© 2001 The Chemical Society of Japan Bull. Chem. Soc. Jpn., *74*, 991—996 (2001)

# A Novel Photosensitive Silicone Ladder Polymer: Synthesis, Photochemical, and Thermal Characteristics

**Naoki Yasuda,*,# Shigeyuki Yamamoto, Hiroshi Adachi, Suguru Nagae, Yuji Wada,† and Shozo Yanagida†**

Advanced Technology R&D Center, Mitsubishi Electric Corporation, Tsukaguchihonmachi, Amagasaki, Hyogo 661-8661

†Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0877

(Received October 12, 2000)

A negative working photosensitive silicone ladder polymer (PVSQ) based on polyphenylsilsesquioxane with vinyl groups as a reactive substituents in the side chain, and 2,6-bis(azidobenzylidene)-4-methylcyclohexanone (BA) as a photocrosslinker, has been developed. The monodisperse PVSQ was synthesized by co-polymerization of trichlorophenylsilane and trichloro(vinyl)silane with potassium hydroxide in isobutyl methyl ketone. The PVSQ film showed excellent transparency above 280 nm and high solubility in organic solvents. The photosensitive PVSQ containing 3 wt% of BA showed the sensitivity of 40 mJ cm$^{-2}$ when it was exposed to 365 nm light (i-line) followed by development with a mixture solution of anisole and xylene at 25 °C. The photosensitive PVSQ film also showed high thermal stability (decomposition temperature: 520 °C) and low dielectric constant (3.2/1 MHz), demonstrating a high potential for application to LSI production.

Silicone ladder polymer (PPSQ; Polyphenylsilsesquioxane) is an inorganic polymer with a ladder type structure consisting of siloxane bonds as a main chain and phenyl groups as a side chain.[1–7] PPSQ has received considerable interest in the microelectronic industry due to its high thermal and chemical stability and low dielectric constant. We have developed a simple and easy synthetic process of PPSQ with high purity, which is useful in semiconductor manufacturing of insulators and dielectrics.[8–11] PPSQ soluble in solvents can be processed into films without shrinkage and degasification during curing so that it has been applied not only as a protection layer but also as insulation layers in the multilayer writing method.[12]

On the other hand, polyimides are well-known as protection layers and insulators in semiconductor manufacturing.[13,14] In particular, photosensitive polyimides are very useful, since the number of processing steps is reduced by avoiding the use of classical photoresists.[15] However, being insoluble in most common solvents, polyimides are usually processed in the form of their precursors, poly(amic acid), which are then thermally converted to the imide structure.[16] Since polyimide precursors suffer from high shrinkage (~50%), which causes distortion to a substrate and enough degasification to contaminate devices during thermal curing for imidization, it is quite difficult to apply polyimides to insulation layers in the multilayer writing methods.

If PPSQ structure can be supplied with photosensitive characteristics, it will become much more attractive than photosensitive polyimides, as the number of processing steps in microelectronic fabrication can be reduced by eliminating the photoresist. Polyimides and non-photosensitive PPSQ need baking processes over 350 °C for making them insoluble in common solvents. On the other hand, photosensitive PPSQ requires no high thermal curing, so that it is also capable of being applied to the manufacture of devices sensitive to heat.

A strategy for the photosensitive PPSQ polymer with negative tone image at i-line ($\lambda = 365$ nm) is the introduction of reactive groups into the side chain of PPSQ with the photoreactive crosslinking reagent. We partially substituted phenyl groups of PPSQ with vinyl groups as a reactive moiety (Fig. 1, denoted as PVSQ). As PVSQ showed high transmittance in the range of the wavelength of $\lambda > 280$nm, it didn't have photoreactivity at the i-line alone. We selected 2,6-bis(azidobenzylidene)-4-methylcyclohexanone (BA) having azide groups on both ends as a photocrosslinker in this system. BA has high absorption in the wavelength of i-line and often has been used as a photocrosslinker of UV negative working photoresists.[17–18] Figure 2 shows the photocrosslinking reaction expected between the side chain groups of PVSQ and BA as a photocrosslinker. When BA is irradiated with i-line, the azide groups

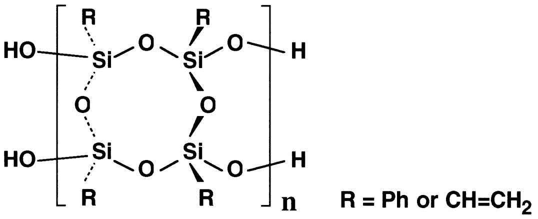

Fig. 1. Structure of PVSQ.

---

# Material and Life Science, Graduate School of Engineering, Osaka University.

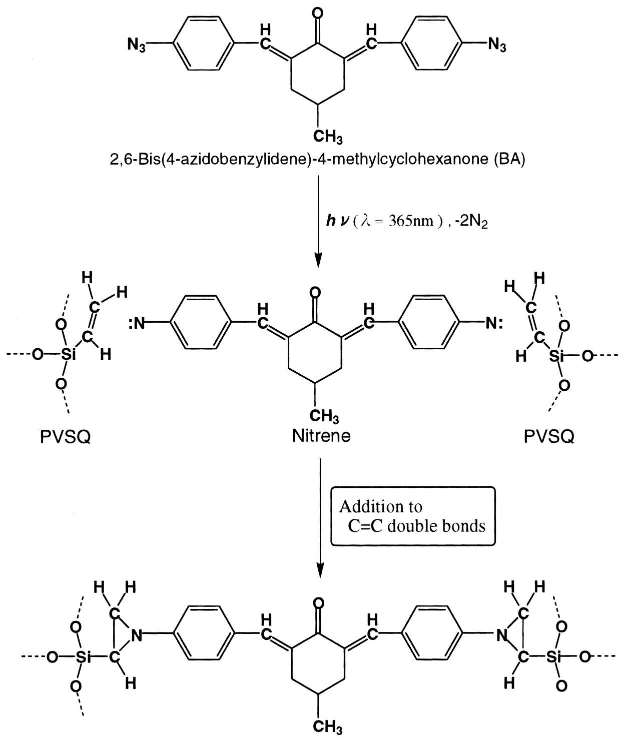

Fig. 2. Photocrosslinking reaction between PVSQ and BA.

are decomposed to form active nitrene intermediate by releasing nitrogen molecules. Nitrene adds to vinyl groups to crosslink PVSQ, giving films which are insoluble in any kinds of solvents.[19–25]

In this article, the preparation and characterization of a novel photosensitive silicone ladder polymer system consisting of PVSQ and BA are reported. Pattern fabrication of the films required for microelectronic application has been successfully demonstrated.

## Experimental

**Chemicals.** The raw materials of PVSQ, trichlorophenylsilane and trichloro(vinyl)silane, were purchased from Shin-Etsu Chemical Industry Ltd., and were purified by distillation before use. Isobutyl methyl ketone (MIBK), anisole, and xylene were purchased from Kanto Chemical Industry Ltd.. Tetrahydrofuran was purchased from Tokyo Chemical Industry Ltd.. 2,6-bis(azidobenzylidene)-4-methylcyclohexanone as a photocrosslinker was obtained from Aldrich Co., and used without further purification.

**Apparatus.** The apparatus for identification and characterization of synthesized PVSQ is as described below. Fourier transform infrared (FT-IR) spectra were measured on a JASCO Model FT/IR-230 spectrometer. $^1$H and $^{29}$Si NMR data were obtained with a Bullker Model MSL-300 (230 MHz) instrument in $CDCl_3$, with tetramethylsilane (TMS) as an internal standard. Determination of molecular weight of PVSQ was obtained with a JASCO Model TRI ROTER-IV gel permeation chromatograph (GPC). UV-vis absorption spectra were obtained with a Shimadzu MPS-2000. Thermogravimetric analyses (TGA) were performed with a heating rate of 5 °C/min in air by a Du Pont Model 951 thermogravimetric analyzer. $O_2$-RIE (Reaction ion etching) resistance was estimated on an ANELVA Model DEM-452T. A mask aligner of a Mikasa Model MA-10, and a spin developer (Kyoei Semiconductor Co.) were used for evaluating applicability for pattern fabrication. Film thickness was measured by a Dektak 3030 system (Veeco Instrument Inc.). The patterning profiles were observed by a JASCO Model JSM-T20 scanning electron microscope (SEM).

**Preparation of Photosensitive PVSQ Varnish.** The photosensitive PVSQ varnish was prepared by the following procedure. In a flask equipped with a magnetic stirrer, PVSQ and anisole were mixed at room temperature. After BA was added into it, the mixture was stirred for 10 h, and then filtered by a membrane filter of 0.1 μm. The varnishes used by PVSQ with various vinyl group contents from 0 mol% to 50 mol% in the side chain were prepared.

**Dielectric Measurements.** The dielectric measurements of the PVSQ film were carried out using a HP multifrequency analyzer. Medium frequency (10 kHz to 4 MHz) capacitance and loss tangents were measured at room temperature. The specimens for dielectric measurements were prepared by vacuum deposition of a gold electrode (3 mm in diameter) on the spin coated PVSQ film (10 μm thickness) with the back surface of the low resistivity Si wafer serving as another electrode.

**Photoirradiation and Photosensitivity.** PVSQ films spin-coated on a silicon wafer were prebaked at 130 °C for 2 min on a hot plate and exposed to i-line with 500 mJ cm$^{-2}$ using a filtered 250 W super high pressure mercury lamp with glass filters (Toshiba, UV-35 and UVD40A). Imagingwise exposure through a mask was carried out in a contact-printing mode with a proximity mask aligner. Exposed films were developed in a mixture of anisole and xylene at 25 °C and subsequently rinsed with xylene. The characteristic sensitivity curve was expressed by plotting a normalized film thickness against the logarithmic exposure energy.

## Results and Discussion

**Synthesis of PVSQ.** PVSQ was prepared in the two steps, i.e., hydrolysis and condensation of organotrichlorosilane as shown in Fig. 3.[8–11] At first, the starting materials, a mixture of trichlorophenylsilane and trichloro(vinyl)silane in the desired mol ratio, were hydrolyzed in MIBK under stirring at 0 °C. After removal of the acid layer of the hydrolysate product, the MIBK solution was washed with pure water to be neutralized, and then the prepolymer was obtained. The average molecular weight ($M_w$) was about 2,000. The prepolymer solution was heated under refluxing in the presence of potassium hydroxide as a catalyst, resulting in further polymerization by dehydration condensation reaction. The reaction mixture was purified by pouring into a methanol aqueous solution to give a white precipitate of PVSQ. The PVSQ was dried in vacuo. The yield of the resulting PVSQ was 70%. This process gave the molecular weight over $10^4$. We synthesized PVSQ of the molecular weight of about $3\times10^4$ with various vinyl group contents from 0 mol% to 50 mol% and PVSQ of the molecular weight of about $1.54\times10^5$ with 5 mol% vinyl groups by the above-mentioned synthetic method.

FT-IR and NMR were measured for confirming the structure of PVSQ random copolymers of $M_w = 3.1\times10^4$ with 50 mol% vinyl group content and $M_w = 1.54\times10^5$ with 5 mol% vinyl group content.[26] In the FT-IR spectra of both PVSQ, the IR bands of 1130 cm$^{-1}$ and 1038 cm$^{-1}$ attributed to Si–O–Si asymmetrical stretching vibration indicated the presence of the cis-syndiotactic double-chain structure of PVSQ.[4] In the $^{29}$Si NMR spectra of both PVSQ, only one sharp single peak as-

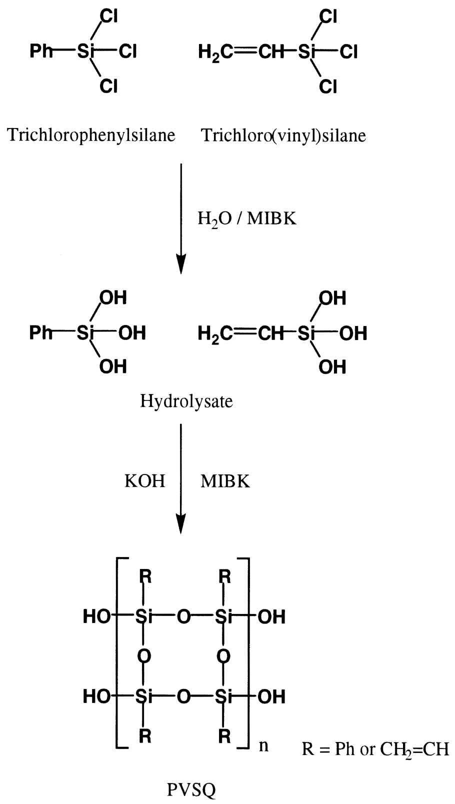

Fig. 3. Synthesis of PVSQ.

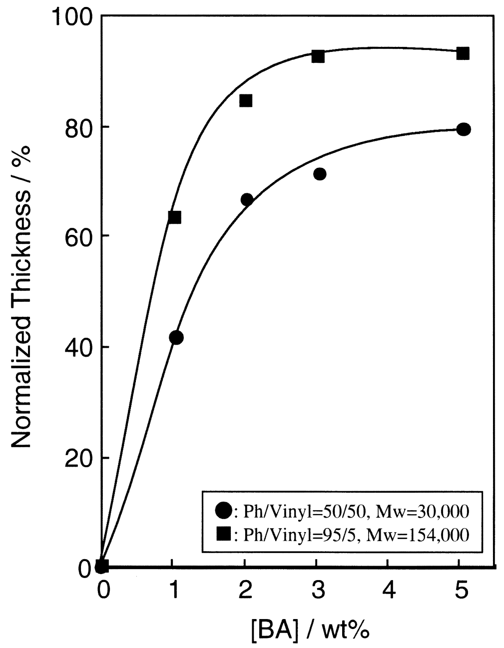

Fig. 4. Dependence of photocrosslinking behavior of the PVSQ films on the BA content. After i-line exposure at 500 mJ $cm^{-2}$, PVSQ film (●: $M_w$ = 30,000, Ph/Vinyl = 50/50) and PVSQ film (■: $M_w$ = 154,000, Ph/Vinyl = 95/5) were developed with anisole or a mixture of anisole/xylene = 1/2, respectively.

signed to trifunctional siloxane: $RSi(–O–)_3$ at $\delta$ −78 (s) was observed while the peaks assigned to monofunctional siloxane: $RSi(–O–)(OH)_2$ and difunctional siloxane: $RSi(–O–)_2(OH)$ were not observed, also indicating the presence of the cis-syndiotactic double-chain structure of PVSQ.[27,28]

**Photochemical Characteristics of Photosensitive PVSQ.** The PVSQ varnish of the molecular weight of about $3\times10^4$ with 50 mol% vinyl groups was spin-coated onto Si wafers and prebaked at 120 °C for 2 min on a hot plate to produce films of about 2 μm thickness. After photocrosslinking by i-line exposure at 500 mJ $cm^{-2}$, the samples were dip-developed in anisole for 30 s and rinsed in xylene for 30 s. Figure 4 shows the dependence of the normalized remaining film thickness on the BA content. The remaining thickness increased gradually with increasing of BA content, and reached 78% at 5 wt%.

The content of vinyl groups in the side chain of PVSQ also affected the photosensitivity, as did the BA content. We synthesized PVSQ of the molecular weight of about $3\times10^4$ with various vinyl group contents from 0 mol% to 50 mol%. Figure 5 shows the relationship between the vinyl content and the normalized remaining film thickness. The BA content was held constant at 5 wt% of the PVSQ weight therein. The higher vinyl content of PVSQ showed the higher remaining thickness. The starting point of weight loss on a TGA curve in air was adopted as a measure of the thermal decomposition temperature. The thermal decomposition temperature of PVSQ containing vinyl content less than 5 mol% stayed at 475 °C (Fig. 5), but decreased suddenly with increase of the vinyl content. Optimization of the vinyl content is the most important step in realizing practically favorable PVSQ characteristics. Judging from the ability of PPSQ to maintain the heat resistance, we chose the 5 mol% vinyl polymer for further evaluation of this material.

When we employed PVSQ polymer (vinyl content: 5 mol%, molecular weight: $1.54\times10^5$) and a mixture of anisole and xylene as a developer, the thickness of the film remaining after development was high. The plots (■) in Fig. 4 show dependence of the normalized remaining thickness on the BA content for PVSQ ($M_w$ = $1.54\times10^5$) by dip-development in anisole/xylene = 1/2. The film of the initial thickness, 4.2 μm, made of PVSQ was employed for the evaluation. The normalized remaining thickness increased with increasing of the BA content and reached 92% above the BA content of 3 wt%. The decrease of the solubility in anisole due to the enormous molecular weight of PVSQ and the change of the developer composition brought both the higher normalized remaining thickness, over 90%, and the high decomposition temperature of 480 °C (Fig. 5). Consequently, for the following evaluations we used the varnishes consisting of PVSQ ($M_w$ = $1.54\times10^5$, 5 mol% vinyl content) as a base polymer and BA content of 3 wt% as a photocrosslinker, and a mixture of anisole/xylene = 1/2 as a developer.

Figure 6 shows the photosensitivity curve of PVSQ. The PVSQ varnish was spin-coated onto Si wafers and prebaked at 130 °C for 120 s on a hot plate to produce a film of 4.2 μm. Exposures were carried out with a mask aligner for i-line. The samples were developed in an anisole/xylene = 1/2 mixture for 30 s and rinsed in xylene for 30 s with a spin developer. The sensitivity to i-line was 40 mJ $cm^{-2}$ at the expose dose of 50% normalized remaining film thickness after development

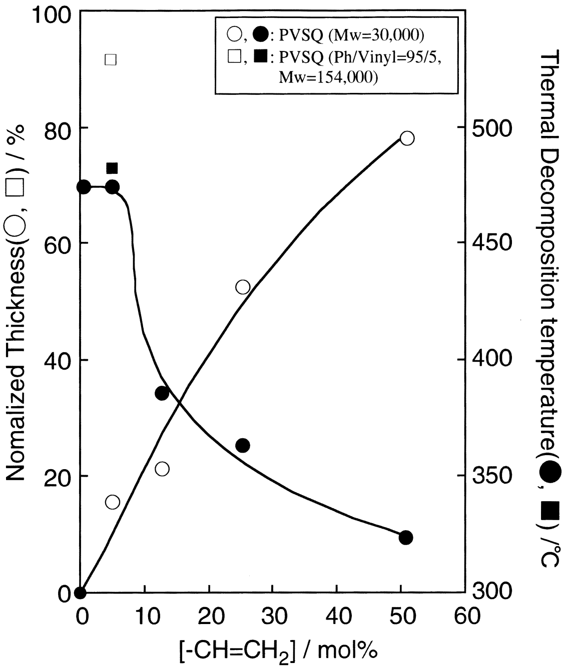

Fig. 5. Dependence of thermal decomposition temperature and photocrosslinking behavior of PVSQ films on the $-CH=CH_2$ content. The plots (●) show the thermal decomposition temperature of PVSQ ($M_w$ = 30,000) polymers with different vinyl content in the side chain. The plot (■) shows the thermal decomposition temperature of PVSQ polymer ($M_w$ = 154,000, Ph/Vinyl = 95/5). After i-line exposure at 500 mJ $cm^{-2}$, PVSQ film (○: $M_w$ = 30,000) and PVSQ film (□: $M_w$ = 154,000, Ph/Vinyl = 95/5) were developed with anisole or a mixture of anisole/xylene = 1/2, respectively.

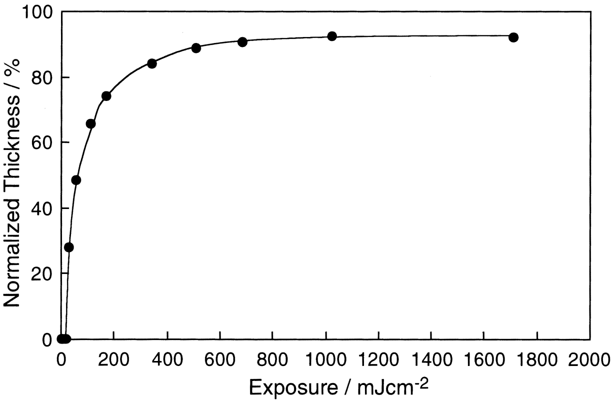

Fig. 6. Sensitivity characteristics of photosensitive PVSQ ($M_w$ = 154,000, Ph/Vinyl = 95/5, BA: 3wt%). The PVSQ varnish was spin coated onto Si wafers and initial thickness was 4.2 µm. The wafers were developed with a mixture of anisole/xylene = 1/2 and rinsed with xylene.

($D_n^{0.5}$). The suitable exposure dose was determined to be 500 mJ $cm^{-2}$. In spite of a rigid structure of PVSQ, a photosensitivity value high enough for practical use as protecting films of LSI was obtained.

**Thermal Properties of Photosensitive PVSQ Films.** The thermal stability of PVSQ photocrosslinked with 3 wt% BA by being exposed to i-line and baked at 350 °C was determined by TGA in comparison with PVSQ without photocrosslinking. The TGA curves (Fig. 7) showed that the thermal decomposition of the photocrosslinked PVSQ started at 520 °C, showing much higher stability than that without photocrosslinking (480 °C). The photocrosslinking reaction of PVSQ molecules by BA should improve its thermal resistance. The inset of Fig. 7 shows FT-IR spectra of PVSQ films after being baked at 350 °C and 600 °C for 60 min under air. In the spectrum of PVSQ film baked at 350 °C, the IR bands near 1050 and 1140 $cm^{-1}$ attributed to Si–O–Si asymmetrical streching vibration indicated the presence of the cis-syndiotactic double-chain structure of PVSQ and the IR band of 1430 $cm^{-1}$ assigned to Si–Ph streching vibration was observed. The IR band of 1405 $cm^{-1}$ assigned to $Si-CH=CH_2$ was below the noise level because of the very low content of vinyl groups. In the spectra of PVSQ films baked at 600 °C, the IR bands assigned to Si–Ph disappeared. Furthermore, the double peak assigned to Si–O–Si changed to a single peak at 1080 $cm^{-1}$ and the Si–O streching vibration of $SiO_2$ appeared at about 800 $cm^{-1}$. These changes in IR spectra demonstrated that the baking at higher temperature than the decomposition temperature of PVSQ causes the phenyl groups to dissociate, and the *cis*-syndiotactic double-chain structure of PVSQ to change to the three dimensional network structure of $SiO_2$.

Figure 8 shows the retention of the PVSQ film thickness after being baked at 350 °C for 60 min. The initial thickness of the films after being exposed to i-line and prebaked at 130 °C for 2 min on a hot plate was 4.2 µm. Little film thickness loss was observed after being baked at 350 °C. Desorption of only a slight amount of $H_2O$ was detected below 350 °C, suggesting that the dehydration condensation of silanol groups occurred at the end of the chain in the insoluble polymer. On the other

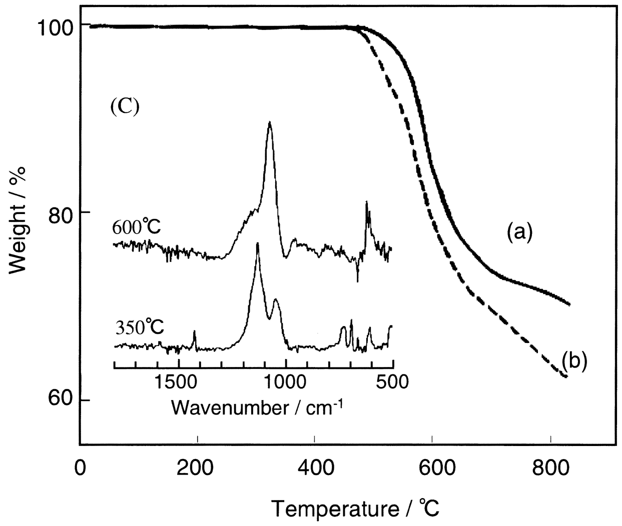

Fig. 7. TGA spectra of PVSQ films ($M_w$ = 154,000, Ph/Vinyl = 95/5), (a) PVSQ film with BA after irradiated and baked at 350 °C for 60 min and (b) PVSQ film without BA after baked at 350 °C for 60 min. (C) shows FT IR spectra of PVSQ films ($M_w$ = 154,000, Ph/Vinyl = 95/5) after baked at 350 °C, 600 °C for 60 min in air.

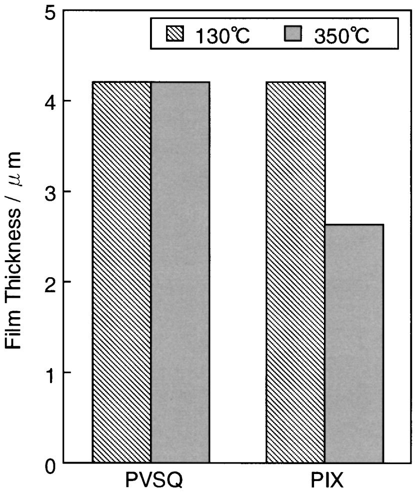

Fig. 8. The retention of (a) PVSQ film ($M_w$ = 154,000, Ph/Vinyl = 95/5, BA: 3 wt%) after irradiated and baked at 350 °C for 60 min and (b) polyimide film (PIX) after baked at 350 °C for 60 min.

hand, in the commercially available polyimide film (PIX-3500; Hitachi Chemical Inc. Co.), the baking process induced reduction of the film thickness by 40% due to degasification. Application of Polyimide film to the layer insulating films should be quite difficult, since degasification contaminates devices. Therefore PVSQ film is suitable for application to microelectronics as insulating films between layers in the multilayer writing method to attain the higher integration circuits or large-scale integrated circuits.

**Physical Properties of Photosensitive PVSQ Films.** The dielectric constant for the PVSQ film after being exposed to i-line light and baked at 350 °C for 60 min was 3.21 (1 MHz), as determined from the dielectric measurements; this value was substantially lower than those of polyimide films (3.4~).[29] PVSQ may thus be applicable not only to protection layers but also to insulation layers of LSI production, thanks to this value.

When PVSQ was employed as an interdielectric in the multilayer writing structure, PVSQ must possess very high resistance to $O_2$-RIE used at the ashing process of photoresists on the fabrication of the upper layers, i.e., metal electric wiring, and inorganic films.[30] So we estimated the $O_2$-RIE resistance of PVSQ. PVSQ was spin-coated onto Si wafer. After baking at 130 °C for 120 s, PVSQ film on the wafer was exposed to i-line of 500 mJ cm$^{-2}$, and then the wafer was baked at 350 °C for 60 min. A parallel plate rector was employed to study the $O_2$-RIE resistance of PVSQ. The etchings were carried out under $O_2$ (25.6 Pa pressure) and 300 W rf power. The flow rate of $O_2$ was fixed at 200 sccm. Figure 9 shows the residual thickness of the PVSQ film versus the etching time in comparison with that of a novolak photoresist, OFPR-800 (Tokyo Ohka Kogyo Corp). The etching rate of PVSQ was 22.5 Å min$^{-1}$ and was much lower than 4062.5 Å min$^{-1}$ of OFPR-800, showing the much higher resistance of PVSQ to $O_2$ plasma. On the surface of PVSQ, organic groups in PVSQ contained as the side chains were dissociated by chemical etching during $O_2$-RIE. The surface of PVSQ film became an inorganic layer, i.e., $SiO_2$ during $O_2$-RIE. This layer was considered to play an important role as a protective layer for interception of $O_2$ plasma.[31]

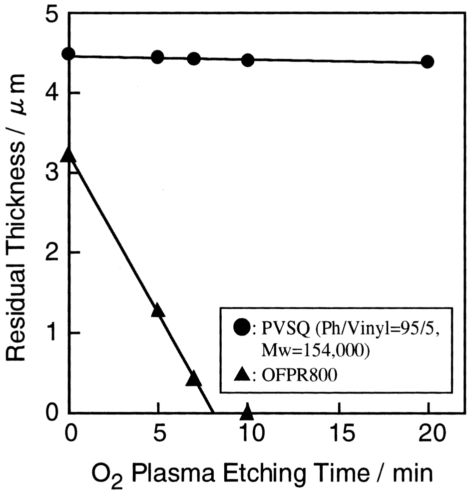

Fig. 9. The residual thickness of (a) PVSQ film ($M_w$ = 154,000, Ph/Vinyl = 95/5, BA: 3 wt%) after irradiated and baked at 350 °C for 60 min and (b) photoresist (OFPR800) versus the $O_2$ plasma etching time using a parallel plate rector. The etchings were carried out under the following condition. Gas: $O_2$, Flow: 200 sccm, Pressure: 25.6 Pa, Incident Power: 300 W, Electrode Voltage: 460 V, Plate Current: 200 mA.

**Pattern Fabrication.** The pattern formation represented in Fig. 10 has been attempted. First, PVSQ was spin-coated on a Si wafer and baked at 130 °C for 120 s on a hot plate to yield a 4.20 μm thick film. After i-line exposure at 500 mJ cm$^{-2}$ through a photomask with patterns, the film was developed in a mixture of anisole/xylene = 1/2 for 30 s and then rinsed in xylene for 30 s with a spin developer. The resolution of the obtained patterns was evaluated by SEM. The film thickness after the development was 3.90 μm, that is 92% of the initial thickness. The pattern edge exhibited a taper shape. Figure 10 shows a 18 μm line and 18 μm space pattern and a 18 μm via hole pattern. It was found that the mask patterns were rather accurately transferred into the PVSQ dielectric film.

## Conclusions

A novel photosensitive silicone ladder polymer (PVSQ) based on polyphenylsilsesquioxane with vinyl groups as a reactive substituent in the side chains, and 2,6-bis(azidobenzylidene)-4-methylcyclohexanone (BA) as a photocrosslinker, was developed. The monodisperse PVSQ was prepared by copolymerization of trichlorophenylsilane and trichloro(vinyl)silane using potassium hydroxide as a catalyst in MIBK. This PVSQ having vinyl groups was highly soluble in common solvents. PVSQ containing BA was found to work as a negative-tone photosensitive dielectric with high sensitivity. The PVSQ containing 3 wt% of BA showed a sensitivity of 40 mJ cm$^{-2}$ when it was exposed to i-line, followed by development with a mixture solution of anisole and xylene at 25 °C. This exposed PVSQ film also showed the high thermal decomposition temperature (520 °C) and the low dielectric constant (3.21/1 MHz). The photosensitivity and thermal characteristic were

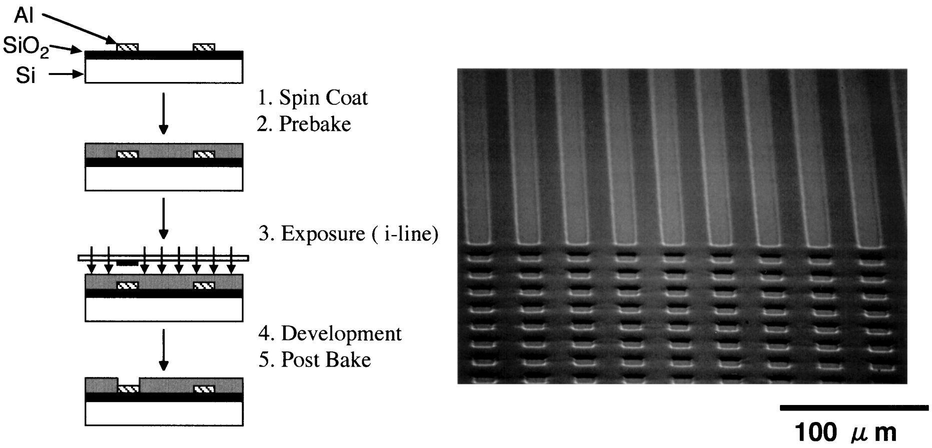

Fig. 10. SEM photograph of patterning profiles after development and baked of PVSQ film (thickness: 3.9 μm).

attributed to the fact that the crosslinking reaction was a chain reaction using the addition reaction between vinyl groups of PVSQ and nitrenes formed from BA. PVSQ also can be processed into films without shrinkage and degasification during curing. Photosensitive PVSQ requires no thermal curing, due to being insoluble in most common solvents. Therefore this PVSQ/BA system can be applied not only to protection layers but also to insulation layers in the multilayer writing method of devices sensitive to heat.

## References

1 J. F. Brown, J. H. Vogt, A. Katchman, J. W. Eustance, K.M. Kiser, and K. W. Krantz, *J. Am. Chem. Soc.*, **82**, 6194 (1960).

2 J. F. Brown, *J. Am. Chem. Soc.*, **87**, 4317 (1965).

3 J. F. Brown, J. H. Vogt, and P. I. Prescott, *J. Am. Chem. Soc.*, **86**, 1120 (1964).

4 J. F. Brown, *J. Polym. Sci. C*, **1**, 83 (1963).

5 J. F. Brown and P. I. Prescott, *J. Am. Chem. Soc.*, **86**, 1402 (1964).

6 K. A. Andrianov, G. A. Krakov, F. F. Suschentsova, and V. A. Miagkov, *Vysokomol. Soedin.*, **7**, 1477 (1965).

7 S. A. Palvlova, V. I. Pahomov, and I. I. Tverdokhlebova, *Vysokomol. Soedin.*, **6**, 1275 (1964).

8 H. Adachi, E. Adachi, O. Hayashi, and K. Okahashi, *Rep. Prog. Polym. Phys. Jpn.*, **28**, 261 (1985).

9 H. Adachi, E. Adachi, S. Yamamoto, and H. Kanegae, *Mater. Res. Soc. Symp. Proc.*, **227**, 95 (1991).

10 H. Adachi, E. Adachi, O. Hayashi, and K. Okahashi, Japanese Patent Kokai-H-1-26639, 1989; *Chem. Abstr.*, **111**, 58577 (1989).

11 H. Adachi, E. Adachi, O. Hayashi, and K. Okahashi, Japanese Patent Kokai-H-1-92224, 1989; U. S. Patent 5,081,202, 1989; *Chem. Abstr.*, **111**, 154663 (1989).

12 N. Yasuda, S. Yamamoto, and H. Adachi, *J. Soc. Electr. Mater. Eng.*, **7(1)**, 28 (1998).

13 M. Morita, S. Imamura, A Tanaka, and T. Tamamura, *J. Electrochem. Soc.*, **131**, 2402 (1984).

14 R. Rubner, H. Ahne, E. Kuhn, and G. Kolodziej, *Photogr. Sci. Eng.*, **23**, 303 (1979).

15 N. Yoda and H. Hashimoto, *J. Macromol. Sci. Chem.*, A, **21**, 1641 (1984).

16 H. Ahne, L. Rainer, and R. Rubner, *Polym. Adv. Technol.*, **4**, 217 (1993).

17 T. Iwayanagi, T. Kohashi, and S. Nonogaki, *J. Electrochem. Soc.*, **127**, 2759 (1980).

18 C. C. Han, J. C. Corelli, and J. F. Mcdonald, *J. Electrochem. Soc.*, **134**, 1036 (1987).

19 L. S. Efros and T. A. Yurre, *Vysokomol. Soedin. A*, **12**, 2211 (1970).

20 S. Patai, "The chemistry of the Azido Group" in "The Chemistry of Functional Groups," ed by S. Patai, Interscience Publishers, London (1971).

21 W. D. Closson and H. B. Gray, *J. Am. Chem. Soc.*, **85**, 290 (1964).

22 L. Horner, *Angew. Chem.*, **75**, 707 (1963).

23 L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963).

24 W. Lwowski and T. W. Mattingly, *J. Am. Chem. Soc.*, **87**, 1947 (1965).

25 W. Lwowski and G. T. Tisue, *J. Am. Chem. Soc.*, **87**, 4022 (1965).

26 White powder. FT-IR 3435 (Si–OH), 1430 (Si–Ph), 1405 (Si–C=C), 1130, 1038 $\mathrm{cm^{-1}}$ (Si–O–Si). $^1$H NMR (chloroform-*d*/TMS) $\delta$ 7.25 (br, Si–Ph), 5.80 (br, Si–C=C), 1.50 (s, Si–OH). $^{29}$Si NMR (chloroform-*d*/TMS) $\delta$ −78.0 (s, $\mathrm{RSiO_3}$).

27 E. A. Williams, *Ann. Rep. NMR Spectrosc.*, **15**, 235 (1983).

28 A. Ueyama, S. Yamamoto, H. Adachi, and I. Karino, *ACS Polym. Mater. Sci. Eng. Prepr.*, **67**, 246 (1992).

29 R. J. Jensen, J. P. Cummings, and H. Vora, Proceedings of Electronic Components Conf. Proc., 73 (1984).

30 Ch. Steinbruhel, H. W. Lehmann, and K. Frick, *J. Electrochem. Soc.: Solid State Sci. and Thechnol.*, **132(1)**, 180 (1985).

31 J. Paraszcak, E. Babish, M. Hatzakis, and J. Shaw, Proceedings of Int'l. Symp. On Electron, Iron & Photon Beam, New York, 358 (1984).