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A SOLUBLE PHOTSENSITIVE POLYIMIDE

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ABSTRACT

We have been studying an intrinsically photosensitive polyimide derived from cyclobutane dianhydride and oxydianiline which exhibits both good thermal stability (50% weight loss at 460°C) and high deep ultraviolet sensitivity (45 mJ/cm²).⁽¹⁾ However, the insolubility of cured polyimide films complicates the detailed mechanistic investigation of the photochemical process. We have therefore prepared a soluble homolog of this system which is derived from the dimer of methyl maleic anhydride. This material may also be imaged with deep ultraviolet radiation and exhibits good thermal stability. A discussion of the photochemical behavior of this soluble system will be presented.

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 which 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 SiO₂ 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-crosslinkable alcohols.(2) 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 which is photo-insensitive. 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.(3) We have reported the use of 1,2:3,4-cyclobutane-dianhydride to form a polyimide which can be imaged by irradiation at a wavelength which corresponds to energy absorption by the cyclobutane imide moiety.(1,4) This type of polymer has been described for use as a colorless polyimide(5) but its photosensitivity was not reported.(6) Similar polyimides have been prepared by solution polymerization of aliphatic bismaleimides.(7,8)

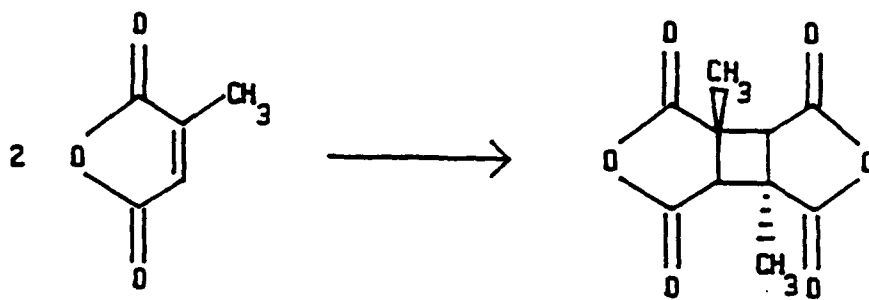
Doses up to 500 mJ/cm² remove approximately 20% of the initial film thickness. Re-irradiation of the film after solvent development and drying solubilizes a further portion of the film. Measurements at lower doses yield a sensitivity of 45 mJ/cm².(4) Preliminary results with model compounds are generally supportive of the conclusion that the enhanced solubility of irradiated films is directly related to a light induced cleavage of the cyclobutane ring, but the insolubility of this polyimide hinders a detailed study of the photochemistry of the retrocyclization process.

We now wish to report the synthesis of an intrinsically photosensitive polyimide which is also soluble.

EXPERIMENTAL PROCEDURE

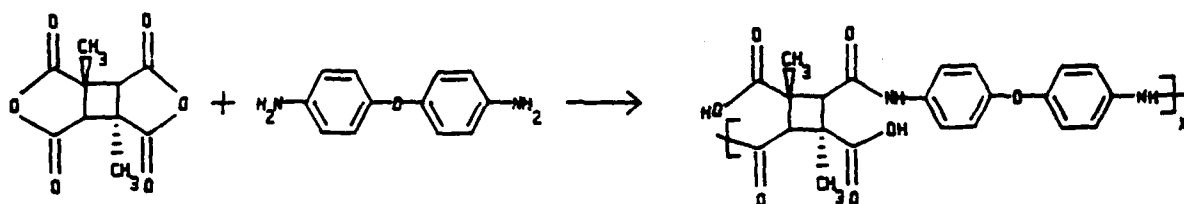
Dimethylacetamide (DMAC) was dried over calcium hydride and distilled at reduced pressure.

A solution of citraconic anhydride and 7-wt% benzophenone in freshly distilled dioxane was irradiated with an unfiltered 450 Watt Hanovia high pressure mercury arc for 18 hours to form 1,3-dimethyl-1,2,3,4-cyclobutanetetracarboxylic1,2:3,4-dianhydride (DMCBDA).(9) The stereochemistry has been shown to be *cis*, *anti*, *cis* by distinguishing between head-to-head and head-to-tail dimerization from examination of the C¹³-H nmr spectra (10).

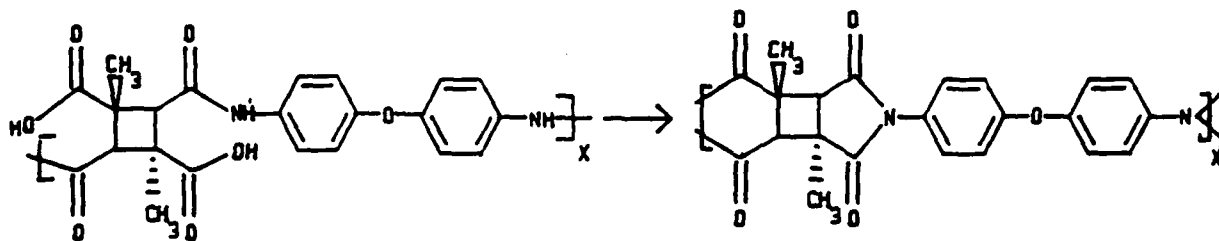


DMCBDA precipitated from solution and was collected by filtration and was purified by successive recrystallizations from ethyl acetate-hexanes.

To a dry, 3-necked, 100 ml round-bottomed flask fitted with a magnetic stirrer, nitrogen inlet and condenser was added 1.17313g (5.2332 mmoles) of DMCBDA, 50 ml of dry DMAC and 1.04790g (5.2332 mmoles) of oxydianiline (Aldrich Gold Label). The reaction was allowed to proceed at room temperature under dry nitrogen for 17 hr, the temperature was then raised to 70°C and the reaction continued for an additional 20 hr. The resulting polyamic acid was precipitated into methanol and dried in vacuo at room temperature for 24 hr. A yield of 65% was achieved.



The polyamic acid was cured to the polyimide by heating films cast by solvent evaporation in a watch glass, in an oven for 2 hr. at 75°C, 2 hr. at 150°C and 2 hr. at 200°C.



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 film thickness (0.6 micron) was measured with a Dektak profilometer.

The polyimide films were irradiated with a high pressure 500 watt Hg-Xe lamp (Hybrid Technology Group) in the range of 230 to 254 nm at incident doses ranging from 100 - 500 mJ/cm² (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, a quartz contact mask was used.

Development was carried out by immersing the samples in ethyl acetate, a non-solvent for the unirradiated polyimide, for 30 seconds and then immersing the samples in deionized water for 15 seconds. After development the samples were baked at 120°C for 30 minutes.

RESULTS AND DISCUSSION

Fig. 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 of 150°C - 200°C. Subsequent rescanning of the sample shows no transitions in this region.

Fig. 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 and one also sees that, once the polyimide is formed, 50% weight loss occurs at about 440°C and after heating the sample to 1200°C there is a residual weight of approximately 28%.

Fig. 3 represents the sensitivity curve for the polyimide. After each exposure the sample was developed, washed, dried and the remaining thickness was measured with a Dektak profilometer. In Fig. 3 doses up to 500 mJ/cm² remove approximately 70% of the initial film thickness. Measurements at lower doses are currently in progress and a sensitivity lower than 45 mJ/cm² is expected. Fig. 4 is an example of non-optimized positive images generated in this material.

Table 1 shows a comparison between the polyimide previously reported and the polyimide derived from DMCBDA. These results clearly indicate that the presence of two methyl groups on the cyclobutane ring in the polyimide facilitate the cleavage of the backbone, perhaps because steric compression favors the reversion reaction. In addition, the added methyl groups solubilize the polyimide, presumably by hindering intermolecular association. The polyimide is soluble in polar aprotic solvents such as DMSO, DMF, DMAC, and NMP.

CONCLUSION

We have successfully prepared a readily synthesized, photopositive, soluble polyimide and demonstrated its utility for image generation. Work

is continuing to extend the limits of sensitivity, to optimize image dimensions and to explore the structure-photosensitivity relationships of the class of polyimides derived from cyclobutane dianhydrides and diamines as well as to explicate the mechanistic underpinnings of this process.

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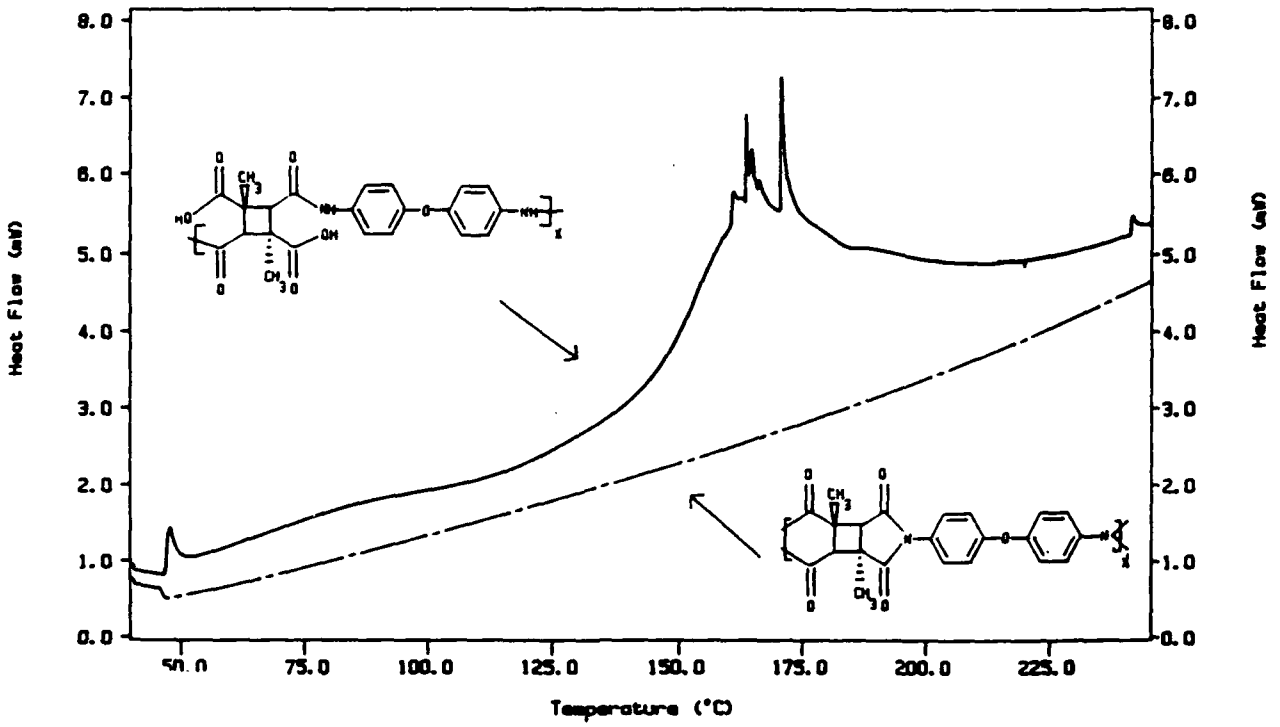


FIGURE 1. Differential Scanning Calorimogram of polyamic acid.

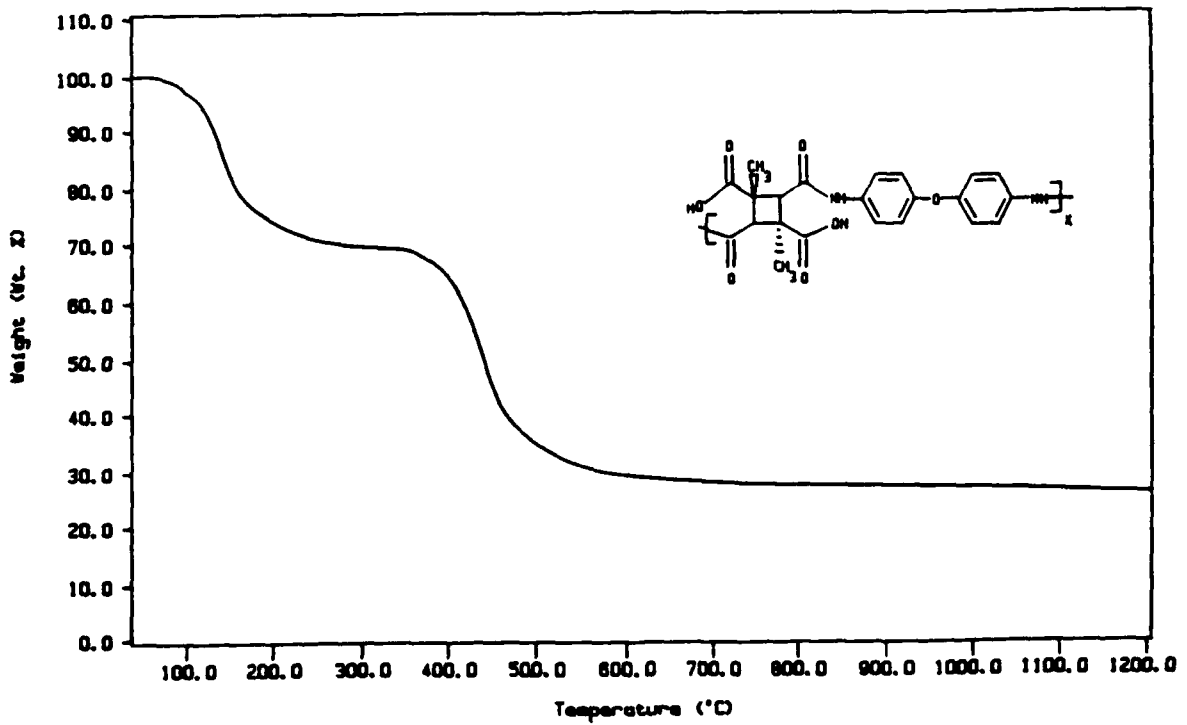


FIGURE 2. Thermogravimetric Analysis of polyamic acid.

Sensitivity curve of Polyimide

Original film thickness 0.6 microns

▲ 30 sec. dev
ETOAC

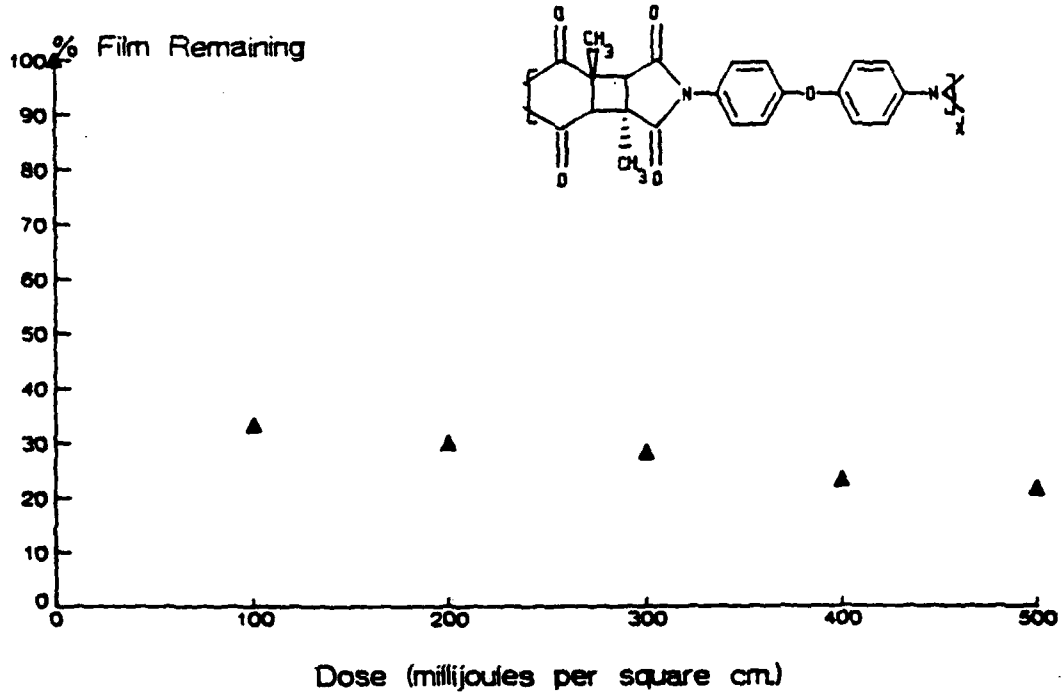


FIGURE 3. Sensitivity curve of polyimide.

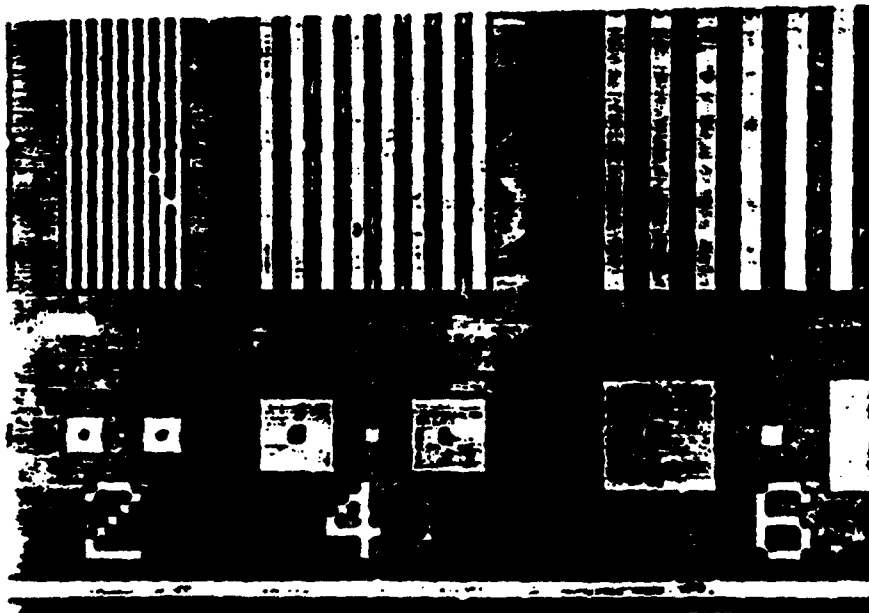


FIGURE 4. 2, 4 and 6 micron lines at dose of 200 mJ/cm².

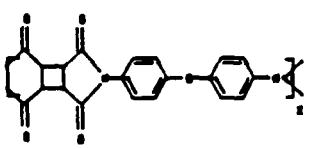
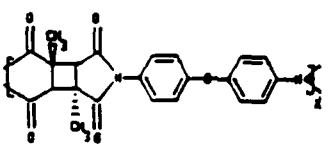
		
DOSE (mJ/sq. cm.)	% Film Remaining	% Film Remaining
0	100	100
100	79.4	33.3
200	76.6	30.0
300	76.9	28.3
400	76.6	23.3
500	75.4	21.7

TABLE 1. Sensitivity of two cyclobutane containing polyimides.