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Abstract. A photosensitive polyimide system based on amine catalyzed imidization of a precursor poly(amic ester) is described. The material is based on the meta ethyl ester of pyromellitic dianhydride and 2,2' bis(trifluoromethyl)benzidine. It acts as a negative tone resist when formulated with a photobase generator. The material exhibits a dielectric constant of 3.0 in the gigahertz range, a coefficient of thermal expansion of 6 ± 2 ppm/K, and can be patterned to aspect ratios of >2 when formulated with a highly quantum efficient cinnamide type photobase generator.

Keywords: photosensitive polyimide; coefficient of thermal expansion; high aspect ratio; dielectric.

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1 Introduction

The recent interest in the development of 3-D architectures has brought renewed interest in polyimide for packaging applications. The requirement for connecting multiple chips into the same circuit requires either a true vertical 3-D architecture complete with through silicon vias (TSV) or an alternate structure with multiple chips on top of a silicon interposer. In the case of the interposer, fine wiring running at the packaging level is necessary to connect the chips, and this requires the use of some lithographic patterning scheme.1

The requirements for the packaging dielectric are quite different than the interlayer material; reduction of the dielectric constant is not the primary objective. The film thicknesses required at the packaging level are also orders of magnitude larger than interlayer materials, making commonly used interlayer deposition techniques such as chemical vapor deposition and atomic layer deposition impractical, prohibitively expensive, and not as mechanically stable as thick films.2 Current methods of patterning the dielectric require the use of a separate photoresist or laser ablation step,3 which can damage low dielectric constant materials such as polymers or organosilicate glasses. The use of photosensitive polyimide (PSPI) presents an intriguing third option. PSPI removes the need for a separate photoresist layer, an etch step, and, in general, simplifies the patterning of the polyimide. PSPI also tends to have desirable material properties such as high mechanical strength and low thermal expansion coefficient (CTE).

A great deal of effort has been focused on the development of PSPIs; however, there remains considerable room for improvement. There are several reports of both positive and negative-working PSPI systems, though most commercial PSPIs are negative tone. The negative tone resists are typically based on photoinitiated cross-linking of pendant methacrylate groups either ionically bonded to poly(amic acids) (PAA) or covalently bonded in the form of amic ester polymers.4,5 More recently, negative resists based on soluble, preimidized PI with crosslinkable side chains have also been patented and these tends to reduce cure shrinkage.6,7 Positive tone PSPI designs have been more varied, though many involve the addition of diazoquinone (DNQ) derivatives to act as dissolution inhibitors for poly(hydroxyimide)s or poly(isoimides).8,9 Most of these methods still suffer from high cure shrinkage (>40%), image distortion, and/or they have undesirable material remaining in the final film. Other positive tone PSPIs have been prepared that are based on polyimides containing t-butoxy carbonyl or o-nitrobenzyl protected phenols.10,11 These designs allow for high aspect ratio and high resolution, though at a loss of the desirable polyimide material properties. Additionally, the o-nitrobenzyl protected PSPI systems typically have poor sensitivity (>5 J/cm²). Finally, a chemically amplified design based on base catalysis has been described. Amine bases catalyze the imidization of PAA, poly(amic esters), and poly(isoimides) and as the imidized material tends to be much less soluble, this creates a chemically amplified positive resist.12–15 Variations on the use of chemical amplification have been reported that include printing PAA by combining a thermal base generator with a photo base generator (PBG) or a photocid generated vinyl ether cross-linking scheme to create lower curing temperature PSPI.16,17 The use of PAAs allows for easy synthesis and the ability to use aqueous tetramethylammonium hydroxide (TMAH)
developer. However, PAAs are very soluble in TMAH and large PBG loadings (15% to 25%) are required for sufficient contrast.14,16,18 Additionally, the solubility of many PAAs that from rigid polymers is limited to 15% to 20 wt. %,19 greatly restricting the obtained final film thickness. Finally, PAAs are unstable upon storage, causing a change in viscosity.20,21

While much work has been done on PSPI, none has demonstrated a PSPI with a simultaneous combination of low CTE, low dielectric constant, low cure shrinkage, and the ability to pattern high aspect ratio features. Many commercial PSPIs, after curing, consist of the PI of pyromellitic dianhydride-co-oxydianiline (PMDA-ODA), a material that has a reasonable combination of these properties and is known by its more common DuPont tradename, Kapton®. However, for implementation into new 3-D architectures, improvement in material properties beyond those of Kapton is required.

This paper describes the patterning of a fluorinated polyimide based on poly(pyromellitic dianhydride-co-2,2′ bis (trifluoromethyl)benzidine) (PMDA-TFMB) by a base-catalyzed mechanism, as shown in Fig. 1. When combined with a photobase generator, the amic ester polymer imidizes upon UV exposure and subsequent baking.22 The imidized polymer is insoluble in standard solvents, creating a chemically amplified negative tone resist. This allows for only a small amount of photoactive compound to be required, lessening the impact on dielectric constant and cure shrinkage.

2 Experimental
TFMB monomer (Combi-Blocks) and 4,4′ oxydianiline were sublimed prior to use. N-methyl 2-pyrrolidone (NMP) used for polymerizations was vacuum distilled from P2O5 and stored over molecular sieves. Toluene, pyridine, and dichloromthane (DCM) were distilled from CaH2 immediately before use. Tetrahydrofuran (THF) was passed through an alumina column under argon prior to use. All other solvents and reagents were used as received from commercial suppliers. NMR spectra were obtained using a 400-MHz Varian DirectDrive 400.

2.1 Photobase Generators
2.1.1 (E)-3-(2-hydroxy-4-methoxyphenyl)-1-(piperidin-1-yl)prop-2-en-1-one (3a)
Prepared according to the literature procedure.23 Recrystallized from ethanol to obtain slightly yellow solid in 22% overall yield. HRMS (ESI) calc.: 284.1257 [M + Na]⁺, found 284.1257; 1H NMR (DMSO-d6) δ 10.17 (br s, 1H), 7.66 (d, 1H), 7.57 (d, 1H), 7.01 (d, 1H), 6.39 (m, 2H), 3.70 (s, 3H), 3.55 (m, 4H), 1.58 (m, 2H), 1.46 (br s, 4H); 13C NMR (DMSO-d6) δ 165.4, 161.7, 157.9, 137.1, 129.8, 115.6, 114.8, 106.1, 101.4, 55.5, 46.4, 43.0, 27.0, 25.9

2.1.2 (E)-3-(2-hydroxy-4-methoxyphenyl)-1-(4-hydroxy piperidin-1-yl)prop-2-en-1-one (3b)
4-hydroxypiperidine (4.0 g, 19.8 mmol, 1 equiv) was dissolved in 150 mL of EtOAc and 75 mL of sat. aq. Na2CO3 was added to obtain a biphasic mixture. Chloroacetyl chloride (2.4 mL, 29.6 mmol, 1.5 equiv) was then added dropwise more than 5 min. The reaction was completed after 4 h by thin layer chromatography (TLC). The organic layer was separated, dried with Na2SO4, and the solvent removed in vacuo to obtain 2b as a slightly yellow oil (3.08 g, 88%). 2b was then heated to 80°C overnight with triphenylphosphine (4.55 g, 17.3 mmol, 1 equiv) in 100 mL toluene. After cooling to room temperature, the solvent was decanted to obtain a slightly oily white solid that was placed in high vacuum to remove the remainder of the toluene. The salt (4.66 g, 10.6 mmol) was diluted with methanol and then 2-hydroxy-4-methoxybenzaldehyde (1.61 g, 10.6 mmol, 1 equiv) was added. Finally, 0.6 g KOH (10.6 mmol, 1 equiv) dissolved in 50 mL methanol was added to form a bright

![Fig. 1](http://nanolithography.spiedigitallibrary.org/pdfaccess.ashx?url=/data/journals/moems/935435/)
yellow solution. After consumption of the starting material as monitored by TLC, the solvent was removed in vacuo and the crude material purified by flash chromatography (5:95 MeOH/DCM) to obtain 0.93 g (32%) of the title compound as an off-white solid. HRMS(ESI) calc.: 300.1206 [M + Na]+, found 300.1208; 1H NMR (DMSO-d6) δ 10.06 (br s, 1H), 7.67 (d, 1H), 7.58 (d, 1H), 7.02 (d, 1H), 6.39 (m, 2H), 4.73 (br s, 1H), 4.00 (br s, 2H), 3.70 (s, 3H), 3.67 (m, 1H), 3.23 (br s, 1H), 3.05 (br s, 1H), 1.72 (br s, 2H), 1.28 (br s, 2H); 13C NMR (DMSO-d6) δ 165.6, 161.8, 158.0, 137.2, 129.8, 115.5, 114.7, 106.2, 101.5, 66.2, 55.5, 43.0, 35.5, 34.5.

2.1.3 (E)-3-(2-hydroxy-4-methoxyphenyl)-1-(4-(hydroxymethyl)piperidin-1-yl)prop-2-en-1-one (3c)

Prepared analogously to 3b using 4-piperidinylmethanol in place of 4-hydroxypiperidine. Recovered white powder in 29% overall yield after chromatography (MeOH/DCM). HRMS (ESI) calc.: 314.1363 [M + Na]+, found 314.1361; 1H NMR (DMSO-d6) δ 10.06 (br s, 1H), 7.67 (d, 1H), 7.58 (d, 1H), 7.01 (d, 1H), 6.40 (m, 2H), 4.47 (br s, 2H), 4.18 (br s, 1H), 3.70 (s, 3H), 3.24 (d, 2H), 2.99 (m, 1H), 2.57 (m, 1H), 1.62 (m, 3H), 1.00 (br s, 2H); 13C NMR (DMSO-d6) δ 165.5, 161.7, 158.0, 137.1, 129.8, 115.6, 114.9, 106.2, 101.4, 66.0, 55.5, 49.0, 30.1, 29.0.

2.1.4 4,5-dimethoxy-2-nitrobenzyl piperidine-1-carboxylate (6-nitroveratryloxycarbonyl piperdine) (4)

Nitroveratraldehyde (5.0 g, 23.6 mmol, 1 equiv) was reduced to the benzyl alcohol by addition of small portions of NaBH4 (total: 1.5 g, 2 equiv) in 100 mL THF. After the reaction was completed by TLC, the solution was partitioned between sat. Na2CO3aq and EtOAc. The organic phase was collected and the solvent removed in vacuo to obtain 4.76 g (94%) of the chloroformate. The alcohol (1.5 g, 7 mmol, 1 equiv) was then dissolved in 40 mL THF and added dropwise to the benzyl alcohol by addition of small portions of phosgene (∼21 mmol, 3 equiv) at 0°C overnight. The excess phosgene was then removed by flowing dry nitrogen over the solution and the rest of the solvent removed in vacuo to obtain 1.90 g (98%) of the chloroformate. Finally, the crude chloroformate (500 mg, 1.81 mmol) was dissolved in 5 mL DCM at 0°C and piperidine (0.43 mL, 2.4 equiv) was added dropwise. After completion of the reaction, the solution was washed with 1N HCl and brine, dried over Na2SO4 filtered, and the solvent removed to obtain the title compound as a light yellow powder (0.500 g, 87%). HRMS (ESI) calc.: 347.1214 [M + Na]+, found 347.1218; 1H NMR (CDCl3) δ 7.69 (s, 1H), 6.98 (s, 1H), 5.52 (s, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 3.47 (br s, 4H), 1.65 to 1.51 (m, 6H); 13C NMR (CDCl3) δ 154.6, 153.3, 148.0, 139.9, 128.5, 110.1, 108.2, 63.9, 56.4, 56.3, 45.0, 25.6, 24.3.

2.1.5 Diethyl 4,6 dichloroisophthalate (5)

In a 1-L round bottom flask, PMDA (100 g, 458 mmol) was refluxed overnight in 400 mL ethanol. The solvent was then removed in vacuo to obtain a white powder. 425 mL of EtOAc was then added to the powder, and the suspension was heated at 90°C for 30 min with vigorous stirring. The heating was stopped, and the solution was stirred overnight. After filtering the precipitated, para-enriched isomer, the solvent from the mother liquor was removed, leaving a white solid containing 66.7 g (46.3%) of 90:10 meta: para isomer mixture by NMR. The meta-enriched isomer (10.0 g, 32.2 mmol, 1 equiv) was then dissolved in 125 mL ethyl acetate and a drop of DMF was added. The solution was then heated to 50°C and oxalyl chloride (8.3 mL, 3 equiv) was added dropwise more than 10 min. After the bubbling had ceased, the solvent and excess oxalyl chloride were removed in vacuo. The crude diacid chloride was then treated with activated charcoal and recrystallized twice from hexanes to obtain 8.50 g (76%) of shiny, snow-white flakes of the title compound in a 95:5 meta: para ratio. 1H NMR (CDCl3) δ 8.38 (s, 1H), 7.93 (s, 1H), 4.45 (q, 4H), 1.42 (t, 6H); 13C NMR (CDCl3) δ 166.6, 163.7, 139.7, 132.1, 131.6, 126.8, 63.2, 13.8.

2.2 Polymerization

Precursor poly(amic ester) was prepared using a slight modification of the literature procedure.20 2.2 Bis(trifluoromethyl)benzidine (TFMB, 1.50 g, 4.69 mmol, 1 equiv) was dissolved in 45 mL NMP then cooled to 0°C. A solution of 5 (1.63 g, 4.69 mmol, 1 equiv) in 7 mL THF was then added dropwise more than 15 min. After the addition was completed, pyridine (0.75 mL, 2 equiv) was added dropwise, and the reaction was stirred at room temperature overnight. The solution was precipitated into water, filtered, washed with water, methanol, and ethyl acetate, and then dried at 50°C for 2 days in vacuo to obtain 2.79 g of a white solid (97%).

The polymer of 4,4'-oxydianiline and 5 (PMDA-ODA ethyl ester) was prepared in a similar manner to obtain a light yellow powder after drying.

2.3 Films and Exposures

Formulations were prepared by dissolving resist polymer and photobase in NMP for 6-nitroveratryloxycarbonyl (NVOC) PBG or 10 wt. % acetic acid in NMP for the cinnamide PBGs. The PBG loading was 5 wt. %, and total solids loading was adjusted to 15 to 30 wt. % to achieve varying film thicknesses. Silicon wafers were surface functionalized with (3-aminopropyl)triethoxysilane (APTES). Then, films were cast on the APTES coated wafers by spin-coating at 1500 rpm. Excess solvent was removed by a post bake at 100°C for 10 min. Patterned exposures were performed using a Suss MA6 near UV mask aligner. Exposed films were then baked on a hot plate for 10 min at 130°C (cinnamide PBG) or 160°C (NVOC PBG). The films were then developed in a solution of 30% NMP in methanol. Final curing was performed at 350°C in a vacuum oven for 1 h.

2.4 Degree of Imidization by IR Spectroscopy

Formulations were prepared using either a 5:95 cinnamide PBG/polymer in 10:90 AcOH:NMP solution or a 5:95 4: polymer solution in NMP; both at 10 wt. % total solids. The solutions were spincoated (1500 rpm) onto APTES treated wafers and baked for 2 min at 100°C to obtain films ~800-1000 nm thick. Half of the samples were exposed to 2 J/cm² of 365 nm filtered light from a Novocure 2100 spot curing system, and then baked alongside unexposed samples at each temperature (120°C to 170°C) for 10 min. All the films were then measured on a ThermoSci Nicolet 6700 FT-IR in transmission mode before being fully cured overnight at 350°C in a vacuum oven. No imidization was
observed in samples after the post apply bake at 100°C. The degree of imidization was then calculated by

\[
\text{Imidization} = \left( \frac{A_{1783}/A_{1491}}{\text{sample}} \right) / \left( \frac{A_{1783}/A_{1491}}{\text{cure}} \right)
\]

where imidization is the fractional conversion of the ester groups to imides, \( A_{1783} \) is the area of the C–O stretch of asymmetric stretch of the imide carbonyl and \( A_{1491} \) is the C–C aromatic stretch used as an internal standard in this study. Subscript "sample" after the ratio refers to the polymer baked at each temperature for 10 min. "Cure" refers to the samples after complete curing.

2.5 Measurements

Exposure doses were measured using a Coherent FieldMaxII-T0 with PowerMax PM3 detector. Dielectric constant measurements at 200 kHz were performed by capacitance: a 450-nm film (after full cure at 350°C overnight) of PI was spincoated onto a 300-nm Al-coated wafer containing 500 nm of thermal oxide. 300-nm Al was evaporated on top of the film through a mask to complete the capacitors. Split post dielectric resonator (SPDR) measurements were performed on free-standing films using a series of GHz range SPDR fixtures (Agilent/Keysight) with a VASE ellipsometer. Thicker films were measured using a Veeco Dektak profilometer. Scanning electron microscope (SEM) micrographs were obtained using a Hitachi S-4500 SEM at 5 kV accelerating voltage; Au/Pd was sputter coated on films prior to imaging to prevent charging.

3 Results and Discussion

The PMDA-TFMB ethyl ester polymer used in this paper is more transparent than the PMDA-ODA found in many commercial Kapton®-based polyimides. As shown in Fig. 2, the PMDA-TFMB ethyl ester is transparent in the visible wavelengths, with absorbance strongly increasing below 370 nm.

The PMDA-ODA ester polymer is more absorbent, even into the visible range, though much less so than the fully cured yellow-brown material, which is colored due to formation of charge-transfer complexes.

The meta isomer of the diethyl ester of PMDA was chosen due to the improved solubility properties it imparts upon the polymers formed from it. This is especially important due to the rigid diamine TFMB used instead of ODA. Incorporating TFMB into polyimides lowers the dielectric constant, water absorption, and coefficient of thermal expansion relative to ODA-based PI. However, ODA imparts a bend in the main chain of the poly(amic ester) while TFMB does not. Polymerizing TFMB with para diethyl esters of PMDA results in rigid rod like polymers. While the noncoplanar structure of the TFMB unit does grant some solubility relative to other rigid diamines such as p-phenylenediamine, polymers of rigid diamines with para diethyl esters of PMDA are still less soluble than the meta versions and typically exhibit liquid crystalline behavior.26 PSPIs are typically deposited by spincoating; the decreased solubility and liquid crystalline behavior are both detrimental for this process. Casting the many micron-thick films required for packaging applications requires very high-solid content solutions. Additionally, spincoating liquid crystalline materials tends to align the polymer chains, which create opaque films because the crystalline domains scatter light. These opaque films cannot be patterned effectively.

3.1 Thin Film Patterning

Even with the increased transparency relative to other PSPIs, multiple micron-thick films of uncured PMDA-TFMB are opaque at wavelengths below 350 nm. As most of the common photobase generators only function in the deep UV, printing PMDA-TFMB with these PBGs would be limited to several hundred nanometer films. NVOC piperidine PBG was used for thin film patterning. The NVOC PBG is a variation on the ortho-nitrobenzyl carbamate class of photobases that red-shifts the absorbance into the near UV, at a significant loss in quantum efficiency.27-29 However, this PBG is easily prepared and thermally stable to 170°C.

Contrast curves for this system were prepared using a 5-wt. % PBG loading for films 1- to 2-μm thick, and are shown in Fig. 3. Low exposure doses (<200 mJ/cm²) were completely developed away, and doses >900 mJ/cm² were sufficient for patterning. The intermediate region, however, experiences considerable swelling during the development, causing significant roughness, and produced films that are thicker than the initial film thickness. Also, unusual compared to standard cross-linking type negative tone resists is the noticeable loss in film thickness after the development. As the resist material goes from the amic ester form to the polyimide, ethanol is generated and diffuses out of the film, resulting in cure shrinkage. The reaction reaches higher conversion with increasing temperature due to both reaction kinetics and base diffusion; this can be observed in the thinner films remaining after the 170°C post exposure bake (PEB) compared to the 150°C bake. Even after a 10-min bake at 170°C, however, the imidization is incomplete and further shrinkage occurs during a final cure step. Contrast likely could be improved by post exposure baking at a higher temperature to further enhance the base-catalyzed reaction and diffusion, but attempts were unsuccessful due to the
thermal decomposition of NVOC PBG, as shown in background imidization in Fig. 4.

A film of 2-μm thickness was cast onto a silicon wafer. After exposure to 1500 mJ/cm² (365 to 435 nm), the film was baked at 160°C for 10 min. The film was then developed in 25% NMP in MeOH. Final curing was accomplished by heating to 350°C for 1 h. The resulting 1.5-μm thick, 2.5-μm lines/space pattern is shown in Fig. 5. While the sidewall profile is smooth and vertical, noticeable footing is observed. The cure shrinkage of 25%, while much lower than commercial PSPIs, likely is the cause of the sidewall shape. The originally printed image was an equal line/space pattern, and the fully cured material has considerably narrower lines than spaces; the footing at the bottom, however, appears to correspond to the original printed image.

3.2 Thicker Film Patterning

Due to the high absorbance of NVOC photobase in the near UV, patterning PMDA-TFMB using this PBG only worked well in the case of relatively thin films. A thicker, 12-μm film was also printed at various aspect ratios, as shown in Fig. 6. While the large 25-μm pitch patterns are printed, the smaller pitches begin to show many defects. The resist is strongly absorbing, so the bottoms of the films are underexposed and they swell, as indicated by the holes at the bottom of the film. Bridging defects also began to appear on the tops of lines for the smaller pitches, which we attributed to the volatility of the piperidine base causing the base to evaporate out of the film and imidize the film surface.

3.3 Cinnamide PBGs

The less i-line absorbent and more quantum efficient cinnamide piperidine photobase 3a were also used to print thicker films. It was prepared according to the literature procedure and is reported to have an extinction coefficient of 260 M⁻¹ cm⁻¹ at 365 nm, which should allow for patterning multiple micron-thick films. Substituted versions 3b and 3c have been reported and were prepared in a similar way, though the yields are low (~10%). The EDC coupling of hydroxyl substituted piperidines with cinnamic acids always resulted in poor yields in our hands as well. However, the procedure shown in Fig. 7 improved overall yields to 30%. In this process, the substituted piperidine was reacted with chloroacetyl chloride to exclusively form N-acylated product 2. 2 was then heated with PPh₃ to form the Wittig salt before being...
reacted with 2-hydroxy-4-methoxybenzaldehyde and base to form 3 in a Wittig reaction.

The cinnamide class of photobases has been used in PSPI to print PAA.23,30 However, when we attempted to print the PMDA-TFMB ethyl ester polymer using the same conditions as the NVOC PBG, no images were formed. Mechanistically, the photobase is known to work in a two-step process in which the molecule is first isomerized to the cis form then ring closes to the lactone and loses amine base in the second step.32,33 The lactone forming step is catalyzed by acid and does not proceed well in organic solvents without a small amount of weak acid present.32 We also exposed THF solutions of the cinnamide PBG to broadband UV and monitored the changes in absorbance by UV–Vis for a sample containing 1% acetic acid and a pure THF sample. These data are shown in Fig. 8. While the reaction is completed after 1000 mJ/cm² in both cases, the shapes of the curves are very different. In the pure THF case, the PBG is quickly isomerized to the cis form, with conversion back to the more stable trans form not observed on the timescale (~5 min) of the experiment. Also, interesting is that strong photobleaching in the near UV is observed. The bleaching is beneficial for thick film patterning as PBG that has already reacted no longer competes with unreacted PBG for light. This is not the case in the NVOC system where the byproducts are even more absorbent in the near UV than the starting PBG.

Films on the order of 20-μm thick were spin coated onto 2"-silicon wafers. The edge bead was removed before exposure to 1200 mJ/cm² of near UV light. PEB was performed at 130°C for 10 min followed by the development for 6 min.

**Fig. 6** Scanning electron micrographs of 1:1 line/space patterns printed using NVOC PBG. The film thickness is 12 μm after cure. Full pitch is (a) 25 μm, (b) 20 μm. Note the defects in the higher aspect ratio images (b).

**Fig. 7** Synthesis of cinnamide type photobase generators.

**Fig. 8** UV–Vis spectra from broadband UV exposures of cinnamide PBG 3a. (a) 97 μM in THF and (b) 96 μM in 1% acetic acid/THF. Base is not generated in the absence of weak acid.
in 25% NMP in MeOH. The film was then fully cured by heating to 350°C. The thickness of the resulting fully cured film was 14 μm. Figure 9 shows a 6-μm line pattern that was printed in the resist. The shrinkage is 30% in thick films compared to 25% in the thinner films. This is likely due to the higher light absorption in the thick films, which results in underexposure of the bottom of the images. The developer attacks those regions more quickly, resulting in a retrograde slope to the sidewalls. The sidewall profile in these patterns has a retrograde slope. This is noteworthy as this is the opposite of the slope produced in most commercially available PSPI.

The substituted piperidine cinnamide PBGs were also tested for catalysis of imidization in films of PMDA-TFMB. Higher boiling amines were expected to alleviate some of the problems in thick film printing due, in part, to base volatility. As shown in Fig. 10, both 3b and 3c imidized PMDA-TFMB ester films better than unsubstituted 3a at a constant 5-wt. % loading. We attribute this to the decreased volatility of generated base, with both hydroxypiperidine and piperidinyl methanol having normal boiling points in excess of 200°C. The unexposed films performed essentially the same regardless of the cinnamide PBG used. There was very little imidization below 140°C, but imidization increased to more than 10% at 160°C. The catalyst loading was varied as shown in Fig. 11. Little difference is seen between the 5- and 10-wt. % loadings, but the 15 wt. % loading performed significantly better. However, this amount of PBG causes noticeably more background imidization compared to both 5% and 10% loadings. It is also important to note the relatively small amount of imidization occurring in this system compared to other base-catalyzed ester systems.22 The difference in imidization in the exposed and unexposed regions for this system is only 20% to 25%. Much of the difference is likely due to the backbone rigidity of PMDA-TFMB compared to the more flexible polymers having decreased UV absorbance but larger CTE. The curing process requires diffusion of generated amine catalyst, a process that is quickly inhibited as the polymer is imidized and glass transition temperature (T_g) increases. The diffusion rate in a glassy polymer is orders of magnitude slower than it is above T_g. The smaller size of the hydroxypiperidine and ease of diffusion compared to the piperidinyl methanol may also explain the more efficient curing for 3b.

### 3.4 Material Properties of Cured PMDA-TFMB

The dielectric constant and dissipation factor of the fully cured resist were determined for the GHz range using an SPDR. Additionally, a thin-film capacitor was constructed to obtain these measurements at 200 kHz. The data from both experiments are shown in Fig. 12. The dielectric constant is around 3.0 and the dielectric loss is between 0.01 and 0.015 over the frequency range studied. SPDR induces a circular electrical field in the plane of the material, so the dielectric constant that is measured is the in-plane value rather than the through plane value measured by capacitance. Typically, PIs tend to be quite anisotropic with different material properties in-plane and perpendicular to the plane, but the measured dielectric constants are nearly equal for this material.

This material is known to have a water absorption of around 2%,34 so the dielectric constant was measured after allowing the material to sit in air as well as immediately

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**Fig. 9** Six-micrometers of lines printed in 14-μm thick PMDA-TFMB using cinnamide PBG 3a.

**Fig. 10** Comparison of cinnamide type PBGs on curing PMDA-TFMB. Exposure dose 2 J/cm² filtered 365 nm light. Five weight percentage of PBG to polymer. 10-min PEB.

**Fig. 11** Comparison of curing for different loadings of 3b in PMDA-TFMB. Exposure dose is 2 J/cm² filtered i-line, PEB 10 min.

**Fig. 12** Dielectric properties of fully cured PMDA-TFMB after drying.
after baking at 150°C in vacuum for 2 h. As shown in Table 1, polymer that is stored in air has a significant increase in both dielectric constant and dissipation factor compared to dried polymer presumably due to water uptake from the air. This water uptake process occurred quickly; a rapid rise in dielectric constant and dissipation factor were observed during testing, allowing for only a handful of points on a sample to be measured.

The coefficient of thermal expansion is important from a device integration standpoint. During the solder reflow step employed to attach the die to the package, temperatures of around 250°C are required to melt the solder. Upon cooling, stresses are generated from CTE mismatch that can lead to cracks and via delamination. As such, the CTE of the dielectric should be less than that of the copper metallization (17 ppm/K) and close to that of silicon (3 ppm/K). These values are quite low for purely organic materials; CTEs of 50 to 100 ppm/K are more typical for commercially important polymers. Aromatic polyimides tend to have a low CTE due to the rigid rod like structure of cured material. The incorporation of TFMB monomer results in an even more rigid material than standard PMDA-ODA polyimide, with a corresponding reduction in CTE. The CTE of a film of PMDA-TFMB was obtained by thermomechanical analysis to be 6 ± 2 ppm/K in the temperature range 0°C to 150°C. The CTE was also measured by silicon wafer deflection from 50°C to 300°C and these data were found to be in good agreement at 9 ppm/K.

Taken together, the properties of low CTE, low dielectric constant, and high aspect ratio, smooth printed features are fairly unique for a PSPI material. This combination of properties is rare and represents a significant improvement over commercially available acrylic or DNQ-based PSPI.

4 Conclusions
A base-catalyzed chemically amplified PSPI was demonstrated. The material has a lower dielectric constant, lower CTE, and lower cure shrinkage than commercially available PSPI. PBG loadings of only 5 wt. % were sufficient for patterning. Cinnamide PBGs allowed for patterning of much thicker films due to the greatly improved efficiency and decreased i-line absorbance compared to traditional NVOC PBGs. Films with aspect ratio > 2.0 and film thicknesses of 14 μm were obtained using this PSPI system. Using less volatile piperidine derivatives resulted in increased imidization contrast relative to unsubstituted piperidine.

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References


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