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Poly(aryline imides) as E-Beam Resist: Sensitivity and Resolution

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Synopsis

Polyamic acids synthesized from di-trifluoromethyl methane bis(phthalic anhydride) and 4,4'-diaminophyenyl sulfone (F-1) and 4,4'-diaminophenyl ether (F-4) were found to have excellent negative E-beam resist properties. The best materials contain about 90% imidized structural units having sensitivities of 1.5 to 2.5 μC/cm² and contrast of 1.0 to 1.3. Polyamic acid of pyromellitic dianhydride and 4,4'-diaminophenyl sulfone (P-1) imidized to 97% exhibits useful positive E-beam resist properties. Radiation induces imidization and chain scission to alter the solubility of the resist polymers resulting in the formation of latent images.

INTRODUCTION

Polymeric materials are used in conjuction with the technology of VLSI in two main areas. The first is the E-beam resist applications. Several monographs are now available on the subject. In our laboratory, we have investigated the halogen atom sensitization effect[1-5] and low ceiling temperature polymers[6,7] in E-beam lithography especially concerning the possibility of self-developing direct imaging positive resists.

Thermally stable polymers found the following usages in VLSI: (1) passivating overcoat, (2) interlevel dielectrics, (3) multi-level multi-conductor substrates, (4) adhesive for bonding a substrate to the chip[8-10]. Polyimides are the preferred materials in these applications.

There have been proposals to use polyimides in photo-imaging systems.[11,12] So far, photo-active ingredients are needed which are not heat stable. The photosensitizers need to be decomposed and volatilized; their complete elimination had been one of the technical difficulties. The other shortcomings are the limited shelf-life stability and shrinkage in curing resulting in image distortion and stress build-up.

The central purpose of this work is to discover a polyimide resist system which does not need a sensitizing additive and forms high resolution image without shrinkage. The preparation of the polyimide resists and their radiolytic behaviors are given in the accompanying paper.13

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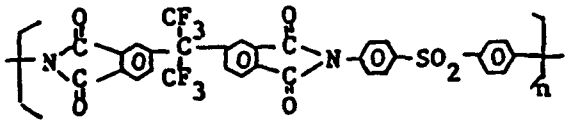
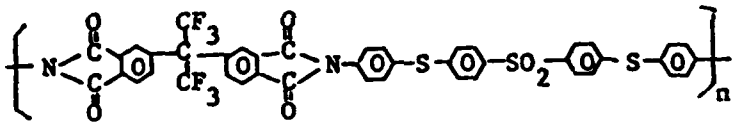
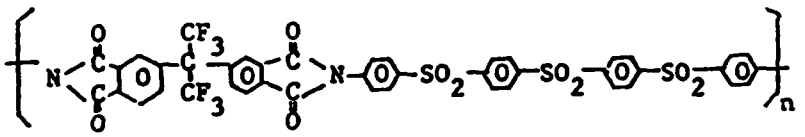
EXPERIMENTAL

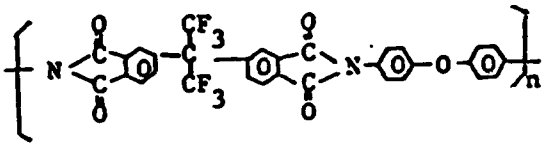
Materials

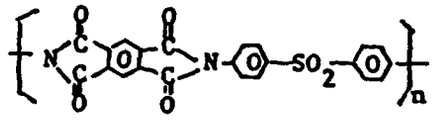
The synthesis of polyamic acids are given in detail elsewhere[13]; their structures are given below:

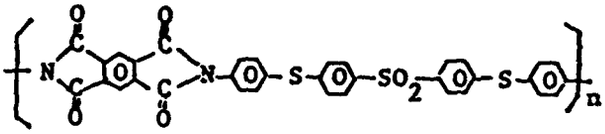
F-1 

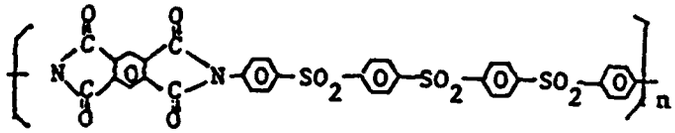
F-2 

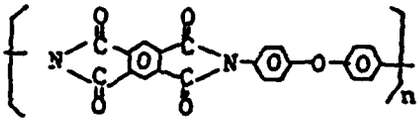
F-3 

F-4 

P-1 

P-2 

P-3 

P-4 

The F series polymers were prepared from di-trifluoromethyl methane bis(phthalic anhydride) (F6 dianhydride) and the P series polymers were prepared from pyromellitic dianhydride.

Imidization

Imidization was carried out in a thermal reactor under an atmosphere of nitrogen monitored by 1380 cm^{-1} and 1780 cm^{-1} band intensities for the C-N and C=O vibrations respectively.[14] The degree of imidization (D.I.), is estimated from the ratio of optical density at 1380 cm^{-1} following heat treatment to the optional density after 15 min. of heating at 300°C, the latter corresponds to complete imidization. Figure 1 shows the IR spectral changes with imidization; figure 2 plots the degree of imidization versus temperature of heating for 5 min.

Polyimide samples with various degree of imidization were prepared as described in Table I.

Gamma irradiation

Gamma irradiation was performed with a ^{137}Cs source and the dose rate determined by Fricke dosimetry.

E-beam lithography

Polymer was dissolved in dimethyl formamide (10% in DMF) and the solution spin-coated on a silicon waffle and prebaked for 10 min. at 120°C. The resist film, about one micron thick, was exposed to a 20 keV electron beam with a JEOL JSM-35 CF scanning electron microscope, and the image

Table I Imidization of polyamic acids

polyamic acid	Degree of imidization (D.I.), %				
	170°C	200°C	250°C	280°C	300°C
F-1	38	73	91	98	~100
F-2	45	80	96	98	~100
F-3	54	79	90	97	~100
F-4	62	81	90	96	~100
P-1	41	69	87	97	~100
P-2	66	72	90	96	~100
P-3	33	65	89	98	~100
P-4	68	75	91	98	~100

After 5 min. of heating at indicated temperatures except it was >15 min at 300°C to affect complete imidization.

developed with a i-propanol/DMF mixture for 2 min. and rinsed with i-propanol. The thickness of resist was measured with interference microscopy.

RESULTS AND DISCUSSION

F-1 and F-4 were found to be excellent negative resists; these performances vary with D.I. Figure 3 gives the variation of thickness with dose. From these curves the values of sensitivity and contrast, γ were calculated (Table II). Figure 4 and Table III contain the results for F-4.

Neither the polyamic acid nor the polyimide of either polymer acts as resist but the copolymer does. The structure of the random copolymer may be represented by

$$-(\text{imide})_{\text{D.I.}}-(\text{amic acid})_{\text{100-D.I.}}$$

Table IV summarized the results of these and other polymers. The best performing polymers have D.I. between 90-97%. Figure 5 is a plot of sensitivity versus D.I. for F-1 and F-4. F-3 and P-3 are useless as resists because they are

Table II. Properties of F-1 polyimides in E-beam lithography

D.I.,%	Developer DMF: i-propanol volume ratio	Sensitivity μ C cm^{-2}	γ	Resolution
0	1:20	-	-	poor
38	1:4	10	-	poor
73	1:3	5	1.2	good
91	3:4	2.5	1.1	excellent
98	1.1	3	1.0	excellent

Table III.Properties of F-4 polyimides in E-beam lithography

D.I.,%	Developer DMF: i-propanol volume ratio	Sensitivity μ C cm^{-2}	γ	Resolution
0	1:20	-	-	poor
62	1:3	8.0	0.96	good
81	1:2.5	4.5	0.89	good
90	1:1	1.5	1.3	excellent
96	1:0.5	2.0	1.1	poor

insoluble at any D.I.

P-1 is the only material which acts in the positive mode to E-beam irradiation. Figure 6 and Table V give the detail results.

Table IV Summary of E-beam lithographic properties

Sample	D.I.,%	Developer DMF: i-propanol	Sensitivity μ C cm^{-2}	Resolution	Mode	Usefulness
F-1	91	3:4	2.5	excellent	neg.	excellent
F-2	96	2:1	6.5	excellent	neg.	excellent
F-4	90	1:1	1.5	excellent	neg.	excellent
P-1	97	1:0	8	good	pos.	useful
P-2	90	1:0	8	good	neg.	poor
P-4	75	1:0	-	poor	neg.	useless

The excellent negative E-beam resist properties found for the F-series polyimides and and their dependence on D.I. are both unexpected. The polymers were synthesized with the hope that they will be good positive E-beam resist based on

Table V Properties of P-1 polyimides in E-beam lithography

D.I.,%	Developer DMF:i-propanol volume ratio	Sensitivity, $\mu C\ cm^{-2}$	γ	Resolution
0	0:1	-	-	-
41	1:3	-	-	-
69	1:2	-	-	-
87	2:1	7	0.9	good
97	1:0	8	1.0	good
~100	1:0	10	1.7	good

the sensitivity of sulphone moiety to energetic radiation.[15-17] Alternating copolymers of olefin and SO_2, poly(alkylene sulfones), have G-values of up to twenty SO_2 and olefins produced per 100 eV. It was reported in the accompanying paper[13] that the F-series polyimides has G_s values between one and two scissions per 100 eV. These G_s values are comparable to that for poly(methyl methacylate) which is a commerically used E-beam positive resist.

Therefore, some other mechanism is responsible for the negative E-beam resist action of the F-series polyimides.

Sample of F-1 with 73% D.I. was irradiated with γ-radiation for five days. Infrared spectra (Figure 7a) showed that the D.I. was raised to 88%. Similarly, an F-1 sample with 91% D.I. was irradiated, the D.I. increased to 99% after 5 days of irradiation (Figure 7b). Since the solubility of the polymer decreased with the increase of D.I., the exposed region has lowered solubility. In this way, this discovery of negative E-beam resist properties for the F-series polyimides and their dependence on D.I. can be explained. The superior properties of the F-series than the P-series may be simply because the former have better solubility characteristics. The positive E-beam behavior of the P-1 material is different from the F-series but is along the line of our initial expectation.

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References

1. G.N. Babu, A. Narula, S.L. Hsu, and J.C.W. Chien, Macromolecules 7, 2749 (1984).
2. G.N. Babu, A. Narula, P.H. Lu, X. Li, S.L. Hsu, and J.C.W. Chien, Macromolecules 17, 2756 (1984).
3. G.N. Babu, P.H. Lu, S.L. Hsu, and J.C.W. Chien, J. Polym. Sci. Polym. Chem. Ed. 22, 195 (1984).
4. G.N. Babu, P.H. Lu, S.L. Hsu, and J.C.W. Chien, J. Polym. Sci. Polym. Chem. Ed. 23, 1421 (1985).
5. G.N. Babu, P.H. Lu, and J.C.W. Chien, Macromolecules 17, 276 (1984).
6. J.C.W. Chien and P.H. Lu, Macromolecules submitted.
7. J.C.W. Chien, Zhao, B. Xu, and D. Khanna, J. Polym. Sci. Polym. Chem. Ed. in press.
8. A.M. Wilson, Thin Solid Films 83, 145 (1981).
9. P.P. Ghate, Thin Solid Films 93, 359 (1982).
10. S.D. Senturis, R.A. Miller, D.D. Denton, F.W. Smith, III, and H.J. Newhaus, Proc. 2nd Intu. Conf. Polyimides 107 (1985).
11. W.H. Shen, A.J. Yo, and B.M. Gong in "Polyimides, Synthesis, Characterization and Applications," K.L. Mittal, Ed. Plenum Press, NY, 1984, p. 947.
12. J. Pfeifer and O. Rohde, Proc. 2nd Int. Conf. Polyimides, 130 (1985).
13. J.C.W. Chien and Z.S. Cheng, J. Polym. Sci. Polym. Chem. Ed. submitted.

14. S. Nishizake and A. Fukami, Kogyo Kagaku Zasshi 66, 3822 (1963); 67 474 (1964).

15. M.J. Bowden and L.F.Thompson, J. Appl. Polym. Sci. 17, 3211 (1973).

16. T.W. Bonmer and J.H. O'Donnell, J. Polym. Sci. Polym. Chem. Ed. 19, 45 (1981).

17. T.W. Bonmer, J.H. O'Donnell and P.R. Wells, Makromol. Chem. Rapid Commun. 1, 1 (1980).