A New Positive-Type Photosensitive Alkaline-Developable Alicyclic Polyimide Based on Poly(amic acid silylester) as a Polyimide Precursor and Diazonaphthoquinone as a Photosensitive Compound

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ABSTRACT: A new positive working photosensitive alicyclic polyimide precursor based on poly(amic-acid *tert*-butyldimethylsilylester) **(3)** and 2, 3, 4-tris[2-diazo-1(2*H*)-naphthalenone-4-sulfonyloxy]benzophenone **(D4SB)** as a photosensitive compound has been developed. Polymer **3** was prepared by ring-opening polyaddition of bicyclo[2.2.1]heptane-2-methanecarboxylic-3,5,6-tricarboxylic-2,3:5,6-dianhydride **(2)** with 5-*tert*-butyldimethylsilylamino-*N*-*tert*-butyldimethylsilyl -1,3,3-trimethylcyclohexanemethyl -amine **(1)** in toluene / *N*, *N*-dimethyl acetamide (DMAc) (2 / 1 weight ratio) at 20 °C for 3 h . The film of polymer **3** showed an excellent transparency at the wavelengths above 250 nm. The dissolution behavior of polymer **3** containing 30 wt% **D4SB** after exposure was studied, and it was found that the difference of dissolution rate between the exposed and unexposed areas was enough to get a high contrast due to the photochemical reaction of **D4SB** in the polymer film. The photosensitive polyimide precursor containing 30 wt% **D4SB** showed a sensitivity of 60 mJ / cm^2 and a contrast of 1.7 when it was exposed to 365 nm light and developed with a 2.38 wt% aqueous tetramethylammonium hydroxide solution at 25 °C. A fine positive image of 10 μm-line and space patterns was also printed in a film which was exposed to 300 mJ / cm^2 by a contact mode. The positive image in polymer **3** was converted to the positive image in the polyimide(PI) film by thermal treatment. The optically estimated dielectric constants of the polyimides with and without **D4SB** are 2.45 and 2.44, respectively. These values are significantly lower than those of conventional aromatic polyimides.

Introduction

Polyimides **(PIs)** have been widely used as the protection and insulation layers for very large scale integration circuits (VLSI) and multi-chips modules for computers because of their high thermal stability and excellent mechanical property. Photosensitive PIs **(PSPIs)** have been developed to simplify the processing steps.

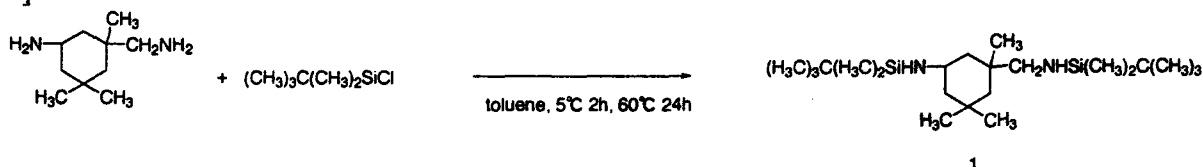
Recently, **PIs** having low dielectric constants are required to increase the circuit speed. Especially, aliphatic and alicyclic **PIs** are interesting as optoelectronic and interlayer dielectric materials. Therefore, partially aliphatic **PIs** derived from aliphatic dianhydrides and aromatic diamines or vice versa have been developed as **PIs** with low dielectric constants.[1-13] Several reports have been published on the synthesis of wholly aliphatic PIs **(APIs)**. However, the reported **APIs** were of low molecular weight. Quite recently, we developed a synthetic method to give wholly alicyclic **PIs** with high molecular weights via poly(amic acid silyl ester)s, which can be employed as a **PSPI** precursor.[14] These findings prompted us to develop a new alicyclic PSPI having a lower dielectric constant.

In this study, we report a new positive working alkaline developable thermally stable and photosensitive polymer based on poly(amic acid *tert*-butyldimethylsilylester) **(3)** and 2, 3, 4-tris[2-diazo-1(2*H*)-naphthalenone-4-sulfonyloxy] benzophenone **(D4SB)** as a photoreactive compound.

Results and Discussion

Synthesis of 5-*tert*-butyldimethylsilylamino-*N*-*tert*-butyldimethylsilyl -1,3,3-tri-methylcyclohexanemethyl-amine (1)

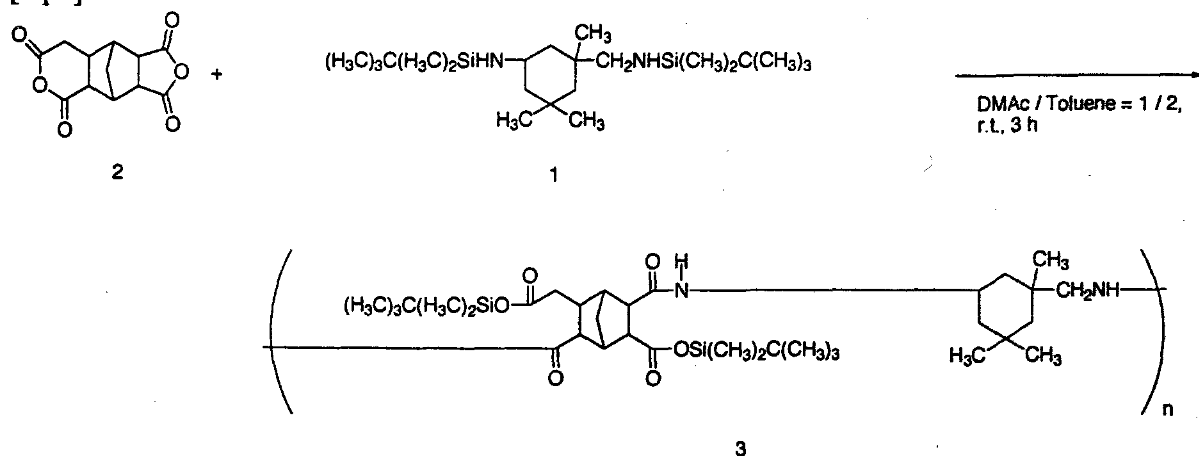
Monomer **1** was prepared by the reaction of 5-amino-1,3,3-trimethylcyclohexane-methylamine with *tert*-butyldimethylchlorosilane in the presence of TEA as an acid acceptor in toluene for 2 h at 5 °C, then 24 h at 60 °C. The structure of **1** was identified as the corresponding *N*-silylated alicyclic diamine by IR spectroscopy and elemental analysis. [eq. 1]



eq. 1

Synthesis of poly(amic acid *tert*-butyldimethylsilyl ester)

The ring-opening polyaddition of **1** with alicyclic dianhydride, bicyclo[2.2.1]heptane-2-methanecarboxylic-3,5,6-tricarboxylic-2,3:5,6-dianhydride **2** was carried out in DMAc and toluene at room temperature. Polymerization proceeded smoothly to give a desired poly(amic acid *tert*-butyldimethylsilylester) **(3)** with a number average molecular weight of 19,000 and a polydispersity of 2.1. The structure of polymer was identified as the corresponding poly(amic acid silylester) by IR spectroscopy. The IR spectrum showed characteristic amide and silyl ester absorptions at 1658 and 1708 cm^{-1}.
[eq.2]



eq. 2

Polymer **3** was readily converted to the corresponding PI by thermal treatment. The traces of TG for polymer **3** and the corresponding PI are shown in Figure 1. A rapid weight loss was observed at 200-350 °C for polymer **3**. In this range, the weight loss of 37 % is in good agreement with the value (40.8 %) calculated from the elimination of *tert*-butyldimethylsilanol due to the imidization. A 10 % weight loss temperature of PI is 420 °C. The IR spectrum of the thermally treated PI exhibited characteristic imide absorptions at 1778 and 1704 cm^{-1}.

Lithographic Evaluation

The UV-visible spectrum of polymer **3** film with 2.8 □m thickness (Figure 2) shows an excellent transparency in the region above 250 nm. This means that 2,3,4-tris[2-diazo-1(2H)-naphthalenone-4-sulfonyloxy]benzophenone **(D4SB)** which has a strong absorption in the range of 350-420 nm can be used as a photoactive compound. **D4SB**

is photochemically transformed to 3-sulfoindenecarboxylic acid. [15][eq. 3]

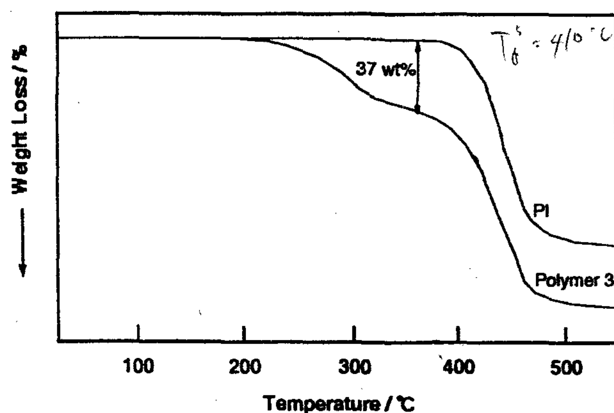


Figure1. TG curves of polymer 3 and the corresponding PI.

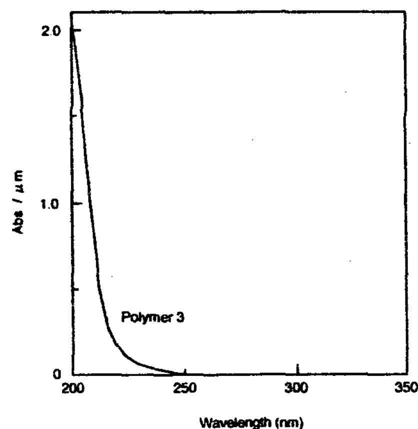


Figure 2. UV-visible spectra of polymer 3 film.

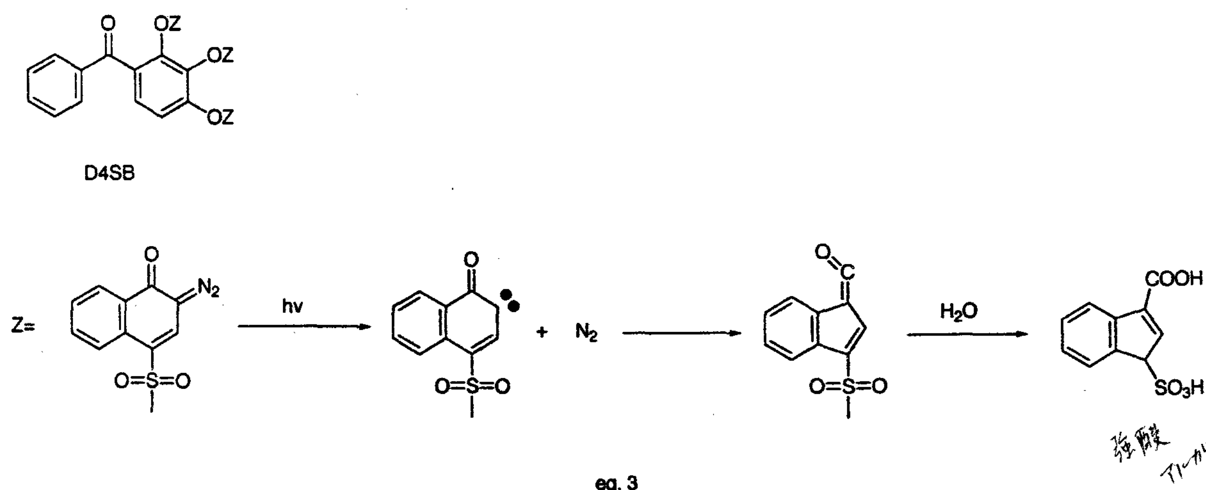


Figure 3 shows the changes in the UV-visible spectra of a polymer **3** film containing 30 wt% **D4SB** upon 365 nm UV (i-line) irradiation. The intensity of the characteristic absorption band in the range of about 350-420 nm gradually decreased, and this absorption band disappeared completely at 200 mJ / cm^2. Therefore, the resist consisting polymer **3** as a matrix and **D4SB** as a photoactive compound would be expected to work as an i-line sensitive **PSPI** system.

To clarify the difference of dissolution behavior between the exposed and unexposed areas, the effect of **D4SB** loading on the dissolution rate in the developer (2.38 wt% TMAH) was studied, and the results are shown in Figure 4. The films spin-cast on silicon wafers were pre-baked at 80 °C for 5 min, and then exposed to a filtered super-high pressure mercury lamp (365 nm, 300mJ / cm^2). The dissolution rate was estimated by measuring the film thickness after development. The unexposed areas were not dissolved in the TMAH solution. On the other hand, the solubility of the exposed areas increased gradually with increasing **D4SB** contents. The difference of the dissolution rates between the exposed and unexposed areas reached almost 800 times at the 30 wt% **D4SB** loading.

The most widely used positive resists are two-component materials consisting of an alkaline soluble matrix resin that is rendered insoluble in an aqueous alkaline solution through addition of hydrophobic radiation-sensitive materials.[16,17] In our case, hydrolysis of polymer **3**

might occur in the exposed areas by aqueous alkaline solution because the developer can penetrate easily into polymer film **3** due to the existence of hydrophilic groups such as carboxylic acid and sulfonic acid groups.

Therefore, this dissolution-accelerating behavior in the exposed film is considered to be the polarity change of polymer **3** due to the photochemical reaction of **D4SB** and the hydrolysis of polymer **3** in the developing process.

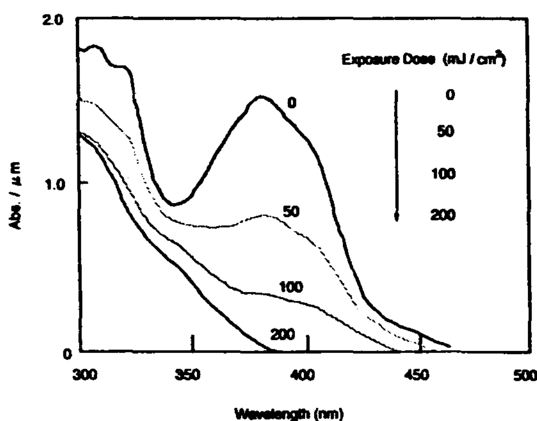


Figure 3. the changes in the UV-visible spectra of a polymer **3** film containing 30 wt% **D4SB** upon 365 nm UV (i-line) irradiation

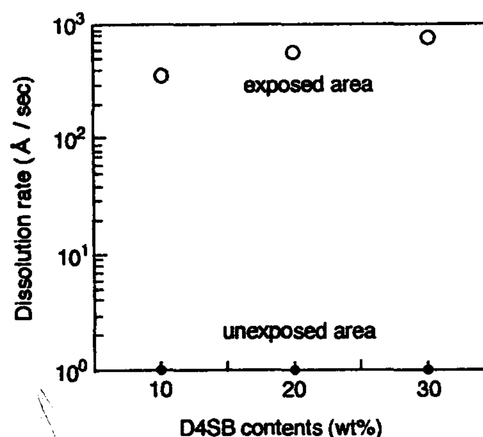


Figure 4. Relationship between dissolution rate and **D4SB** content

A photosensitive polymer system consisting of polymer **3** and 30 wt% **D4SB** in DMAc and toluene was formulated. The sensitivity curve for a 2.8 μm-thick polymer film **3** shown in Figure 5 was consistent with the dissolution behavior studied above, indicating that the sensitivity (D^0) and contrast (γ^0) were 60 mJ / cm^2 and 1.7, respectively.

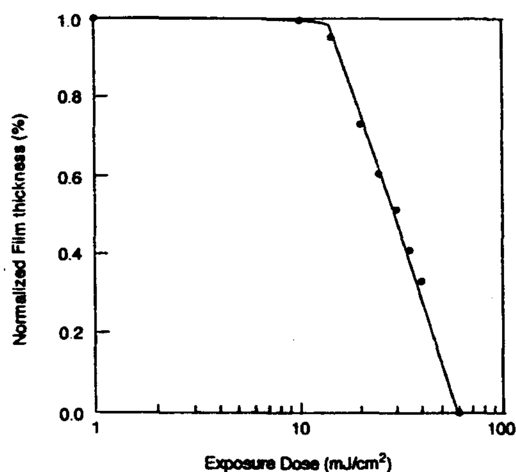


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Figure 5. Exposure characteristic curve for the system of polymer 3 and 30 wt% **D4SB.**

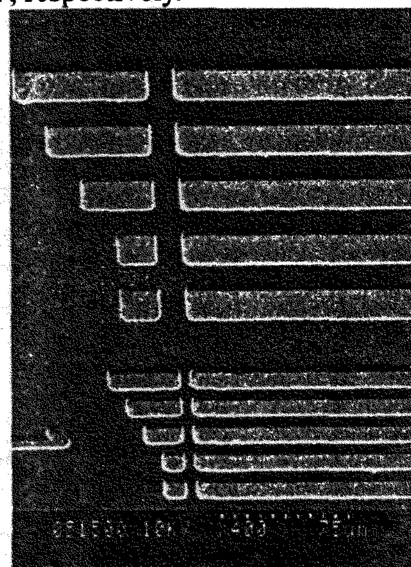

Figure 6. Scanning electron micrograph of the pattern from polymer 3 containing **D4SB.**

exposure of 300 mJ / cm^2 light, followed by development with the 2.38 wt% aqueous TMAH solution. Clear positive patterns with 10 μm resolution were obtained. Furthermore, this positive image in polymer film **3** was converted to a positive image of PI film by high-temperature treatment without any deformation.

Table.1 Refractive indices and estimated dielectric constants of polyimide films

polyimide	d (μ m)[a]	n_{TE}[b]	n_{TM}[c]	n_{AV}[d]	Δn[e]	ε[f]
Polymer 3	3.4	1.4908	1.4909	1.4908	-0.0001	2.44
Polymer 3 + D4SB	5.1	1.4927	1.4885	1.4913	0.0042	2.45

[a]Film thickness. [b]In-plane refractive indices. [c]Out-of plane refractive indices. [d]Average refractive index; $n_{AV} = (2n_{TE} + n_{TM})/3$. [e]Birefringence; $\Delta n = n_{TE} - n_{TM}$. [f]Optically estimated dielectric constant; $\varepsilon = 1.10 n_{AV}^2$.

Refractive Indices and Estimated Dielectric Constants

Average refractive index (n_{AV}) was calculated using the equation, $n_{AV} = (2\, n_{TE} + n_{TM}) / 3$, and in-plane/out-of-plane birefringence (Δn) is given as n_{TE}-n_{TM}. The results are listed in Table 1 along with those of a **D4SB**-containing polyimide. The n_{AV} of the PI (from polymer **3**) film is almost same as that of PI (from polymer **3** + **D4SB**). The dielectric constants (ε) of the material at optical frequencies can be estimated from the refractive index n according to the Maxwell's equation, $\varepsilon \fallingdotseq n^2$. The value of ε around 1 MHz has been evaluated as $\varepsilon \fallingdotseq 1.1\, n_{AV}^2$, including an additional contribution of approximately 10 % from the infrared absorption.[4, 18] The refractive indices of 1.4908 and 1.4913 determined for PI (from polymer **3**) and PI (from polymer **3** + **D4SB**) can be translated into dielectric constants of 2.44 and 2.45, respectively. These values are lower than the optically estimated ε of an alicyclic polyimide reported by Matsumoto et al. (2.55). The estimated value of ε (2.44) is ca. 22% smaller than that of a conventional aromatic polyimide (pyromellitic dianhydride + 4,4'-oxydianiline, 3.14). The incorporation of **D4SB** into PI is advantageous because it gives high photosensitivity without increase in dielectric constant.

Since birefringence is related to inherent anisotropy in molecular polarizability and degree of orientation of refracting units, it provides additional information regarding the orientation of polyimide. It has been reported that aromatic polyimides may exhibit large birefringence, indicating the preferential orientation of polymer chains to the film plane.[19] The Δn of the PI (from polymer **3**) film is nearly equal to zero, while that of PI (from polymer **3** + **D4SB**) exhibits a small positive value of Δn. The negligibly small birefringence of PI (from polymer **3**) implies that this polymer has small polarizability anisotropy, and the polymer chains are randomly oriented. On the other hand, the positive Δn of PI (from polymer **3** + **D4SB**) could be ascribed to the residual aromatic groups oriented in the film plane which were generated from thermally treated **D4SB** molecules.

Conclusions. Polymer **3** with a high molecular weight was prepared by the ring-opening polyaddition of *N*-silylated alicyclic diamine **1** and alicyclic dianhydride **2**. The photochemical reaction of **D4SB** in polymer **3** film occurred smoothly because of its excellent transparency in the UV region above 250 nm. Polymer **3** containing 30 wt% **D4SB** functioned as a positive type photosensitive polymer, and its sensitivity and contrast were 60 mJ / cm^2 and 1.7 with 365 nm light, respectively. The positive image of polymer **3** film after development was converted to the corresponding PI image by thermal treatment. A 10 % weight loss of the corresponding PI (from polymer **3**) under nitrogen was 420 °C. The optically estimated dielectric constant is 2.44, which is ca.22% lower than that of a conventional aromatic polyimide. The incorporation of **D4SB** into PI is advantageous because it gives high photosensitivity without an increase in the dielectric constant.

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