Recent Development in Photosensitive Polyimide (PSPI)

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Photosensitive polyimides (PSPIs) are attracting much attention as an insulating materials for microelectronic applications. PSPIs can be directly patterned, simplify processing steps and do not need a photoresist to be used in the micro-lithographic stage, nor a toxic etchant. This review introduces the recent development of PSPIs with emphasis placed on the chemistry responsible for images.

Keywords: photosensitive polyimide, positive-type, negative-type, dielectric constant, porous polyimide

1. Introduction

Photosensitive polyimides (PSPIs) are widely used as protection and insulation layers in semiconductor manufacturing because of their excellent properties such as thermal and chemical stabilities and low dielectric constants. In addition, they are used as insulating films for print wiring boards (PWBs), and the application area in the microelectronics field still continues to expand. PSPIs are also attractive since they simplify processing and avoid the use of photoresist in microelectric industry. Patterning process of polyimide is shown in Fig. 1.

Both photoresists for semiconductor processing and PSPIs have been used for image formation process. However, PSPIs are finally mounted to the electronic devices as a polyimide film, whereas photoresists are removed after processing. Therefore, polymer design of PSPIs must consider two factors as shown in bellow, 1) image formation, (sensitivity, resolution, development system, heat treatment condition (imidization), etc.).

2) film properties as a polyimide (mechanical strength, electrical characteristics, dimensional stability, adhesive property, purity).

Imaging technique is depending on how to introduce a photosensitivity and how to design a polymer chemical structure that affects the film properties. So, it is considered to be a promising way that these two important requirements are satisfied simultaneously for the development of PSPIs.

Fig.1 Pattering Process of Polyimide

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This review addresses the recent progress of PSPIs, and focuses on how to introduce photochemistry to polyimides (PIs). Other related reviews have been reported elsewhere [1,2].

2. Negative-type Photosensitive-polyimide

Most commercial PSPIs are based on polyamic acid (PAA) where cross-linking sites are introduced to amic acids through ester [3] and acid-amine ion linkages [4] as shown in eq. (1).

Although these two representative PSPIs have a similar polymer structure with methacrylate groups, the mechanism of photochemical reaction is different. In case of ester-type PSPI, the methacrylate of PAA exposed to UV irradiation results in a cross-linked PI-precursor. On the other hand, the charge-transfer complex between PAA and a sensitizer (N-phenyldiethanolamine) is formed without the cross-linking reaction by UV irradiation in the ionic bond-type PSPI. The radical formed undergoes an intersystem crossing to a triplet state, and the anion radical pair is formed in pyromellitic diamide part in the polymer matrix. The charge separation by this UV irradiation is considered to be the image formation mechanism. In addition, this system has higher sensitivity than the ester type PSPI, because the polymer structure itself functions as a sensitizer. To develop these PSPIs, the mixture of polar solvents such as N-methyl-2-pyrrolidone and alcohol are used as a developer. After removing the unexposed polymer by developing, the negative image is formed. Then, the cross-linked methacrylate groups are thermolyzed during curing to give PI. The final film thickness decreases to a half compared to the thickness before developing due to volatilization of the cross-linked methacrylate moiety of PSPI precursor.

PSPI (eq. (2)) without using photoreactive amic acid moiety has been reported [5]. The polyimide synthesized from 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA) and diamine having alkyl group in ortho position. After exposed to UV light, the polymer becomes insoluble to organic solvent as a developer. This is due to the formation of cross-linked polymer as a result of radical coupling, which is caused by hydrogen abstraction from the alkyl group by the triplet state benzophenone generated by UV irradiation. Decrease of film thickness after the heat treatment is drastically improved, because the imaging process completes simply by removing the soluble part [6].

The following PI containing chalcone moiety in the main chain was reported as negative-type PSPI using photo-crosslinking reaction [7]. Its sensitivity and contrast were 33 mJ/cm² and 1.5 respectively, upon UV irradiation (eq. (3)).

PSPI system composed of PI having furan moiety and fullerene (C₆₀) as a photosensitizer have provided a negative-tone image (eq. (4)) [8].
Photo-chemical reaction of PI containing pendant propargyl ester groups was examined using various photo-acid generators (PAG) (eq. (5)). Insoluble polymer film was obtained upon UV irradiation as a result of photo-generated acid catalyzed cationic polymerization [9].

3. Positive-type Photosensitive-polyimide

Positive working PSPIs are consistent with the trend of using an aqueous base solution as a developer for the photore sist processing technology in the microelectronic industry. Positive working photoresists based on novolac resins with diazonaphthoquinone (DNQ) are standard materials used in LSI manufacturing, where DNQ acts as a dissolution inhibitor for aqueous base development (eq. (6))[10].

3-1. 2-Nitrobenzylester-type

It is well known that aromatic nitro compounds containing benzylic hydrogens at the ortho to the nitro group are light sensitive (eq. (7)). A positive working PSPI was prepared from pyromellitic dia[α-(2-nitroph enyl)ethyl]ester employing this mechanism [11]. The photo-rearrangement of the 2-nitrobenzyl ester causes a cleavage of the ester bond (eq. (8)), and the exposed area is converted to alkaline soluble film. Thus, this dissolution contrast provides a positive image.

Phenol compounds have adequate solubility to the aqueous alkaline solution. Because pKa values of phenol compounds are about 10, while pKa value of a carboxyl group in PAA is about 5. Alkaline-soluble polymers were prepared from PAAs, which are introduced to the phenolic hydroxyl groups through ester (eq. (9)) or acid-amine ion linkages (eq. (10)). These polymers were formulated with DNQ to make PSPI precursors and provided positive images [12]. Although the loss of final film thickness after converting into the polyimide seems to be larger than that of conventional negative-type PSPIs, these PSPI precursors can be developed using an aqueous alkaline solution with a practical sensitivity.

3-2. System of Polyamic Acid (PAA)/Dissolution Controller

The resist system consisting of an alkaline-soluble polymer matrix and a certain
dissolution inhibitor such as a DNQ [13] has been reported. However, it is difficult to get large difference of solubility between the exposed and unexposed area, because the solubility of PAA to the aqueous alkaline solution is too high. To overcome this problem, the system consisting of PAA having hydrophobic structure and DNQ was investigated (eq. (11, 12)). These PSPI precursors have a high sensitivity and good resolution [14].

The PSPI was successfully applied to development of the second-order nonlinear optical (NLO) materials (eq. (14)) [17]. The PAA containing NLO units and DNQ system functioned as an alkaline developable resist and then was converted to the PI by corona poling during the thermal imidization process. The second harmonic coefficient (d33) of the resulting PI at the wavelength of 1064 nm was 53 pm/V and remained unchanged at higher temperature (180 °C).

The PSPIs consisting of PAAs and dissolution controllers have industrially great advantages due to no restriction for the chemical structure of PIs.

4. System of Polyhydroxyimide (PHI) as a Matrix Polymer

4-1. System of PHI/DNQ [18]

Polyhydroxyimide (PHI) having phenol units in polymer chains has an appropriate solubility to an aqueous base solution. Thus, positive working alkaline-developable PSPIs based on PHI and DNQ have been reported. The PHI containing 30 wt% of diazodihydroxynaphtoquinone-4-sulfonate showed a good sensitivity of 250 mJ/cm² and excellent contrast of 5.2 when it was exposed to 436 nm light followed by developing with a 1% aqueous TMAH (tetramethylammonium hydroxide) solution at 35 °C (eq. (15)). The thermal stability after post-development bake is almost the same as for the neat resin of PHI.
4-2. System of Chemical Amplification based on PHI (Positive-type: Deprotection reaction) [19]

PSPI employing the chemical amplification mechanism has been developed (eq. (16)). PHI was converted to the alkaline-insoluble polymer by protecting the phenolic hydroxyl group. Two-component resist system consisting of photo-acid generator (PAG) and the protected PHI as a matrix polymer has been investigated. The tert-butoxycarbonylated (t-BOC) matrix polymer can be deprotected by the photo-generated acid (eq. (17)). In exposed area, diffusing the photo-generated acid from PAG accelerates the deprotection reaction, and the matrix becomes the alkaline soluble polymer to provide a positive tone image.

4-3. System of Chemical Amplification based on PHI (Negative-type: Cross-linking reaction) [20]

The negative-type alkaline developable PSPI has also been reported. Three-component resist system containing PHI and 2,6-bis(hydroxy-methyl)-4-methylphenol (BHMP) as a cross-linker, and a photo-acid generator; diphenyldiodonium-9,10-dimethoxyanthracene-2-sulfonate (DIAS) was developed (eq. (18)). The PSPI containing 70 wt% PHI, 20 wt% BHMP, and 10 wt% DIAS showed a sensitivity of 70 mJ/cm² and a contrast of 3.8 when it was exposed to 365 nm light and post baked at 120 °C, followed by developing with a 2.5 % aqueous TMAH solution at 40 °C. The photo-generated acid catalyzes the formation of benzylc carbocation species, which undergo electrophilic aromatic substitution to produce a C- and O-alkylated polymers. This reaction converts the soluble linear polymer to the insoluble cross-linked polymer.

Hyperbranched polymers have been attracting great interest for their unique properties such as intrinsic globular structure, low viscosity, high solubility and large number of terminal functional groups [21].

The hyperbranched polymer, poly(ether imide) was successfully employed as matrix polymer for PSPIs. Thus this matrix containing a cross-linker and a photo-acid generator worked as a negative-type PSPI and showed a high sensitivity and a good contrast. (eq. (19)) [22].

5. System of Polyamic Ester (PAE) or Polyimide with Pendant Carboxylic Acid

To optimize the dissolution rate of base polyimide precursor in a TMAH solution, polyamic ester (PAE) with pendant carboxylic acid (PAE-COOH) was prepared (eq. (20)). The dissolution rate of PAE-COOH was controlled by the content of pendant carboxylic acid. It was found that the photosensitive system composed of PAE-COOH and a DNQ compound showed a good sensitivity and resolution. The obtained patterns were fully cured at 330 °C to the PI ones [23].

The PSPI system composed of PIs having pendant carboxyl groups and DNQ were also studied. The sensitivity and the contrast of this
resist system were 1,200 mJ/cm² and 1.3 for 15 µm of film thickness, respectively (eq.(21)).[24]

6. System of Polyimide with Acid Degradable Unit

A series of PIs with carboxyl groups in the ends of main chain was synthesized and used for three-component PSPIs, consisted of the polyimide, vinyl ether monomer, and photo-acid generator (DIAS) (eq. (22)). An increase in the acid value and decrease in the molecular weight enhance the sensitivity based on dissolution rate by cleavage reaction. This PSPI act a positive-type resist with the process of UV irradiation and PEB, and showed a sensitivity of 137 mJ/cm² and a gamma value of 2.9 [25].

The PIs having cyclobutane and aromatic sulfonloxyimide units in the main chain also function as positive-working photodegradable polymers [27].

7. System of Polyimide (PII) as a Polyimide-precursor [28]

PIIs have an excellent solubility and lower glass transition temperature (Tg) than those of the corresponding PIs, and are easily isomerized to the corresponding PIs without elimination of volatile compounds such as water. Furthermore, the isomerization is accelerated by acid or base catalyst. Therefore, the new PSPI system consisting of PII, dissolution controller, and photobase generator (PBG) has been reported.

7-1. System of PII/DNQ[29]

PSPI precursor based on PII and DNQ derivative was investigated. The sensitivity and contrast of the PSPI system consisting of PII and 20 wt% of diazonaphothoquinone-4-sulfonate (eq. (24)) were 250 mJ/ cm² and 2.4, respectively when it was exposed to 436 nm light. This PSPI system is capable of resolving a 2.5 µm feature when a 5 µm thick film is used.
PII copolymer as shown in eq. (25) is soluble in organic solvents, and gives positive image by combination of diazonaphthoquinone-5-sulfonate. The PI obtained from the PII showed an excellent dimensional stability and their thermal expansion coefficients ($\alpha$) can be controlled within 0-60 ppm.

7-2. System of PII / photo-base generator (PBG)[30]

\[
\begin{align*}
\text{PII} + \text{PBG} \xrightarrow{\text{UV}} & \text{PI} + \text{H}_{2}\text{N}\text{C} \\
\text{PI} \xrightarrow{\text{PEB}} & \text{PII}
\end{align*}
\]

PSPI using isomerization of PII by the photo-generated amine has been reported. The isomerization degree of the exposed PII film containing 30 wt% of photo-base generator (PBG) (eq. (26)) reached to 70% at PEB temperature of 150°C for 5 min, while no significant isomerization was observed in the unexposed film. This isomerization reaction is catalyzed by photo-generated base (dimethyl piperidine) (eq. (27)).

The PII containing 10 wt% of PBG functioned as a negative type PSPI with good contrast due to a large difference in the solubility between PII and PI. This system is utilized isoimide-imide isomerization by base catalyst.

8. System of Alicyclic Polyamic Acid Silylester/DNQ [31]

Alicyclic structures are effective to decrease a molecular density because of their bulkiness and no multiple bonds, giving PIs with a low dielectric constant.

Recently, a positive working photosensitive alicyclic polyimide precursor based on polyamic acid tert-butyldimethylsilylester and DNQ was developed (eq. (28)). This resist system showed a sensitivity of 60 mJ/cm² and a contrast of 1.7 upon 365 nm light, followed by developing with a 2.38 wt% TMHA solution. The positive image in this polymer was converted to the PI film by thermal treatment. The optically estimated dielectric constant of the PI film was 2.45.

9. Next generation PSPI: Low Dielectric Constant PSPI

9-1. Non-porous Low Dielectric Constant PSPI

Propagation velocity ($V$) of electrical signal through the wiring and dielectric loss ($\text{Ad}$) can be calculated according to the eq. (29) and eq. (30). These relationships indicate that the lower $\varepsilon$ gives higher $V$ and lower $\text{Ad}$. Furthermore, materials with small dielectric dissipation factor in the high frequency range are required.

\[
V = k \cdot C \cdot 1/\varepsilon^{1/2} \quad (29)
\]

\[
\text{Ad} = 27.3 \times f/c \times \varepsilon^{1/2} \times \tan \delta \quad (30)
\]

(\(f\): frequency; \(\varepsilon\): dielectric constant; \(C\): velocity of light; \(k\): constant)

Table 1. $P$ and $V$ values of various atomic groups

<table>
<thead>
<tr>
<th>Atomic group</th>
<th>$P$(cm$^3$/mol)</th>
<th>$V$(cm$^3$/mol)</th>
<th>$P/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-F$</td>
<td>1.80</td>
<td>19.9</td>
<td>0.01</td>
</tr>
<tr>
<td>$-CF_3$</td>
<td>5.37</td>
<td>37.3</td>
<td>0.14</td>
</tr>
<tr>
<td>$-CH_3$</td>
<td>5.64</td>
<td>23.9</td>
<td>0.24</td>
</tr>
<tr>
<td>$-NH_2$</td>
<td>4.05</td>
<td>18.8</td>
<td>0.25</td>
</tr>
<tr>
<td>$-Ph$</td>
<td>2.50</td>
<td>65.5</td>
<td>0.04</td>
</tr>
<tr>
<td>$-O$</td>
<td>5.20</td>
<td>30.0</td>
<td>0.18</td>
</tr>
<tr>
<td>$-CO_2$</td>
<td>15.0</td>
<td>23.0</td>
<td>0.65</td>
</tr>
<tr>
<td>$=CN$</td>
<td>11.0</td>
<td>25.5</td>
<td>0.71</td>
</tr>
<tr>
<td>$-CONH_2$</td>
<td>10.0</td>
<td>25.4</td>
<td>0.75</td>
</tr>
<tr>
<td>$-CONH$</td>
<td>30.0</td>
<td>20.8</td>
<td>1.48</td>
</tr>
<tr>
<td>$-OH$</td>
<td>17.0</td>
<td>9.70</td>
<td>1.75</td>
</tr>
</tbody>
</table>

\[\varepsilon = \frac{(1 + 2 \cdot \Sigma P/EV)}{(1 - \Sigma P/EV)} \quad \text{P: Molar Polarization}(\text{cm}^3/\text{mol})\]

\[V: \text{Molar Volume}(\text{cm}^3/\text{mol})\]
Thus, low dielectric materials, which are used as coating film of wiring, are useful for communication and microelectronic industries. Eq. (31) is the well-known Clausius-Mossotti equation used for calculating the value of dielectric constant ($\varepsilon$) of polymers [32].

$$\frac{(\varepsilon - 1)}{(\varepsilon + 2)} P / V$$

Where $P$ is the molar polarization (cm$^3$/mol) and $V$ is the molar volume (cm$^3$/mol). To make a polymer with low dielectric constant, it is very effective to select the atomic groups comprising the molecule having lower $P/V$ values. The $P$ and $V$ values of various atomic groups are listed in Table 1.

From this table, fluorine-containing polyimides are expected to have a small molar polarization. In facts, these PIs with the lower dielectric constant were reported [33]. These monomers, however, require the multi-step synthesis.

<table>
<thead>
<tr>
<th>R: Diamine</th>
<th>$\alpha$ (ppm)</th>
<th>$\varepsilon$ Found.</th>
<th>$\varepsilon$ calc'd</th>
</tr>
</thead>
<tbody>
<tr>
<td>FKRT-1</td>
<td>54</td>
<td>2.6</td>
<td>2.5</td>
</tr>
<tr>
<td>FKRT-2</td>
<td>57</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>FKRT-3</td>
<td>62</td>
<td>2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>FKRT-4</td>
<td>60</td>
<td>2.5</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Table 2. Properties of various 6FDA polyimides

To achieve the lower $P/V$ value, diamines introducing non-fluorinated atomic groups have been developed (eq.(32)) [34]. Dielectric constant of PIs prepared from these diamines and fluorinated dianhydride (6FDA) are 2.5-2.6 (Table2). By copolymerizing these PIs with low thermal expansion PIs (eq.(33)), low dielectric constant PSPIs (FK-1 – FK-4) that have excellent dimensional stability were developed. Thermal expansion coefficients ($\alpha$) of these polymers were 18-20 ppm (Table 3).

Moreover, the propagation velocity of signal in copper wire insulated with this low dielectric constant PSPI was 7% faster compared to that of conventional PI (Table 4). This result clearly showed low dielectric constant PSPIs effective to improve the propagation velocity of signal transmission on PWB [34].

9-2. Porous Polyimide

An advantage of foam formation is clearly apparent to make a low dielectric constant PI, because pores are filed with air (dielectric constant =1). According to the advancement on the
shrinkage of dimension in integrated circuits, low-k insulators are receiving much attention for application for LSI industries [35]. Recently, studies and reviews on the porous polyimide have been reported [36]. Hedrick et al. prepared the block copolymer containing PPO (polypropylene oxide) into the PI backbone as shown in Fig.2 [37]. PPO was chosen as a thermally labile component for the porous PI precursor synthesis because of its ability to withstand temperatures of 300 °C when heated in an oxygen-free atmosphere. Incorporation of pore sizes in the nanometer scale was achieved by using a block copolymer approach for the preparation of porous PIs in which a thermally labile block is uniformly dispersed in a matrix polymer. Subsequent thermal treatment degrades the thermally unstable component leaving pores with size and shape corresponding to the original morphology of the phase separated block copolymer.

Another modification of the labile block approach is the formation of poly(amic alkyl ester) precursor, where thermally labile PPO chain is attached to the carboxylic acid of PI precursor through ester linkage (Fig.3)[38]. The PPO-containing poly(amic alkyl ester) undergoes imidization without PPO decomposition. PPO can be selectively removed via thermal degradation by heating the PI/PPO composite at 240 °C in the presence of oxygen (in air) without degradation of the PI matrix. The dielectric constant of the porous PI was reported bellow 2.0.

The monomer synthesis, however, is required each time the polymer structure is changed, and this change also influences the performance of polyimide. Therefore, these techniques seem to have many problems for developing the porous PSPIs. Thus, another new concepts would be required to develop photosensitive porous polyimides in the next future.

10. Summary

The representative PSPIs using the various image formation mechanisms were introduced. The simple mixture of PAA and photosensitizer is the most convenient, and is industrially important. To make such PSPI system with a high sensitivity and a high resolution, it is necessary to develop a new dissolution controller for PAA.

Although the system of polyhydroxyimide (PHI) and DNQ provide a positive tone image using aqueous alkaline developer, moisture absorption is high because of the remaining of hydroxyl groups after imaging process. On the other hand, polybenzoxazole (PBO) precursor can utilize a hydroxyl group dose not remain after thermal cyclization. This chemistry is important to develop PSPIs with low dielectric constants.

PSPIs will meet most of the material requirements for microelectronics, and it is desirable to improve the electrical performance of these materials by reducing the dielectric constant and dielectric dissipation factor.

References


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