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An Intrinsically Photosensitive Polyimide

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A polyimide that is intrinsically photosensitive (λ_{max} = 232 nm) has been synthesized from the maleic anhydride photodimer and oxydianiline. An intermediate polyamic acid of $[\eta]_{DMAC}$ = 1.47 dL/g (25 °C) was cast from a dimethylacetamide (DMAC) solution to yield films that were thermally dehydrated to a tough, colorless, thermally stable polyimide. Upon exposure of the DMAC-insoluble polyimide in the range 230–254 nm, the irradiated regions could be dissolved in DMAC (45 s, room temperature) to generate micron-sized images. A sensitivity of ≃45 mJ/cm^2 was determined.

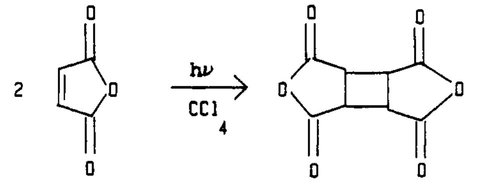
Introduction

We have been studying the synthesis of an intrinsically photosensitive polyimide for use in integrated circuits (IC). In the fabrication of multilevel metal–insulator IC structures, Kapton polyimide has proven to be a good insulator between metalization layers because of its thermal stability, chemical resistance, and dielectric properties. The intermediate polyamic acid formed is soluble and can be spun to films that can be cured to insoluble polyimide structures. Once the material is cured, it is generally insoluble and infusible and is extremely thermally stable.

The insolubility and infusibility of Kapton require that patterning of polyimide layers be accomplished indirectly by photoresist technology. This process entails the spinning and curing of the polyimide layer, formation of a polysulfone lift-off layer, and deposition of a SiO$_2$ masking layer followed by a top layer of resist coating. The pattern is defined by electron beam or optical lithography, the underlying layers are etched with reactive ion etching, metal is deposited, and the polysulfone and excess metal are "lifted off" with solvent. If the polyimide layer *itself* could be made to be intrinsically photosensitive, it is obvious that the process of image generation in the polyimide layers could be greatly simplified. Several photonegative polyimide precursor systems have been developed. In the most common type, the intermediate polyamic acid is partially esterified with photo-cross-linkable alcohols.[1] Irradiation of these esters causes them to become insoluble and enables them to be used to form negative images upon treatment with solvent. *After* imaging, the films are thermally converted to polyimide that is photo*in*sensitive. A photopositive system is much more desirable because of the swelling attendant upon solvent development of negative images. A photopositive polyimide containing photosensitive sulfonium salt units has recently been described.[2]

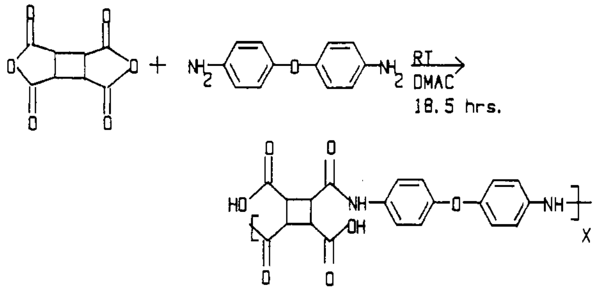
We report here a simple preparation of a polyimide that is *intrinsically* photosensitve so that direct, *positive* photoimaging can be accomplished, even after complete thermal curing to form the polyimide structure.

Upon irradiation of a maleic anhydride solution at 280 nm the excited anhydride molecule dimerizes to form a cyclobutane unit (eq 1).[3]



(1)

Because the olefin is consumed in the dimerization process, the ultraviolet absorption of the cyclobutane unit shifts to shorter wavelength. The dimer anhydride can be used to form a polyimide by standard procedures (eq 2 and 3).



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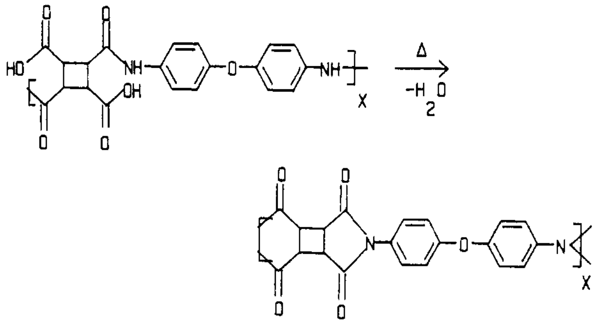
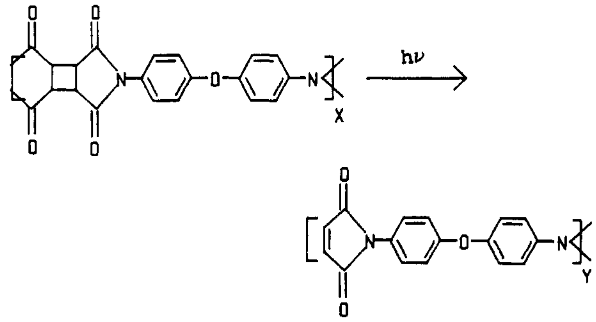


(3)

This material can be imaged by irradiation at a wavelength that corresponds to energy absorption by the cyclobutane imide (eq 4).



(4)

This type of polymer has been described for use as a colorless polyimide.[4,5] Similar polyimides have been

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[1] Kubota, S.; Moriwaki, T.; Ando, T.; Fukami, A. *J. Macromol. Sci., Chem.* **1987**, *A24*, 1407–1422. We note that the polyimide produced in this approach is *not* photosensitive; rather, the polyamic acid ester is subject to a photo-cross-linking reaction.

[2] Crivello, J. V.; Lee, J. L.; Conlon, D. A. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 3293–3309.

[3] Boule, P.; Lemaire, J. *Tetrahedron Lett.* **1976**, *11*, 865–868.

[4] Noriaki, K.; Toyohiko, A.; Kanji, O.; Hideo, S. *Eur. Pat. Appl.* EP 130481, 1985.

[5] Nakanishi, F.; Hasegawa, M.; Takahashi, H. *Polym. J.* **1973**, *14*, 440–444.

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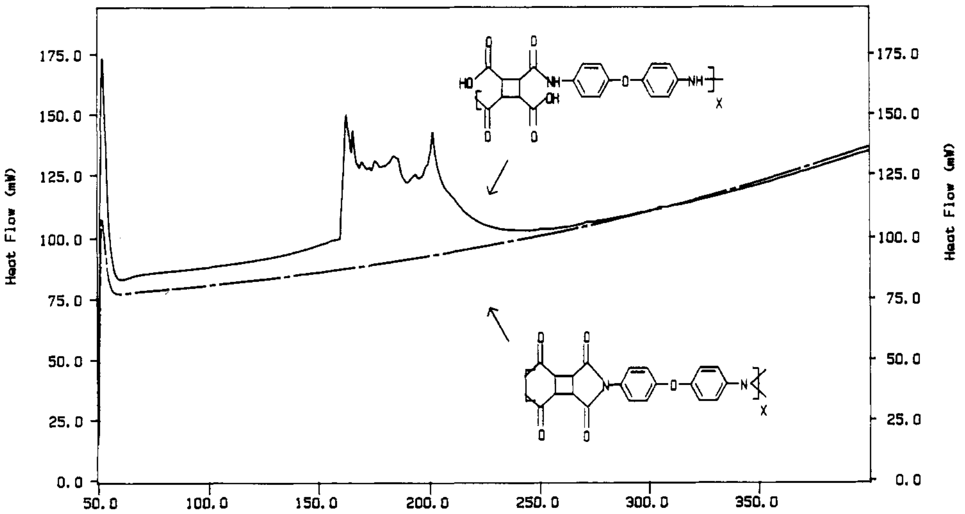


Figure 1. Differential scanning calorimogram of polyamic acid.

prepared by solution polymerization of aliphatic bismaleimides.[6,7]

Experimental Procedure

Dimethylacetamide (DMAC) was dried over calcium hydride and distilled at reduced pressure.

A solution of maleic anhydride (λ_{max} = 280 nm) in carbon tetrachloride was irradiated with an unfiltered 450-W Hanovia high-pressure mercury arc for 1 h to form 1,2,3,4-cyclobutanetetracarboxylic 1,2:3,4-dianhydride (CBDA). CBDA precipitated from solution and was collected by filtration. CBDA (λ_{max} = 232 nm) was purified by successive recrystallizations from acetic anhydride (until the filtrate was colorless) to give a white solid.

To a dry, three-necked, 100-mL round-bottomed flask fitted with a mechanical stirrer, nitrogen inlet, and condenser was added 0.640 31 g (3.1977 mmol) of oxydianiline (Aldrich Gold Label), 60 mL of dry DMAC, and 0.627 14 g (3.1977 mmol) of CBDA. The reaction was allowed to proceed at room temperature under dry nitrogen for 18.5 h. The resulting polyamic acid was precipitated twice into methanol and dried in vacuo at room temperature for 24 h.

The intrinsic viscosity of the resulting polyamic acid was 1.47 dL/g measured with an Ubbelohde viscometer at 25.00 °C in DMAC.

The polyamic acid was cured to the polyimide by heating films cast by solvent evaporation in a watch glass, in an oven for 2 h at 100 °C, 2 h at 175 °C, and 2 h at 250 °C. The resulting polyimide films were colorless.

Silicon wafers were spin-coated with a 7% solution of the polyamic acid. The polyamic acid was then thermally converted to polyimide according to the previously given heating cycle, and the resist thickness (1.3 μm) was measured with a Dektak profilometer. The resulting colorless films showed an absorption maximum at about 250 nm and a more intense absorption around 195 nm.

The polyimide films were irradiated with a high-pressure 500-W Hg–Xe lamp (Hybrid Technology Group) in the range 230–254 nm at incident doses ranging from 10 to 1000 mJ/cm^2 (intensity measurements were made with a Black-Ray short-wavelength intensity meter). The samples for dissolution rate studies were irradiated by flood exposures. In those instances where patterns were generated, appropriate masking procedures were used.

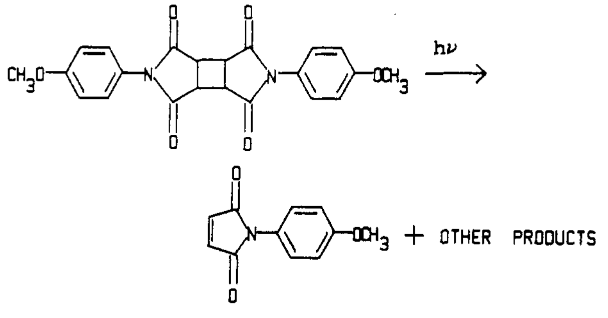
Development was carried out by immersing the samples in DMAC, a solvent in which the unirradiated polyimide is insoluble, for 45 s and then immersing the samples in deionized water for 15 s. After development the samples were baked at 140 °C for 30 min.

Results and Discussion

Figure 1 shows a differential scanning calorimogram, under nitrogen, of the polyamic acid. From this scan it is apparent that conversion of polyamic acid to polyimide takes place in the range 150–250 °C. Subsequent rescanning of the sample shows no transitions in this region.

Figure 2 shows the thermogravimetric behavior, under nitrogen, of the polyamic acid. The weight loss corresponding to the curing of the polyamic acid to the polyimide structure can be seen between ≃150 and 250 °C. The observed 20% weight loss in this region includes the expected 9.09% weight loss caused by the conversion shown in eq 3 as well as volatilization of low molecular weight molecules other than water. The further weight loss in the region 400–700 °C is approximately 40%, indicating that despite the incorporation of an aliphatic repeat unit in the chain, the thermal stability of this polyimide is relatively high.

Figure 3 represents the sensitivity curve for the polyimide. After each exposure the sample was developed, washed, and dried, and the remaining thickness was measured with a Dektak profilometer. In Figure 3 doses up to 500 mJ/cm^2 remove approximately 20% of the initial film thickness. Reirradiation of the film after solvent development and drying solubilizes a further portion of the film. The photoproduct is apparently more absorptive than the cyclobutane ring. Measurements at lower doses yields a sensitivity in the region of 45 mJ/cm^2. Figure 4 is an example of nonoptimized positive images generated in this material. Insolubility of the cured films complicates mechanistic studies of this process, but preliminary results with a model compound derived from the reaction of CBDA with *p*-anisidine are supportive of the conclusion that the enhanced solubility of irradiated films is directly related to a light-induced cleavage of the cyclobutane ring (eq 5). Thus, HPLC (Waters Model 6000, UV detection



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[6] DeSchryver, F. C.; Boens, N.; Smets, G. *Macromolecules* **1974**, *7*, 399–406.

[7] DeSchryver, F. C.; Boens, N.; Smets, G. *J. Am. Chem. Soc.* **1974**, *96*, 6463–6469.

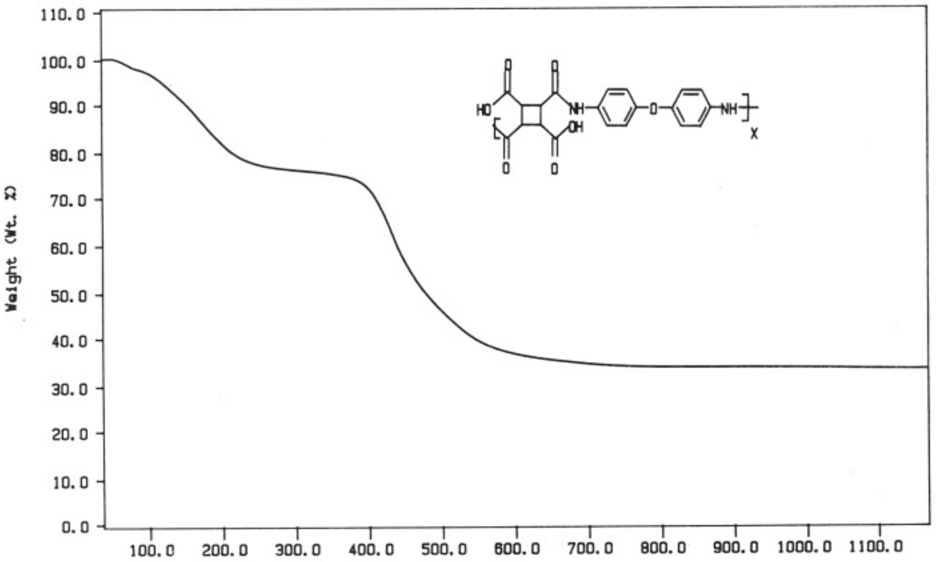


Figure 2. Thermogravimetric analysis of polyamic acid.

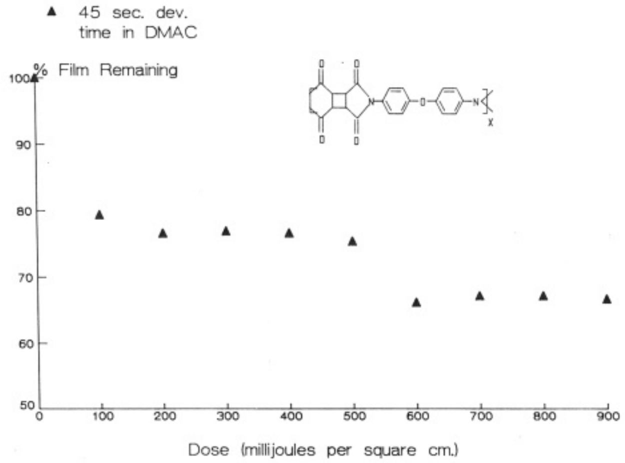


Figure 3. Sensitivity curve of polyimide (original film thickness 1.3 μm).

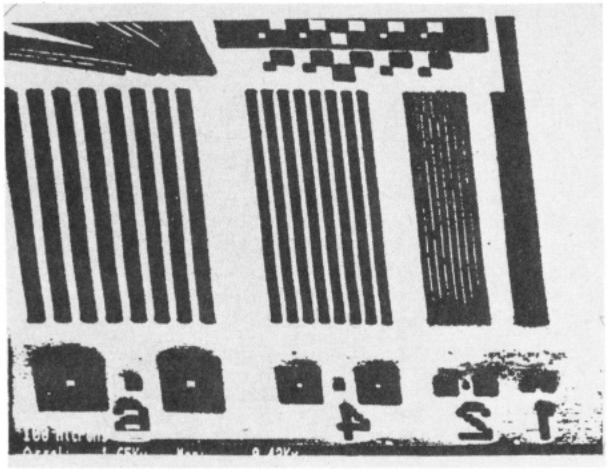


Figure 4. Ultraviolet 2-, 4-, and 6-μm lines at dose of 2.5 J/cm^2 (DMAC; developed for 30 s).

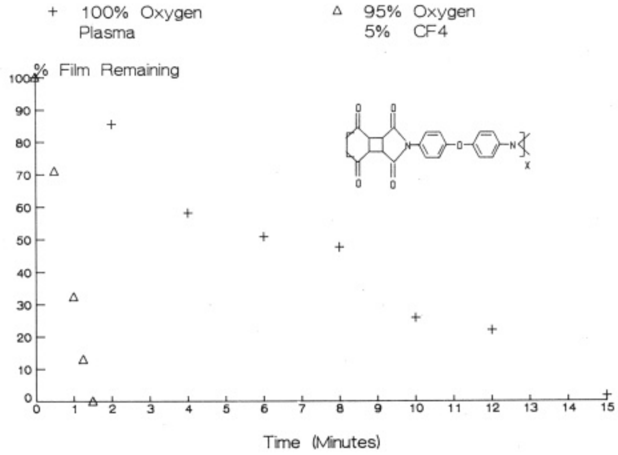
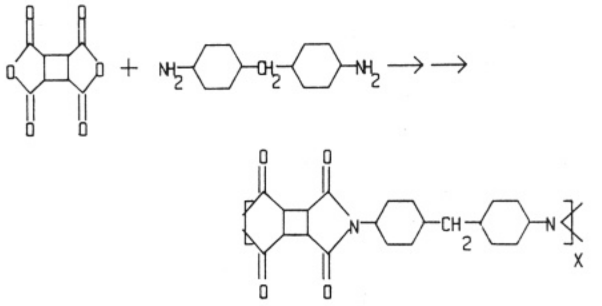


Figure 5. Polyimide plasma resistance.

at 254 nm) of the photolysis mixture obtained upon irradiation of the model compound dissolved in sulfolane under the same conditions used to image the polymer revealed the generation of *p*-anisidine maleimide (among other products), which was identified by co-injection of the authentic material. Preliminary attempts to image a film derived from CBDA and an alicyclic diamine were unsuccessful (eq 6). These results indicate that in accord



(6)

with the mechanism proposed by Lamola,[8] sensitization of the cleavage process by aromatic residues may be necessary.

Thick films of this polyimide (film derived from CBDA and oxydianiline) are resistant to a pure oxygen plasma (Technics Planar Etch II, pressure equal to 300 mTorr and power equal to 300 W) but can be rapidly removed in oxygen plasma containing 5% CF_4 under similar operating conditions, as shown in Figure 5.

Conclusion

We have successfully prepared a readily synthesized photopositive polyimide and demonstrated its utility for image generation. Work is continuing to extend the limits

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[8] Lamola, A. A. *J. Am. Chem. Soc.* **1966**, *88*, 813–819.

of sensitivity, to optimize image dimensions, and to explore the structure–photosensitivity relationships of the class of polyimides derived from cyclobutane dianhydrides and diamines.

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