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A photosensitive polyimide resist that consists of a soluble polyimide 5 and bisPFPA 6 as a cross-linker has been formulated. Polyimide 5 containing 11 wt% of bisPFPA has a deep-UV sensitivity of 30-35 mJ cm^{-2} while polyimide 5 itself has a deep-UV sensitivity of 350-400 mJ cm^{-2}. Under our present conditions, features of about 0.5 um could be resolved with this resist system.

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A Novel Photosensitive Polyimide Resist Consisting of a Soluble Polyimide and a Bis(perfluorophenyl Azide) as a Cross-Linker

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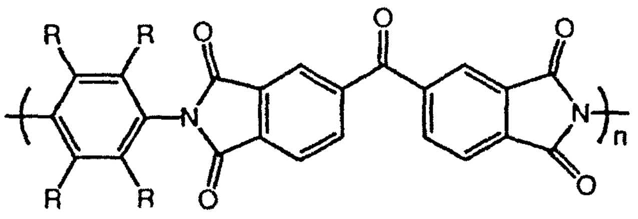
Abstract: A photosensitive polyimide resist that consists of a soluble polyimide **5** and bisPFPA **6** as cross-linker has been formulated. Polyimide 5 containing 11 wt % of bisPFPA **6** has a deep-UV sensitivity of 30-35 mJ cm ^{2} while polyimide **5** itself has a deep-UV sensitivity of 350-400 mJ cm^{-2}. Under our present conditions, features of about 0.5 μm could be resolved with this resist system.

Polyimides are widely used by the microelectronic industry as protection layers and interlayer dielectrics in integrated circuits because of their thermal stability, chemical resistance and dielectric properties. Polyimides are generally insoluble and infusible, thus patterning of polyimide layers has to be accomplished indirectly. The development of soluble and photosensitive polyimides are therefore highly desirable and continue to be an important objective.[1]

Many approaches for the preparation of photoactive polyimide have been reported.[2,3,4,5,6,7,8,9,10,11] For example, Pfeifer and Rohde[12] have developed the negative photosensitive polyimide **1** with a benzophenone unit in the polymer backbone as the photoactive group and alkyl substituents (R) as hydrogen donors. The photoactivated triplet benzophenone groups abstract hydrogen from the alkyl groups, leading to the formation of radical pairs and cross-linking of the polymer by subsequent radical coupling.[13,14] The alkyl substituents also render the polymer soluble in common organic solvents. Moore and Dasheff[15] have developed the intrinsically photosensitive polyimide **2**, a positive resist that uses a maleic anhydride dimer as a photochemically cleavable unit.



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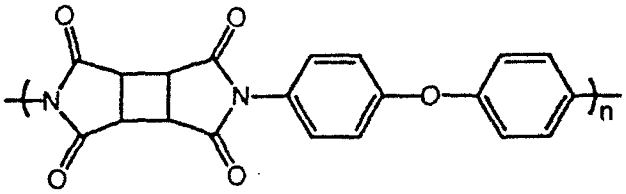

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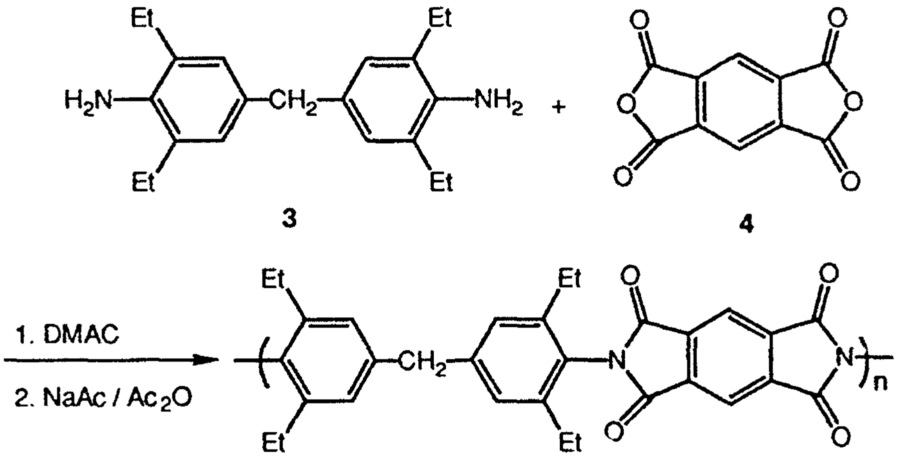
We have recently developed bis(perfluorophenyl azides) (bisPFPAs) as novel efficient cross-linkers for cyclized poly(isoprene),[16] polystyrene,[16] and poly(3-octylthiophene)[17] and demonstrated their application in deep-UV and electron beam lithography. BisPFPAs have proven to be superior to non-fluorinated analogues as cross-linkers in polystyrene based deep-UV resists. Utilization of bisPFPAs significantly reduces the required amounts of cross-linkers in PS-based resists and increases the sensitivity of the resists.[18] Herein, we report the development of a novel photosensitive polyimide resist by utilization of bisPFPA 6 as a cross-linker for the newly synthesized soluble polyimide 5.

The procedure of Lin *et al*[13] was adapted for the preparation of polyimide **5**. Reaction of 4,4'-methylene-bis(2,6-diethylaniline) (**3**, 0.7787 g, 2.508 mmol) (Ethyl Corp.) with 1,2,4,5-benzenetetracarboxylic dianhydride (**4**, 0.5470 g, 2.508 mmol) (Aldrich) in N,N-dimethylacetamide (DMAC, 50 mL) at 25°C overnight was followed by addition of acetic anhydride (4 mL) and sodium acetate (2 g) and the mixture was heated at 85°C for 4 h. The polymer was isolated by addition of the reaction mixture to ice-water (300 mL) and stirred overnight, giving a white precipitate which was filtered, washed with diluted aqueous Na_2CO_3, water, methanol and dried. The polyimide was further purified by dissolution in $CHCl_3$, precipitation by addition of the $CHCl_3$ solution to methanol, and exhaustive washing of the precipitated polymer in a Soxhlet extractor with methanol. The polymer after purification is fully soluble in $CHCl_3$, due to the presence of the four ethyl substituents.[19] The ethyl groups are also designed to provide accessible CH bonds for the CH insertion-based cross-linking reaction by the photochemically generated highly reactive perfluorophenyl nitrenes[20,21] derived from bisPFPA 6.[16-18]



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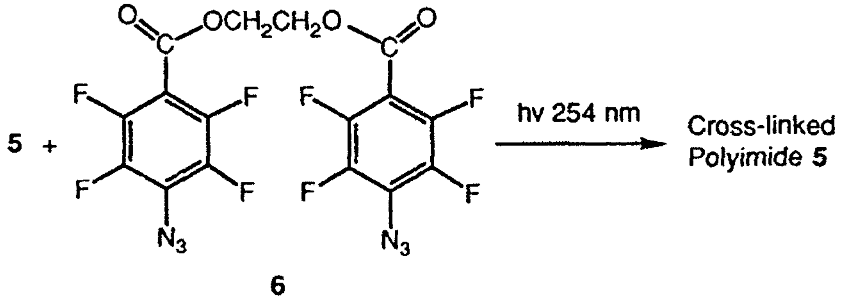
The ability of bisPFPA **6** to cross-link polyimide **5** was evaluated as follows. Various amounts of bisPFPA **6**,[16] ranging from 0-15.3 wt % based on polyimide **5**, were added to solutions of polyimide **5** (40 mg) in $CHCl_3$ (2 mL). The resist solutions were spin-coated (4000 rpm) on NaCl discs, baked at 50°C for 30 min, photolyzed in a Rayonet photoreactor (254 nm), developed in $CHCl_3$ for 30 s and rinsed in isopropanol for 10 s. Polyimide **5** has strong absorption in the deep-UV range (< 260 nm), therefore films of thicknesses of ~0.2 μm were used for the experiments to allow adequate light penetration. The photolysis was monitored by FTIR and required about 1 min for complete decomposition of the azido groups (2120 cm^{-1}). The intensity of the C=O stretching absorption in the IR spectrum at 1740 cm^{-1} before photolysis and after development was compared and used to estimate the retention of film thickness. For polyimide **5** containing 15.3, 10.2, 8.0, 5.6 and 0 wt % of bisPFPA **6**, the retention of film thickness after photolysis and development was 0.74, 0.71, 0.64, 0.30 and 0.0, respectively. Therefore about 10 wt % of bisPFPA **6** was required for retention of more than 70% of the original polyimide film thickness as estimated from IR spectra.



6

Polyimide **5** containing 15.3 wt % and 8.0 wt % of bisPFPA **6** as well as polyimide **5** itself were evaluated for their sensitivity as deep-UV resists. Figure 1 shows the exposure characteristics for these resists. Polyimide **5** itself is seen to be a negative deep-UV resist with relatively low sensitivity. Qualitatively, the sensitivity of **5** is increased about ten-fold by the addition of bisPFPA **6**.

Lithographic evaluation of the resists was carried out in a KSM Karl Suss deep-UV contact aligner. Polyimide **5** containing 11.0 wt % of bisPFPA **6** was found to have a deep-UV sensitivity of 30-35 mJ cm^{-2}, while a sensitivity of 350-400 mJ cm^{-2} was found for polyimide **5** itself. Figure 2 shows the pattern obtained from a resist of polyimide **5** containing 11.0 wt % of bisPFPA **6** at an exposure dose of 32 mJ cm^{-2}. Some swelling was observed after development under these nonoptimized conditions. The smallest feature in the mask (0.5 μm) could be resolved.

In conclusion, a new photosensitive polyimide resist has been formulated using the newly prepared soluble polyimide **5** and bisPFPA **6** as a photoactivated cross-linker. Polyimide **6** containing 11.0 wt % of bisPFPA **6** has been found to be a sensitive deep-UV resist with sensitivity of 30-35 mJ cm^{-2}, which is about 10 times more sensitive than polyimide **5** itself. Features of about 0.5 μm could be resolved with this resist system under our conditions.

Acknowledgment: This work was supported by grants from the Oregon Resource Technology Development Corporation, the Office of Naval Research and the National Institute of General Medical Sciences GM 27137. We thank Dr. Gary Goncher of Tektronix Inc. for his help in carrying out the deep-UV exposure of the resists and the Ethyl Corp. for a sample of aniline **3**.

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19. Polyimide 5: ^{1}H NMR ($CDCl_3$), δ1.143 (t, 12, J = 7.5 Hz), 2.448 (q, 8, J = 7.5 Hz), 4.085 (s, 2), 7.127 (s, 4), 8.541 (s, 2). IR (film), 2968, 1771, 1727, 1471, 1457, 1309, 1113 cm^{-1}.

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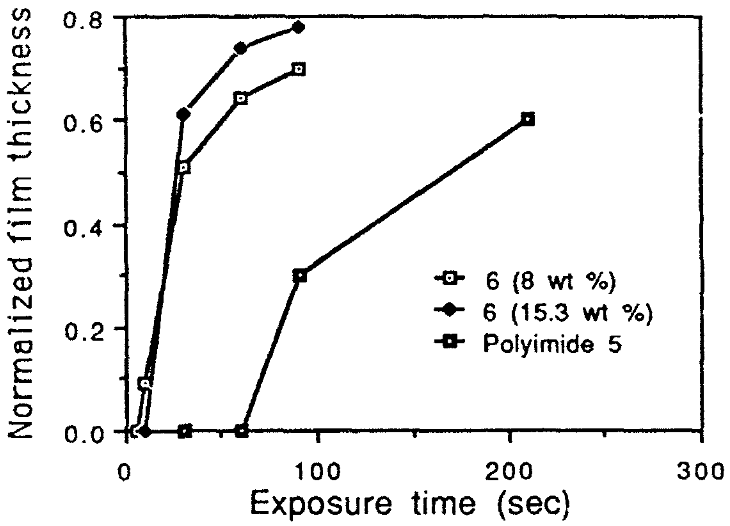
Figure Captions

Figure 1. The exposure characteristics for resists of polyimide **5** containing 8.0 wt % and 15.3 wt % of bisPFPA **6**, and polyimide **5** itself. Resist films were exposed in a Rayonet photoreactor (254 nm) for the time indicated and developed in $CHCl_3$ for 30 s then rinsed in isopropanol for 10 s. The normalized film thickness was determined by IR at 1740 cm^{-1} (C=O absorption) before photolysis and after development.

Figure 2. Optical micrograph of patterns obtained from a resist composed of polyimide **5** and 11.0 wt % of bisPFPA **6**. The deep-UV exposure dose was 32 mJ cm^{-2}. The exposed film was developed in $CHCl_3$ for 30 s and rinsed in isopropanol for 20 s.

Figure 1


Normalized film thickness
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0.4
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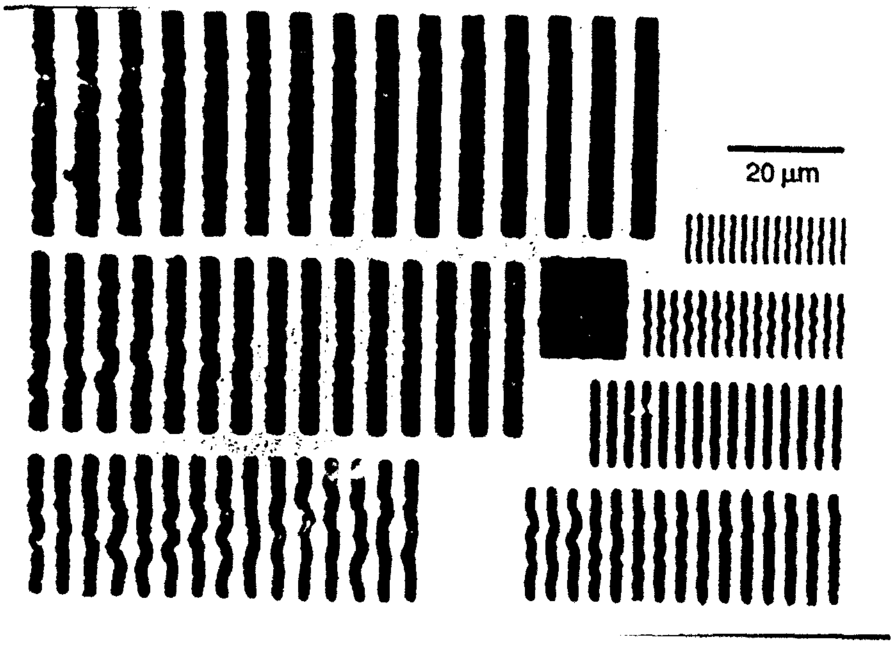
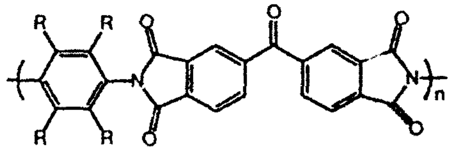
Exposure time (sec)
6 (8 wt %)
6 (15.3 wt %)
Polyimide 5

Figure 2

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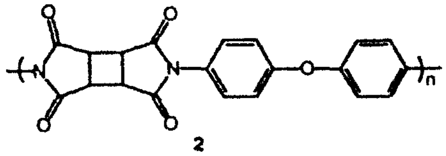
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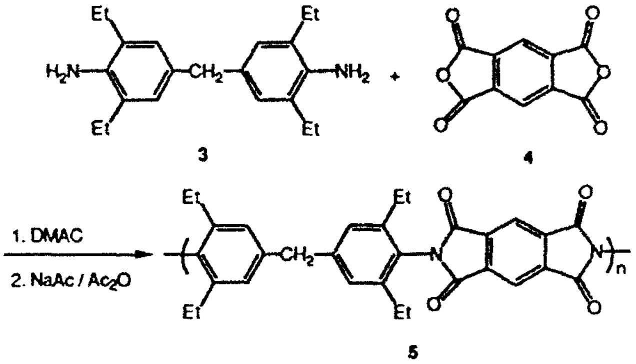
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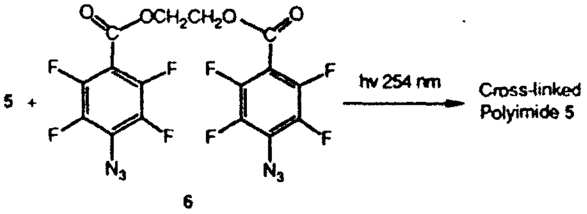
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6
hν 254 nm
Cross-linked
Polyimide 5

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