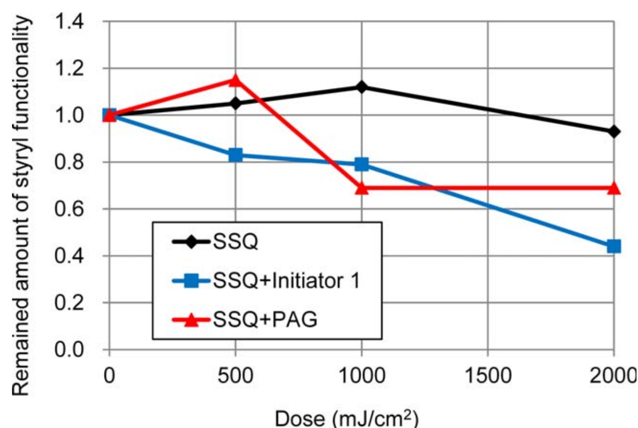

Figure 8. Remained amount of styryl functionality in the films exposed to increasing i-line doses from 0 to 2000 mJ/cm^2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

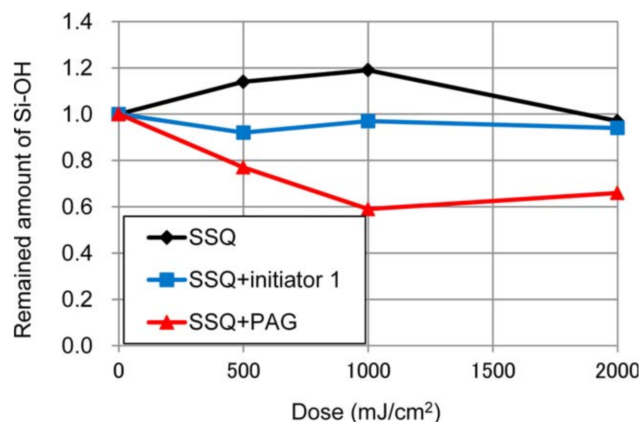

Figure 10. Remained amount of Si—OH in the films exposed to increasing i-line doses from 0 to 2000 mJ/cm^2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymerization and hydrolytic condensation proceed in the film that contains PAG. Figure 9 shows the IR spectra of three unexposed SSQ films loaded with: no additive, initiator 1, and N-hydroxynaphthalimide triflate (PAG). A peak at 1270 cm^{-1} was assigned to the Si—CH_3 related absorption. A region around 900 cm^{-1} was characterized as Si—OH absorption. It was found that there was not an obvious change in the Si—OH amount in the film loaded with initiator 1 after photoexposure when the consumption of Si—OH was accumulated from the normalized area of the Si—OH region based on the Si—CH_3 region (Figure 10). In contrast, decreasing trend of the Si—OH area was observed for the film loaded with the PAG. This can be interpreted that the acid generated from the PAG catalyzes the hydrolytic condensation of the Si—OH in the SSQ. Although increasing the Si—O—Si absorption was predicted with decreasing the Si—OH, severe spectrum overlap between the SSQ and the PAG interrupted the analysis.

Film Properties

One of the most significant features of the material is its thermal stability. Figure 11 shows thermal gravimetric analyses of photo cross-linked SSQ films. The film obtained from a hydrolytic condensation of StTMS with MTMS showed much higher thermal stability than the film given from the sol-gel reaction mixture of 3-(trimethoxysilyl) propyl acrylate and MTMS.

The refractive index (RI) of the styryl SSQ film was 1.56 at 633 nm (Figure 12). This value is comparable to a general acrylic resin. It can be explained by the existence of an aromatic group in the film. RI of methyl SSQs is said to be around the value of 1.46.[32]

High transparent films can be obtained from this material. Transmittance of the 1 um thick film was more than 97% at wavelengths longer than 400 nm as shown in Figure 13. Relatively low transparency was observed at shorter wavelength. Absorption of the residual photoinitiator itself, or its decomposition product, is presumed to cause the transparency loss.

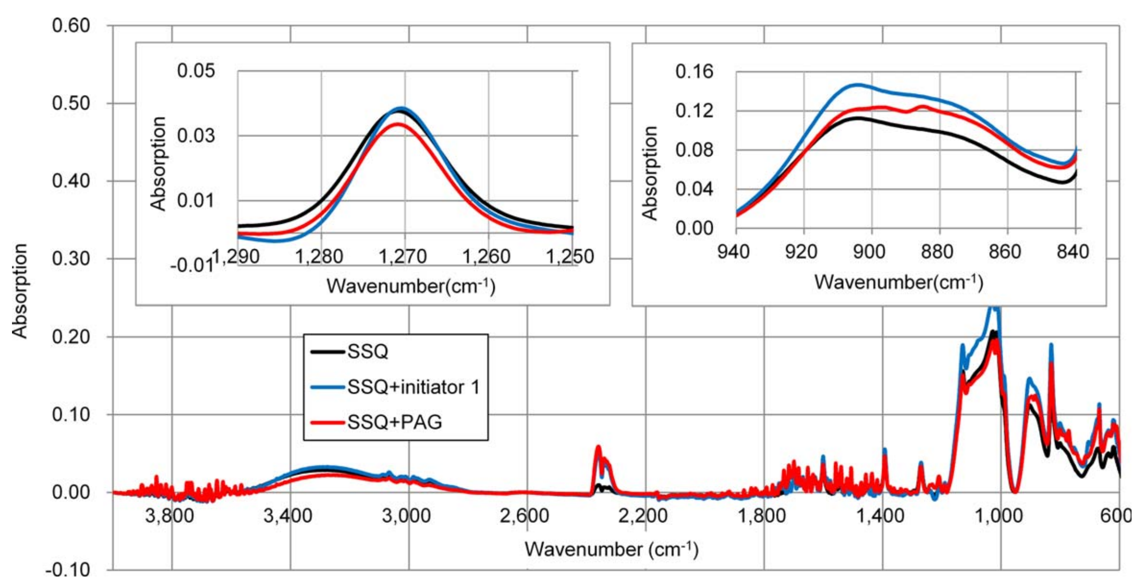

Figure 9. IR spectra of the styryl SSQ films before exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

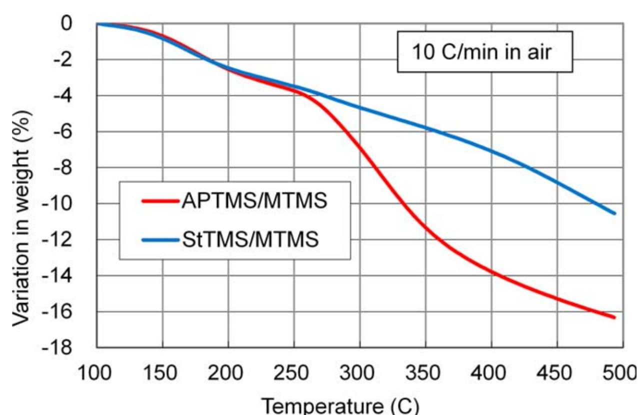

Figure 11. Thermal gravimetric analyses of photocross linked SSQ films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

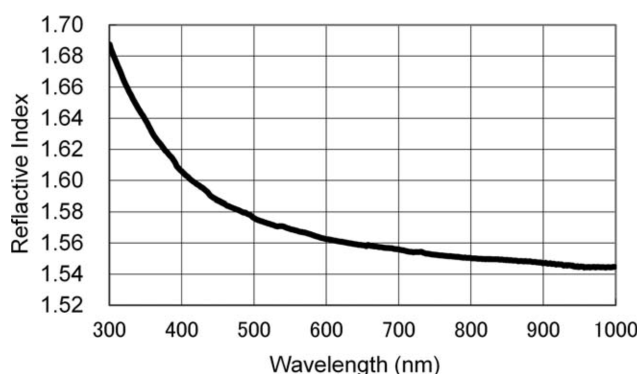

Figure 12. RI of the styryl SSQ film.

A relatively high dielectric constant is also a feature of this material. The value was calculated from the capacitance data of a layered film that consists of ITO-coated glass / the SSQ film 0.6 um thick / evaporated aluminum. It was found that the dielectric constant of this material has a good correlation with the loading amount of StTMS in this material (Table II). Higher loading of StTMS showed higher value.

The film has good resistance to organic solvents, such as acetone, 2-propanol, 2-acetoxy-1-methoxypropane (PGMEA), PGME, and 1-methyl-2-pyrrolidone. No film loss of the resist was observed after a 5 min soak in each of these solvents at 23 C. Tolerance to these solvents offers many options to coat on this material.

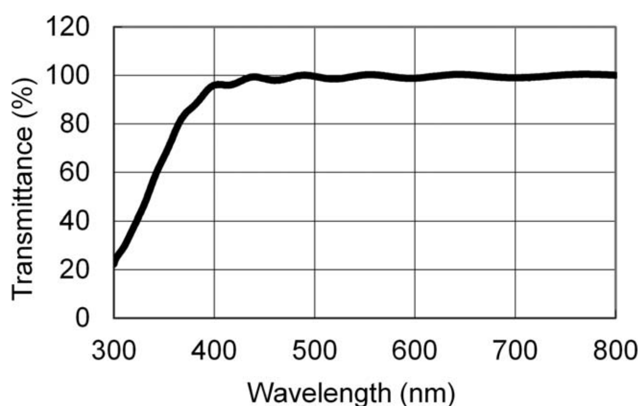

Figure 13. Transmittance of the styryl SSQ film.

Table II. Dielectric Constants[a] of the SSQ Films[b] Having Different Ratios Between Styryl and Methyl Groups

Styryl/Methyl ratio	75/25	50/50	20/80
Dielectric constant (10 kHz)	5.65	5.02	4.52

[a] Capacitance data was collected on a LCR meter.
[b] The films were spin-coated on ITO glass and then exposed to 1000 mJ/cm^2 at 365 nm.

CONCLUSIONS

A styryl SSQ based photoresist was developed. The SSQ sol was synthesized by acid catalyzed hydrolytic condensation of the mixture of styryl TMS and methyl TMS. After loading photo radical initiator in the sol, the resulting solution was spin-coated on an ARC film to create a thin SSQ photoresist film. I-line exposure on the film and subsequent alkaline development was able to form micro patterns of the SSQ. Two key characteristics of photoinitiators were identified, higher photosensitivity, and a nonamine-containing structure. The most effective one among those was initiator **1**, which is called an oxime type photoinitiator. Raman spectroscopy proved the polymerization of styryl functionality in the photoresist. Signal intensity of the vinyl structure decreased in accordance with an increased exposure dose. The resulting film showed remarkably higher heat resistance than the acryl-functionalized SSQ.

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