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REVIEW ARTICLE

Recent Progress of Photosensitive Polyimides

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Photosensitive polyimides (PSPIs) have been attracting great attention as insulating materials in microelectronic industry, and can be directly patterned to simplify processing steps. This article reviews recent works on development of PSPIs. After brief introduction, a typical PSPI formulation was described in comparison with a conventional method, followed by major strategies for the patterning. A number of recent reports on PSPIs were then divided into two major terms; positive-working and negative-working, and highlighted with focus on their chemistries up to pattern formation. In addition to the photosensitivity of PSPIs picked up in this review, other important subjects such as low-temperature imidization and low dielectric constants were also discussed.

KEY WORDS: Photosensitive Polyimide / Poly(amic acid) / Photosensitive Compound / Diazonaphthoquinone / Photochemical Amplification / Photoacid Generator / Photobase Generator / Low Temperature Imidization /

The importance of photosensitive polyimides (PSPIs) as practical packaging and/or insulating materials in microelectronics has increased in recent years. For instance, buffer coatings, passivation layers, alpha particle barriers, interlayer insulations, and wafer scale packages, are widely used in the industrial manufactures including integrated circuits (ICs) and multi-chip packages (MCPs). Advances in outstanding property of polyimides (PIs) as thermally stable polymers along with expanded sources of monomers, have established that PSPIs can function over much broader range.

With regard to the synthesis of PIs, poly(amic acid) (PAA) as a PI-precursor is typically prepared by ring-opening polyaddition of two monomers; a tetracarboxylic dianhydride and a diamine, which produces no side products (Scheme 1). This simple chemistry and environmentally benign process allow us to evaluate photolithographic characterization directly from the polymerization solution (varnish), prompting to employ in industrial manufacturing. The PI films are mostly formed by thermal treatment of PAA (up to 350 °C) after casting the solution on a substrate. Such thermal imidization process addresses recently another aspect to be considered and claims an improvement toward low-temperature cyclization.

Giving photosensitivity onto PIs or PI precursors enables them to produce pattern formation that simplifies the process significantly. Some PSPIs have taken over excellent chemistries developed by photoresists for microlithography, some have been employed with dissolution inhibitors, and some others have been involved in characteristics of own PIs. The most significant difference between PSPIs and photoresists is that PSPIs remain in the final manufactured products whereas the photoresists would be removed after pattern transfer to under-laid materials. Thus, PSPIs are demanded mainly for two distinctive respects as shown in Figure 1; (i) photolithographic properties to make patterns; (ii) quality and durability required as final products. Imaging technique depends on photosensitivity introduced into a PSPI system as well as design of polymer structure which is also effective for the PI film properties. PSPIs should be consistent and satisfied with these factors simultaneously.

Although PSPIs have been greatly contributed to the progress of microelectronics thus far, improving the versatility and robustness as well as resolution of the patterns is still crucial for expanding the utility of PSPIs in this important area.

This review article highlights a recent progress of PSPIs including new concepts such as reaction development patterning, low-temperature imidization and mechanism-induced patterning etc. After brief introduction of a typical patterning process of PSPIs, various chemistries on PSPIs are described along with two major pattering methodologies; positive-, and negative-working PSPIs. The previously and/or originally developed PSPIs have been reviewed in the other literatures.[1–5]

PHOTOLITHOGRAPHIC PROCESS OF PSPI

It is noteworthy that "PSPI" involves not only photopatternable PI with photoactive agents, but also photopatternable PI-precursor such as PAA or poly(amic ester) with photosensitive compounds. Thus, PSPI could be defined as that the origin of photosensitivity relies on either PI (or its precursor) matrix; or additives mixed with the matrix polymer. PI pattern formation by plasma etching through a patterned photoresist layer is not included in the PSPI system, which is known as a conventional fashion.

In this section, comparison of PI pattern formation in a conventional method and that using PSPI is described, followed by typical lithographic strategies—dissolution inhibitor, and chemical amplification (CA).

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Scheme 1. Synthesis of polyimide (PI) *via* poly(amic acid) (PAA).

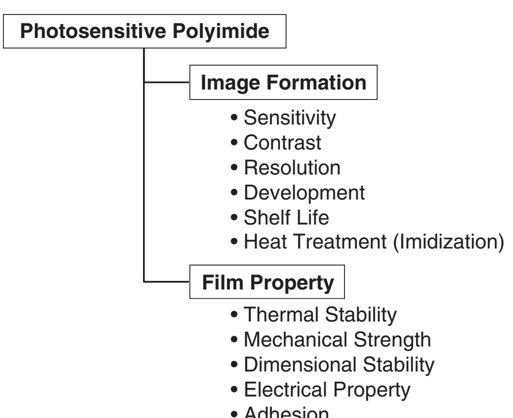

Figure 1. Requirements for development of PSPIs.

Patterning Process of PSPI *vs.* Conventional PI

Schematic representatives of photolithographic processes are shown in Figure 2. In a conventional method (Figure 2(a) and (b)), PIs are shaped into micropatterns by transfer of photolithographic patterns of an additional photoresist coated on a PI layer. Therefore, pattern formation of the photoresist and the following etching procedure are required. On the other hand, by incorporation of photosensitivity into PIs (or PI precursor), PSPIs enable to simplify a patterning process owing to elimination of a photoresist layer (Figure 2(c) and 2(d)). If a PI precursor is utilized for pattern formation, it is possible to convert the precursor pattern into the corresponding PI one by thermal imidization.

After a photosensitive polymer is spin-coated onto a substrate of interest (*e.g.*, a silicon wafer), this coated film is exposed to a UV light through a mask so that pattern information can be transferred to the film. As the source of UV light, wavelength at 436 nm (*g*-line) or 365 nm (*i*-line) is usually chosen for the lithography with PSPI materials. This photo-irradiation allows a coated polymer to undergo a

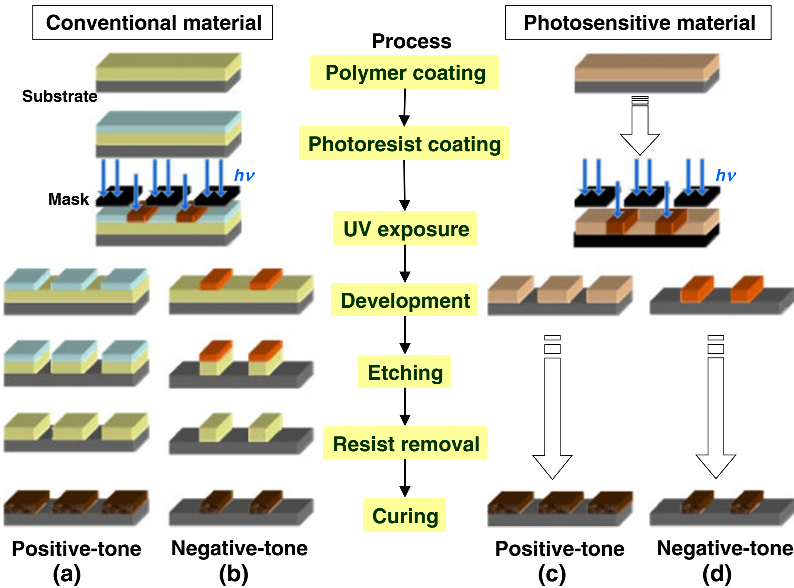

Figure 2. Photolithographic patterning processes in conventional methods using photoresists (a & b) and in advanced methods using photosensitive materials (c & d). Positive-tone can be formed if the exposed area is washed out at the development (a & c), whereas negative-tone can be patterned if the removal of unexposed area is carried out (b & d).

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chemical change such as deprotection, polarity change, chain-scission, cross-linking, imidization up on a post-exposure bake (PEB) (if necessary). In the following step of development, either the exposed or unexposed area is selectively removed resulting in a pattern formation. When the exposed area is washed out, that resist system is categorized in a positive-working (Figure 2(a) and 2(c)). On the other hand, a negative-working refers when the exposed area becomes insoluble in the developer (Figure 2(b) and 2(d)).

In this regard, photolithographic evaluation involves many aspects, in other words, many flexibility to optimize for the best performance of patterning. For instance, the sensitivity of PSPIs depends on the transmittance of the polymer as coated on the substrate and the quantum yield of photosensitive units at the exposure wavelength, whereas the contrast is a function of the rate of cross-linked network formation for a negative resist and the rate of deprotecting reaction for a positive resist at a constant input dose. Furthermore, the rate of change of solubility with the proportion of the deprotection is dependent on the developer. Thus, there is a variety of the photosensitive polymer matrices incorporating additives such as photosensitizers (*e.g.*, diazonaphthoquinones (DNQs) and photoacid generators (PAGs)) or cross-linkers, etc.

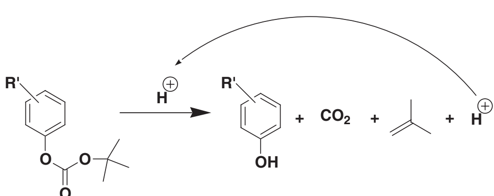
Dissolution Inhibitor Additive

Novolac resins and DNQ compounds as alkaline soluble matrices and dissolution inhibitors, respectively, represent classical positive-working photoresists for microlithography.[6–8] Proposed patterning mechanism of these widely used resists highlights a photochemical transformation of DNQs into indenecarboxylic acid derivatives (Scheme 2) accelerating dissolution in aqueous alkaline solutions, whereas DNQs themselves are hydrophobic to inhibit solubility of matrix polymers. A number of PSPIs with DNQs have been demonstrated, some of which are described below in positive-working PSPIs.

Chemical Amplification (CA) System

CA consists of a chemical reaction that generates species and catalyzes another reaction simultaneously, thus accelerating the consecutive catalyzed reaction. CA can lead to a change in structure and physical properties of a polymeric material with a minimum amount of UV exposure energy. For a typical example of CA, transformation of [(*tert*-butoxycarbonyl)oxy]-phenyl groups in polymer chains to hydroxyphenyl groups catalyzed by a photo-generated acid (Scheme 3) has been utilized in the microlithography.[9]

Scheme 2. Transformation of DNQ derivative upon UV exposure.



Scheme 3. Chemical amplification (CA) system.

Applying this chemistry to PSPIs, Omote *et al.* reported, for examples, PSPIs having pendant acidolytic blocking groups—(*tert*-butoxycarbonyl)oxy[10,11] and tetrahydropyranyl[12] groups (Table I, No. 1)—with a PAG where photochemically generated acid catalyzes deprotection continuously upon a thermal treatment. This system exhibits higher photosensitivity, however, requires more precisely controlled conditions.

POSITIVE-WORKING PSPIs

To avoid a swelling problem often occurred in negative-working resists as well as environmental and safety issues caused by organic solvent developers in the industrial level, positive-working and aqueous alkaline developable PSPIs are desirable. A variety of positive-working PSPIs developed with different chemistries is described in the following sections. Each structure of positive-working PSPIs' is summarized in Table I.

o-Nitrobenylester Type

An *o*-nitrobenzylester is a photosensitive group that can be eliminated upon UV irradiation through a transformation into *o*-nitrosobenzaldehyde and a carboxylic acid as shown in Scheme 4.

A positive-working PSPI based on a poly(amide *o*-nitrobenzylester) was developed (Table I, No. 2),[13] where the ester-bond was cleaved into the PAA and *o*-nitrosobenzaldehyde upon UV exposure.

Recently, two types of positive-working PSPIs having fully imidized backbones with *o*-nitrobenzylester groups as side substituents were reported (Table I, No. 3 and 4).[14,15] Employing PI structure as a polymer matrix instead of PAAs or poly(amic ester) derivatives can avoid problematic volume shrinkage in the stage of thermal treatment. The *o*-nitrobenzylester group was chemically bound to PI chain to overcome the drawback described above. Thus, it allowed developing with an aqueous alkaline solution; however, this resist system had synthetic difficulty and low photosensitivity.

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Table I. Positive-working PSPIs.

No.	Matrix polymer (+cross-linker)	Additive	Ref.
1		PAG	10–12
2			13
3			14
4			15
5		DNQ	16
6		DNQ	17
7		DNQ	18
8		DNQ	20
9		DNQ	23

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Continued.

No.	Matrix polymer (+cross-linker)	Additive	Ref.
10		DNQ	25
11		DNQ	27
12		DNQ	28
13	$-R = -(CH_2)_3CH_3$; -R' = $-SO_2-$ (diazonaphthoquinone) and -H		29
14	$-R_3 = -(CH_3)_2C(CH_3)_3$	DNQ	31
15		DNQ	32
16		DNQ	33
17	$-R- = -(CH_2)_4-$, ...	DNQ	38

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No.	Matrix polymer (+cross-linker)	Additive	Ref.
18		DNQ	39
19	Ali = (two aromatic structures, and)	DNQ	41
20		PBG	43
21	+ cross-linker	PAG	45
22	+ cross-linker; Ali = alicyclic diamine	PAG	46
23	$-R = -CH_2OC_2H_6$ and $-H$	PAG	47
24	-X- = (ether diphenyl) and $-(CH_2)_3-Si-O-Si-(CH_2)_3-$; blended with the polymer No. 15	PAG	49

DNQ: diazonaphthoquinone derivative, PAG: photoacid generator, PBG: photobase generator.

Scheme 4. Photochemical decomposition of *o*-nitrobenzylester.

[PAA/Dissolution Inhibitor] System

PI resist systems based on alkaline-soluble polymeric matrices and certain dissolution controllers such as DNQs have been reported. Generally, PAAs are very soluble in an aqueous alkaline solution. Thereby, a system of PAA and DNQ brings difficulty to obtain a large dissolution contrast between

Scheme 5. Dissolution inhibition mechanism with DHP.

the exposed and unexposed regions. This problem was resolved by (i) introduction of more hydrophobic structure (namely, increasing the aromatic and fluorine contents) into the PAA, and (ii) reducing the content of carboxylic acid in the repeating unit of the polymer (Table I, No. 5 and 6), resulting in reasonably high sensitivity and good resolution.[16,17]

From the point of low coefficient of thermal expansion (CTE), Hasegawa and his coworkers established poly(ester imide)s possessing low CTE values close to copper foil (*i.e.* 17 ppm/K), high modulus, and low water absorption simultaneously (Table I, No. 7).[18] The low water absorption was attributed to decreasing the imide content by introduction of aromatic ester linkages into the main chains. Then, they applied to PSPI system in conjunction with flexible imide sequence to meet suitable solubility toward alkaline developer. This procedure could ensure the precise control of carboxylic acid content compared to thermally induced partial imidization. PSPIs from their work gave fine patterns in the range of 10–20 μm line-and-space as well as low CTE (12–23 ppm/K) close to that of copper foil.

On the basis of newly synthesized PAAs derived from 2,2′,6,6′-biphenyltetracarboxylic dianhydride,[19] Sakayori *et al.* reported a new positive-working PSPI system with DNQ (Table I, No. 8).[20] This PAA demonstrated good solution stability at room temperature and high transparency at 365 nm because of the twisted conformation which could suppress both the intramolecular acidolysis and the π-electron conjugation in the biphenyl structure. The sensitivity and contrast were evaluated to be 110 mJ/cm^2 and 2.0, respectively, when *i*-line was exposed to the 1.3 μm-thick resist film.

As for another type of photoreactive dissolution inhibitor, 1,4-dihydropyridine (DHP) derivatives such as nifedipine known as a medicine were also utilized in PSPI systems. The two types of the photochemical reactions with DHP were proposed as follows: (a) When the temperature for PEB is low, DHP is converted into the corresponding pyridine derivative in the exposed area so that it can solubilize in alkaline developer to formulate a positive-working PSPI (Scheme 5).[21] On the other hand, (b) when the PEB temperature is high (*ca.* 160 °C or higher), the dissolution behavior is reversed because the photo-generated pyridine derivative functions as a base catalyst promoting the thermal imidization to produce a negative-working PSPI.[22]

Phenolic OH-containing PAA or PI Type

Since a poly(hydroxyimide) (PHI) forms final imide structure, there is less concern about film shrinkage upon thermal treatment. A PSPI incorporated with a DNQ (30 wt %) in the PHI film have been reported (Table I, No. 9),[23] where the photosensitivity and contrast were 250 mJ/cm^2 and 5.2, respectively, by development with 1 wt % tetramethylammonium hydroxide (TMAH). It was noted that not only the polymer architecture but the structure of DNQ derivatives played important roles for better lithographic performance including sensitivity and pattern profile.[24]

The photosensitive semi-alicyclic PHI with a low dielectric constant was reported by Jin and Ishii.[25] It was prepared from hydrogenated pyromellitic dianhydride and bis(*o*-amino phenol) (Table I, No. 10), evaluating the dielectric constant to be 2.75 at 1.0 MHz estimated from the refractive index (1.58). The PSPI based on the PHI and DNQ (20 wt %) showed the photosensitivity and contrast of 350 mJ/cm^2, 1.2 (film thickness 7.5 μm), respectively.

By their further investigation, the transparency of the PSPI film strongly depended on the thermal treatment temperatures.[26] Since the polymer was chemically imidized in γ-valerolacton/pyridine mixture at 180 °C, no thermal imidization was generally required after the patterning process. However, post curing at lower temperature than glass transition temperature (T_g) induced higher transparency of the resulting PI film compared to that cured at higher temperature than T_g. Less transparency after the thermal treatment (*ca.* 15 K higher than its T_g) would be attributed to decreasing the film amorphousness as the residual solvent was evaporated from the film and reducing intermolecular free volume. The low-

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Scheme 6. Mechanism of Reaction Development Patterning (RDP).

temperature thermal treatment, however, slightly increased the CTE of the resulting PI film.

Introduction of a phenolic hydroxyl group into a PAA through ester (Table I, No. 11)[27] or ionic linkages (Table I, No. 12)[28] was also demonstrated to obtain similar behavior of PHIs in the presence of DNQs.

Poly(amic ester) Bearing DNQ Moiety Type

Despite of too high solubility of PAA in an aqueous alkaline solution, aqueous development is desirable for practical utilization of PSPIs in the industry. One of the solutions to avoid PAA dissolution in an aqueous alkali is capping a carboxylic acid group to an ester group (*e.g.* poly(amic ester)). Hsu *et al.* reported a formulation of aqueous alkaline developable PSPI based on a poly(amic ester) bearing a phenolic hydroxyl group.[29] The phenol moiety was introduced into the polymer by using bis(aminophenol) monomer, and DNQ was then attached partially to the phenol group (Table I, No. 13). Once the DNQ undergoes photolysis and is converted to indenecarboxylic acid with releasing phenolic groups, this resist system become soluble in an alkaline solution. A 25 mol % DNQ-capped poly(amic ester) containing 25 wt % photosensitive compound showed a sensitivity of 176 mJ/cm^2 and a contrast of 1.68 in a 3-μm film with 1.25 wt % TMAH developer. A pattern with a resolution of 5 μm was obtained.

Wholly Alicyclic Poly(amic silylester) Type

On the demand for low dielectric materials to increase the circuit speed, aliphatic and/or alicyclic PIs have been attracting much attention as desirable interlayer candidates as well as good optoelectronic materials. Wholly alicyclic PIs with high molecular weights was established through the synthesis of the corresponding poly(amic silylester)s as PI precursor polymers.[30]

This type of polymer was applied to alkaline developable PSPI with DNQ, although poly(amic silylester) had no soluble groups in the structure (Table I, No. 14).[31] In the exposed area, a photochemical reaction of DNQ produces a sulfonic acid unit, which promotes penetration of alkaline solution into the film and hydrolysis of a silylester group. Since this hydrolysis gives a carboxylic acid, penetration thus further accelerates and ends up with dissolution of the exposed area into alkaline solution. On the contrary, DNQ can block the dissolution in the unexposed area due to hydrophobicity of both the polymer and DNQ. The resist formulation resulted in showing the photosensitivity with *i*-line exposure and contrast, 60 mJ/cm^2, 1.7 (film thickness 2.8 μm), respectively. This polymer had high T_g (>250 °C), high transparency ($\lambda_{cut\ off} = 230$ nm), and relatively low dielectric constant estimated to be 2.45 at 1.0 MHz.

Reaction Development Patterning (RDP)[32,33]

Tomoi and coworkers reported a new positive-imaging method, RDP, using multi-block copolyimides and DNQ (Table I, No. 15 and 16). Unlike conventional positive-working photoresists in which acidic functional groups (for example, phenolic hydroxyl group, carboxyl group, etc.) are absolutely required to make patterns, the key factor for RDP is unnecessary of alkaline-reactive and photosensitive groups in the polymer structure. During the development with an amine-containing developer (ethanolamine/*N*-methylpyrrolidone/H_2O), chain-scissions of PIs in the irradiated area occur to make a positive-working image (Scheme 6). The pattern formation mechanism in RDP has been described as follows: (i) Indencarboxylic acid is generated through the photo-rearrangement of DNQ upon the UV irradiation, affording an ammonium salt with ethanolamine; (ii) such an acid-base reaction promotes the permeation of the developer into the film in the exposed area; and (iii) the ring-opening of the imide linkage is induced by the nucleophilic attack of the amine, followed by depolymerization successively to form a positive pattern.

RDP is a simple and versatile method because of mixing photosensitive agents into polymers, which can apply to commercially available engineering plastics such as polycarbonates[34] and polyarylates[35] as well as other PIs (Table I, No. 17)[36–38] without specific functional groups for dissolving these polymers in alkaline solution.

Poly(isoimide) Type

PSPIs based on poly(isoimide)s and DNQ was evaluated as alkaline-developable resist system.[39–41] The image formation mechanism is similar to that of RDP. Poly(isoimide)s are insoluble in an aqueous alkaline solution, but are susceptible to a hydrolysis to give an alkaline soluble PAA. In the exposed

Δ or Base

Poly(isoimide) PI

Scheme 7. Photochemical decomposition of oxime-urethane compound.

area, an alkaline solution penetrates into the film due to the existence of sulfonic acids given by photochemical reaction of DNQ. This behavior induces the hydrolysis of poly(isoimide)s, then providing a positive pattern. The sensitivity and contrast of the PSPI with 20 wt% DNQ were 250 mJ/cm^2 and 2.4, respectively when it was exposed to *g*-line (Table I, No. 18). This PSPI exhibited a 2.5 µm-feature resolution with a 5 µm-thick film. Poly(isoimide) has advantages of (i) excellent solubility compared to that of the corresponding PI, and (ii) easy conversion into the PI structure without elimination of any volatile compounds (Scheme 7). For another example, the poly(isoimide) shown in Table I, No. 19 was soluble in organic solvents and functioned as a positive-working PSPI with the DNQ, giving an great dimensional stability as well as low CTE.

[PI/Photobase Generator (PBG)] System

A photolysis of oxime-urethane derivatives can produce the corresponding amines.[42] Applying this chemistry to positive-working PSPIs, a resist consisting of the chemically imidized semi-aromatic PI with carboxylic acid groups at the polymer chain ends and PBG/benzophenone was reported (Table I, No. 20),[43] which could be a complementary system to the negative-working PSPI based on a fully aromatic PAA and a PBG (see "[PAA/PBG] system in the section of negative-working PSPIs").

The alkaline-dissolution mechanism of the PI film with the oxime-based PBG and benzophenone as a photosensitizer has been explained as shown in Scheme 8. In the UV exposed area, an amine can be emerged through the photochemical reaction of oxime-urethane group in the PBG. Such an amine then forms a salt with a carboxylic acid at the end of PI chain, inducing penetration of the developer (ethanol/TMAH) into the film. Thus, solubility of the PI resist film in the exposed area can be changed upon the salt-formation; from being soluble in THF to soluble in a mixture of ethanol and aqueous *tetra-N*-butylammonium hydroxide. A positive tone image with 5-µm resolution was obtained, having the sensitivity of 1.2 J/cm^2 and contrast of 1.08 (film thickness; not described) upon 310 nm UV irradiation.

[Acetal-Containing PAA or PI/PAG] (CA) System

From the point of view that an acetal linkage (*e.g.* tetrahydropyranyl group as represented in Table I, No. 1) is an acid-cleavable group, several positive-working PSPIs have been formulated with vinyl ether derivatives as thermally cross-linking agents to form acetal linkages. Because vinyl ether reacts with both phenolic hydroxyl and carboxylic groups upon thermal treatment (Scheme 9),[44] the resulting polymer can be deformed and soluble in alkaline aqueous solution *via* acidolysis with photogenerated acid.

Yamaoka *et al.* reported a three-component PSPI system comprising PI based on oligoimides (M_w: 3.6×10^3–6.6×10^3) with carboxylic acid end-groups, a bifunctional vinyl ether and a PAG (Table I, No. 21).[45] Because of relatively short chain of PI and carboxylic acids at the chain ends, dissolution in both organic cast solvents and alkaline developers was compatible. The sensitivity and contrast of this resist system were evaluated to be 137 mJ/cm^2 and 2.9, respectively, when *i*-line was exposed to the 1.0 µm-thick film.

A similar PSPI mechanism was established by Okazaki *et al.* from a three-component formulation including a semi-alicyclic PAA, a multi-functional vinyl ether as an cross-linker, and a PAG (Table I, No. 22).[46] This system functioned as a chemically amplified positive-working resist, so that precise controls of prebake for thermal cross-linking and PEB for deformation of the cross-linked structure were required. Since the semi-alicyclic PAA was highly transparent (>90%T @360 nm), this resist had an advantage in use of thick film with *i*-line exposure, resulting in the photosensitivity and contrast, 160 mJ/cm^2, 1.3 (film thickness 23 µm), respectively.

Another type of positive-working and chemically amplified PSPI bearing acetal side-chains was reported by Jung *et al.*[47] In this formulation, an ethoxymethylester group and a norbornene end-capping group were introduced into the PI precursor

I) hν → RNH_2 + CO_2 +

II) RNH_2 < Salt formation >

Insoluble Soluble

Scheme 8. Mechanism of thermal cross-linking and acidlytic decross-linking with vinyl ether compound.

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Scheme 9. Radical generation from benzophenone moiety upon UV irradation.

polymer (Table I, No. 23), each of which played as an acid-cleavable acetal linkage and a post-reactive group for chain-extension and/or cross-linking, respectively, to avoid spoiling the good mechanical properties the PI owned. An optimal protecting ratio of the ethoxymethylester group was determined to be 60 mol %. With 16 wt % of PAG, the resist formulation formed a positive pattern with 5-μm feature in a 15-μm thick film upon *i*-line exposure of 1500 mJ/cm^2.

Further investigation on the effect of the reactive end-capper revealed that the bulky norbornene-type end-capper was efficient for high transparency of the PSPI film.[48] On the contrary, the non-bulky end-capper derived from maleic anhydride resulted in improving the mechanical and thermal properties of the resulting PI film due to the excellent reactivity during thermal imidization.

They also blended an end-capped PAA to the poly(amic ethoxymethylester) described above to improve the mechanical properties of the PSPI film.[49] The PAA was incorporated with a siloxane moiety to improve the adhesion to Si wafers (Table I, No. 24). By controlling PEB temperature to partially imidize the PAAs (130 °C), the dissolution rate of the blend was optimized in alkaline developer, where the resulting PSPI film showed the photosensitivity and contrast as 700 mJ/cm^2 and 0.87, respectively, in a 10-μm thick film with a 13 wt % PAG.

NEGATIVE-WORKING PSPIs

Among Table II summarizing negative-working PSPIs, the most commercially standard PSPIs are based on (a) poly(amic ester) in which cross-linking groups are introduced at the side chains,[50] and (b) PAA with acid-amine ion-linkages[51,52] as shown in No. 25 and 26 in Table II, respectively. Although these two representatives have a similar polymer structure containing reactive methacrylates, the mechanisms of photochemical reactions up to forming negative-working patterns are different. In the case of ester-linkage type (a), methacylates can react upon UV exposure in a radical polymerization fashion, whereas the ionic-bonding type (b) can be patterned by forming charge-transfer complexes between PAA and a sensitizer (such as *N*-phenyldiethanol amine) in an exposed area. A big drawback for these two resist formulations is inevitable use of organic solvents for the development. Therefore, other types of negative-working PSPIs have been reported as much as positive-working ones foresaid.

Poly(amic ester) Type

The commercially available poly(amic ester) type PSPI as shown in Table II, No. 25 had been still research objective to improve the photolithographic performances.[53] Recent PSPI based on poly(amic ester) consisting of glycidyl methacrylate as a side-chain was reported (Table II, No. 27),[54] whereas the corresponding PAA was too soluble in an aqueous alkaline developer. The 2.0 μm-thick film with 20% esterification demonstrated a pattern resolution of 8 μm with an exposure dose of 50 mJ/cm^2 in *i*-line.

Photoinitiator-free Type

A photoinitiator-free PSPI is one of the solutions to avoid loss of thermal- and/or mechanical properties due to the addition of large amount of low-molecular weight additives such as photoactive compounds (*e.g.* DNQ, PAG, PBG, etc.) into a PI system. The photoinitiator-free PSPIs can provide pure PI contents, although most of them need a process of development with organic solvents.

Benzophenone is a well-known photoreactive group that can cross-link without photoinitiator.[55] This type of PSPI depicted in Table II, No. 28 was prepared from 3,3′,4,4′-benzophenone tetracarboxylic dianhydride and diamine having *o*-alkyl groups.[56] In the UV exposed area, the polymer itself was cross-linked through radical coupling to become insoluble in an organic developer. The radical cross-linking was contributed to hydrogen abstraction from the *o*-alkyl group and triplet state of benzophenone moiety excited by the UV irradiation (Scheme 10).

A semi-alicyclic PSPI was formulated in this photoinitiator-free fashion with high transparency of 87% at 500 nm (Table II, No. 29).[57] The resulting negative pattern of the photo-cured PI film exhibited 10-μm resolution and 10 °C higher T_g than that of the PI before UV exposure.

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Table II. Negative-working PSPIs.

No.	Matrix polymer (+cross-linker)	Additive	Ref.
25		PRI	50
26		PRI	51, 52
27		PRI	54
28			55
29			57
30			58
31			59
32			60
33		Silica particle or MMT	66, 67
34		PAG	72
35		PAG	73

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No.	Matrix polymer (+cross-linker)	Additive	Ref.
36		PAG	76
37		PAG	77
38		PBG	80
39		PBG	83
40		PBG	89

PRI: photoradical initiator, MMT: montmorillonite, PAG: photoacid generator, PBG: photobase generator.

Scheme 10. Mechanism of cross-linking *via* photoradical generation.

Another benzophenone-containing PSPI prepared from newly synthesized fluorinated diamine was developed (Table II, No. 30),[58] showing the photosensitivity and contrast of 98 mJ/cm^2 and 1.7, respectively, and producing a 5-μm resolution with *i*-line exposure.

For device fabrication of an organic thin-film transistor, a photoinitiator-free PSPI was utilized in the behalf of inorganic gate insulators since such electrical devices require pure materials.[59] A coumarin-containing diamine was incorporated into a PAA backbone as a photosensitive group (Table II, No. 31). Upon UV irradiation, the coumarin moiety undergoes a cross-linking reaction to give the polymer insoluble to an aqueous alkaline developer.

The PI containing a benzophenone unit in the backbone and a methacryloyl group attached onto the side chain was synthesized, and acted as the photoinitiator-free PSPI (Table II, No. 32).[60] The former group functions as the photosensitive moiety to generate several kinds of radicals upon UV irradiation, and then the latter group can be polymerized in the presence of the radicals (Scheme 11). This PSPI system provides high sensitivity in *i*-line exposure ($D_{0.5} = ca.$ 150 mJ/cm^2, at 2-μm film thickness).

[Inorganic/PSPI] Composite System

In an attempt to improve the mechanical and thermal stabilities as well as to reduce the CTE, composition of PI films with inorganic fillers promises enhancements of these properties. Especially, the preparation of PI/SiO_2 hybrids by sol–gel process has attracted growing attention because of the exceptionally high thermal stability and low CTE of SiO_2 caused by the high Si-O bond energy.[61–63] Although the sol–gel reaction has been one of the most widely used approaches for preparing

Scheme 11. Acid-catalyzed electrophilic substitution of benzylic alcohol cross-linker.

Scheme 12. Isomerization from isoimide to imide structure.

polymer and metallic oxides (*e.g.* SiO_2, TiO_2) hybrid materials,[64,65] mixing with nanosilica or clay such as montmorillonite (MMT) as an inorganic material was carried out in PSPI systems.[66,67] The photosensitivity was originated from the PI own structure derived from benzophenone-3,3′,4,4′-tetracarboxylic dianhydride and 4,4′-diamino-3,3′-dimethyldiphenylmethane (Table II, No. 33) as described above in detail and the literature.[68]

The introduction of well dispersed (preferably on the nanometer scale) inorganic particles into a polymer matrix has been proved to be extremely effective to improve the characteristics of the polymer film.[69–71] Satisfactory photolithographic patterns with a high loading of silica up to 10 wt % was achieved as long as the silica particle size was smaller than the wavelength of the exposure light.

On the other hand, introduction of a small amount (2–3 wt %) of MMT effectively reduced the CTE. This was attributed to the well-dispersed clay layers in the PSPI matrix in exfoliation morphology which can decrease the segmental movement of PSPI matrix.

[PHI/Cross-linker/PAG] (CA) System[72]

A PHI was selected as a non-shrink matrix polymer (Table II, No. 34) unlike PAAs or other precursors as described above in the section of positive-working PSPIs. A benzylic alcohol type cross-linker such as 2,6-bis(hydroxymethyl)-4-methylphenol was effective to make a negative-pattern with an alkaline developer. An acid-catalized cross-linking mechanism was proposed as follows (Scheme 12): Protonation of a benzylic alcohol group occurs by a photo-generated acid. Then alkylation reaction (electrophilic substitution) is undergone through the formation of benzylic cation species. The succeeding alkylations proceed between the cross-linker and the PHI with regeneration of protons, resulting in forming network polymers. The photosensitivity and contrast of the PSPI as PHI matrix/cross-linker/PAG = 70/20/10 by weight were 70 mJ/cm^2 and 3.8, respectively, in a 2.0-μm thick film with *i*-line light exposure.

This cross-linking mechanism was applied to hyper-branched PIs to obtain a negative-working PSPI as well (Table II, No. 35),[73] because hyper-branched polymers have interesting properties such as globular morphology, low viscosity, good solubility, potentially peripheral decoration with many functional groups, etc.[74,75]

[PAA/Cross-linker/PAG] (CA) System

Highly sensitive PSPIs with a combination of a benzylic alcohol type cross-linker and a PAG were reported, where either wholly aromatic (Table II, No. 36)[76] or semi-alicyclic PAAs (Table II, No. 37)[77] as PI precursors was applicable to negative-working lithographic formulations. To suppress the dissolution behavior of the PAA matrices in an aqueous alkaline developer, 25–30 wt % of the cross-linker was required. They suggested that the cross-linker reacted with each other to form a network structure because the matrix polymer was mostly aliphatic structure which could not react with such benzylic alcohol groups. With a 1.8-μm thick film, the photosensitivity and contrast were 30 mJ/cm^2 and 3.0, respectively, for the wholly aromatic PSPI system. Semi-alicyclic PI was advantageous to low dielectric constant because of bulky aliphatic structure such as an adamantane unit.

[Poly(isoimide)/PBG] (CA) System

PBGs have been applied in the preparation of PSPIs for both positive-working as described in "[PI/PBG] system," and negative-working systems. PSPIs with the PBG based

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Scheme 13. Photochemical generation of alicyclic secondary amine.

on poly(amic alkylester)s[78,79] or poly(isoimide) (Table II, No. 38)[80] as the PI precursors have been reported. A key role of PBG which photochemically generates an amine compound (Scheme 13) is promotion of thermal imidization to make a different solubility between the exposed and unexposed regions in these resists. Both types of PSPIs, however, required multi-step syntheses and organic solvents for development due to the absence of carboxyl groups. Thermal conversion of poly(iso-imide) into the corresponding PI was easily carried out by thermal treatment without dehydration, which gave dimensional stability to the final patterned film. The poly(isoimide) containing 10 wt % of the PBG functioned as a negative-working PSPI in *i*-line irradiation with sensitivity and contrast as 900 mJ/cm^2 and 3.4, respectively.

Related to the PBGs in PI films, base-catalysts were found to be efficient for the solid-phase imidization of PAAs at temperatures below 200 °C.[81] Based on this finding, a thermo-base generator was subsequently developed for low-temperature imidization as a latent base-catalyst.[82] Latent catalysts are a group of stable compounds at ambient condition, which acts only under a certain range of external stimulation (*e.g.* heat, UV irradiation).

[PAA/PBG] (CA) System

A negative-working PSPI with PBG was developed from PAA as a matrix (Table II, No. 39) unlike poly(amic alkyl-ester)s or poly(isoimide)s described above, leading to an alkaline developable system as well as direct use of PAA solution (varnish) simply prepared from tetracarboxylic dianhydrides and diamines.[83] In the presence of catalytic amounts of amine given by the PBG, partially induced thermal imidization contributed to pattern formation in the stage of PEB at 160 °C.

Another remarkable aspect for this formulation is that the alicyclic secondary amine generated from the PBG can promote thermal imidization at lower temperature than 200 °C. This low temperature process enables to employ in parallel with thermally unstable componetns and to avoid thermal mismatch between the PI film and the substrate under the PI film. With 15 wt % of PBG, the resist showed the photosensitivity and contrast of 220 mJ/cm^2 and 12 (film thickness: 1.0 µm), respectively, producing a negative pattern with 8-µm feature (Figure 3). The patterned film was then converted into the corresponding PI film up to 200 °C.

Thus, a wide variety of PAA/PI selection, easy synthesis of PAA, and direct use of the PAA polymerization solution without isolation and/or purification are great advantageous to versatile utilization. Current issue to be improved is sensitivity of PBG, however, this patterning process can be theoretically employed in CA fashion.

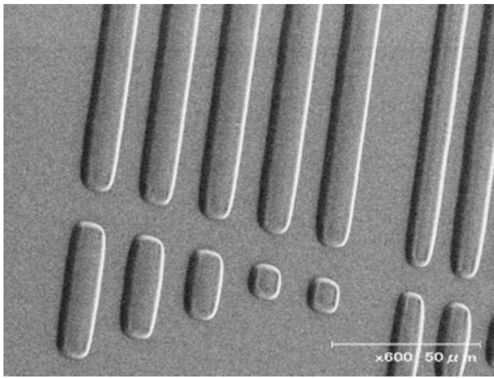

Figure 3. SEM image of negative-working PSPI pattern with PBG (25 wt %).

Porous-introduced PSPI

For high speed and minimum stress between the films and substrates in a multilayer printed wiring board (PWB), PIs having lower dielectric constants (ε) and higher dimensional stability are demanded simultaneously. Among several reports for that purpose in various ways,[84–88] an introduction of pores filled with air in a PSPI film makes it possible and versatile to lower the dielectric constant of the film due to that of air ($\varepsilon_{air} = 1.0$). In addition, the porous PIs for insulation materials must possess a closed-cell structure to prevent any kinds of contaminations.

Mochizuki *et al.* reported that a new negative-working porous PSPI based on PAA, DHP derivatives and poly(ethylene glycol) (PEG) (Table II, No. 40).[89] PEG plays a roll of porogenic agent which can be extracted by supercritical carbon dioxide (scCO_2) before developing steps (Figure 4). Supercritical fluids involving scCO_2 have been explored and found to be low viscosity, high diffusivity, non-wetting property and porous formable, which are useful for synthesis, extraction, impregnation and processing materials as a solvent.

FUTURE PROSPECTS

Focusing on how to incorporate a wide variety of photochemistries into the PI systems is the main theme in this review article. However, optimization for a patterning process takes tremendous times, energy and efforts. Moreover, in the respect of the final properties obtained from the patterned PIs, there are still some concerns and issues to be addressed for the final applications. For example, most of PAA systems might encounter the inherent difficulties such as poor storage stability, volume shrinkage during the thermal imidization due to dehydration, etc.

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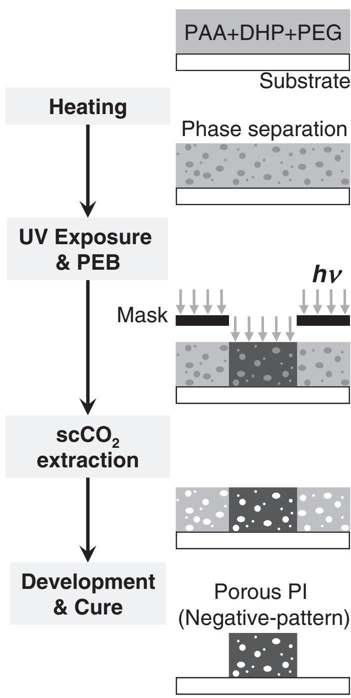

Figure 4. Porous-introduced photosensitive PI.

Recently, PI nanostructures were fabricated by nanoimprint lithography which was different from PSPI.[90] Patterning PIs using the nanoimprint lithography was demonstrated in the following three ways; (i) imprinting into PI at the uncured soft state; (ii) imprinting with low-T_g polymer and subsequent transfer into PI by reactive ion ething; and (iii) direct imprinting into PI at higher temperature than T_g, where each method provided the PI gratings with 200 nm period and 110 nm line-width.

In this growing area, new PSPIs with simplicity, versatility, and environmentally friendly production are still demanded for more improved properties and functionalities; high sensitivity, high transparency, low dielectric constant, low CTE, low thermal imidization and so on as well as new development of photochemical patterning mechanism.

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