Preparation and Characterization of Photoreactive Copolymers Containing Curable Pendants for Positive Photoresist

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ABSTRACT: *tert*-Butyl methacrylate (TBMA) was copolymerized with various comonomers that were selected from methyl methacrylate (MMA), *n*-butyl acrylate (NBA), acrylic acid (AA), and 2-hydroxyethyl methacrylate (HEMA). From film physical properties, poly(TBMA-*co*-HEMA) and poly(TBMA-*co*-AA-*co*-NBA), were selected as resin binders. To introduce unsaturated double bonds onto the side chain of copolymers, they were further functionalized with acryloyl chloride and glycidyl methacrylate. Copolymers synthesized in this investigation were all identified by using FTIR and NMR. The thermal decomposition temperature of functionalized poly(TBMA-*co*-HEMA) showed obvious difference before and after crosslinking. Adding a small amount of EGDMA as the crosslinking agent could increase the degree of crosslinking and obviously improve the physical properties. Functionalized poly(TBMA-*co*-HEMA) was used as a binder resin and composed with a photoacid generator for positive photoresists. From exposure characteristics, the optimal lithographic condition was achieved when exposed for 90 s, PEB at 100°C for 2.5 min, and developed in 10 wt % Na_2CO_3 developer for 30 s. After completing the lithography process, the residual pattern of positive photoresist was further treated at 140°C for 30 min to cure the pendant unsaturated groups. The resolution of the positive photoresist was analyzed by an optical microscope and SEM technique. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 328–333, 2001

Key words: positive tone photoresist; photoacid generator; crosslinking; functionalization; postexposure baking

INTRODUCTION

Positive photoresists based on novolak resin and 1,2-naphthoquinone diazide (NQD) derivatives are extensively utilized in the field of photolithography.[1–5] The photochemical conversion of hydrophobic NQD to hydrophilic indenecarboxylic acid via ketocarbene and ketene intermediates lead to the formation of positive images. On the other hand, several process variations enable us to reverse the tone of the image to create negative images.[6,7] The advancements in IC fabrication processes require the photoresist to withstand elevated temperatures and harsh environments during processing to maximize wafer throughput and device yields. Recent developments in photoresists include modification in materials as well as in the processing conditions, such as use of high molecular weight novolak, resin-bound sensitizer, silicone modified novolak, and changes in processing parameters like postbake cycle and deep UV hardening to enhance thermal stability of the resist.[8,9]

Polyimides are an important class of high-performance polymers. The qualities of a high thermal stability and a low dielectric constant are

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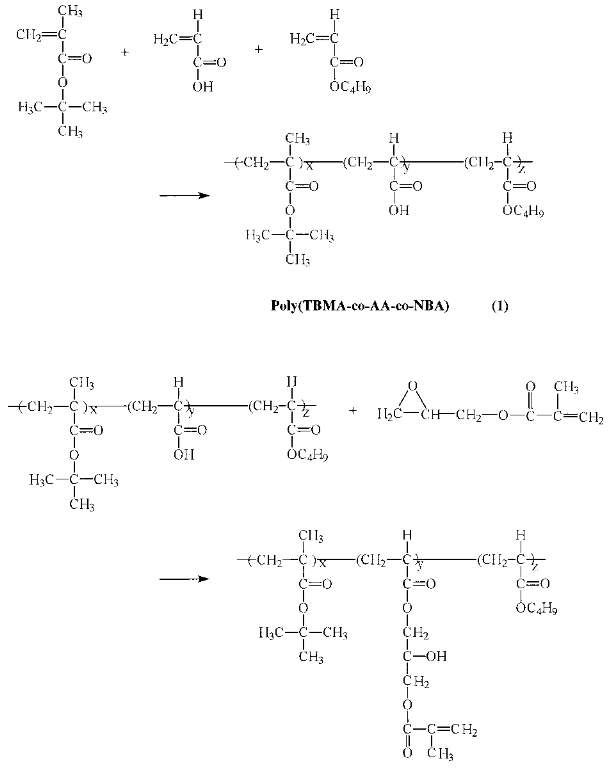


Poly(TBMA-co-AA-co-NBA) (1)

Copolymer (2)

Scheme 1

especially desirable in the manufacturing of semiconductors. However, the process for multilayer fabrication using conventional polyimides is complicated. The flexibility and the adhesion between polyimide and substrate such as silicone wafer are not always satisfactory. In previous research we have reported the syntheses of polyamic acid, polyurea, and poly(amic acid-*co*-urea)s in various contents, and their applications on the negative photoresist in the presence of diazo resin.[10] The chemical behavior of polymers bearing cycloaliphatic bornyl units, and the steric difference of the chiral (+)-bornyl methacrylate [(+)-BMA] and achiral (±)-BMA units appeared on the physical properties of copolymers, and electro-optical properties of liquid crystal display were all investigated.[11]

This article describes the syntheses of functionalized poly(TBMA-*co*-HEMA) and poly(TBMA-*co*-AA-*co*-NBA) by using acryloyl chloride and glycidyl methacrylate. Applications of the copolymers having pendant unsaturated groups on the positive tone photoresists were investigated. The optimal lithographic conditions, developer, and resolution of the photoresist were all estimated in this investigation.

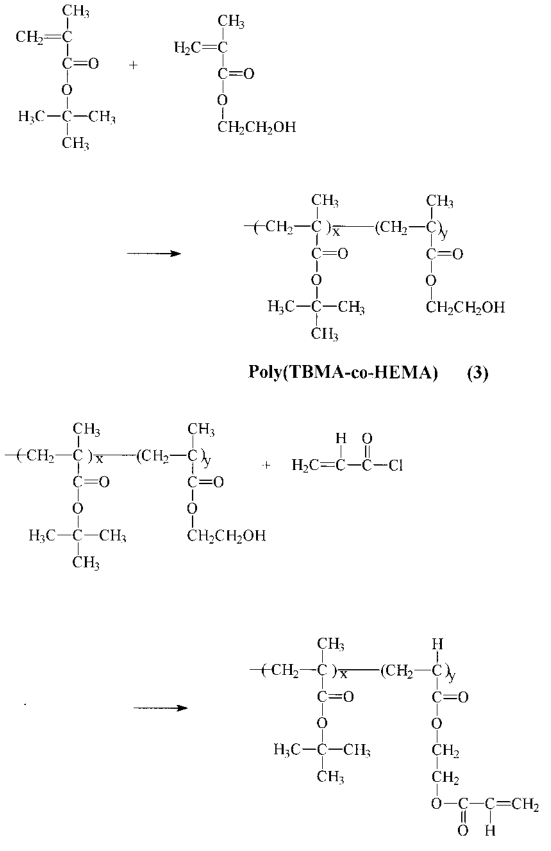
EXPERIMENTAL

Materials

Commercial monomers used in this investigation were obtained from Merck Pure Chemical Industries, Ltd.. Monomers of *tert*-butyl methacrylate (TBMA), methyl methacrylate (MMA), acrylic acid (AA), 2-hydroxyethyl methacrylate (HEMA), and *n*-butyl acrylate (NBA) were purified by distillation technique. The initiator azobisisobutyronitrile (AIBN) was purified by recrystalization in ethanol. Triphenylsulfonium hexa-fluoroantimonate was used as a photoacid generator. Organic solvents used in this investigation were all distilled, and dried with molecular sieves prior to use.

Measurements

The UV-visible spectra of films of the photoresist on quartz substrates were measured with JASCO UV/VIS 7850 double-beam spectrometer. The photoresist was exposed with a Karl Suss MJB-3



Poly(TBMA-co-HEMA) (3)

Copolymer (4)

Scheme 2

Table I Thermal Properties of Poly(TBMA-*co*-AA-*co*-NBA)

Copolymers	$T_{d,5\%}$[a] (°C)	T_{d2} (°C)	T_{d3} (°C)	Char Yield at 550°C
Poly(TBMA-*co*-AA-*co*-NBA)	222.5	254.9	451.4	2.9%
Functionalized Copolymer[b]	233	265.4	454.7	3.2%
Crosslinked polymer[c]	234	267	455	3.5%

[a] Initial degrading temperature at 5% weight loss.
[b] Functionalized poly(TBMA-*co*-AA-*co*-NBA), before crosslinking.
[c] Functionalized copolymer crosslinked at 140°C for 30 min.

aligner. The film thickness was measured with a Tencor Instrument alpha step-200 film thickness monitor. Dissolution rate is defined as the changes of photoresist film thickness per development time. The resist pattern profiles were evaluated using a JEOL JSM-35 and JAX-840 scanning electron microscope. Thermal properties and functional groups of polymers were evaluated and analyzed by using a Du Pont 910 differential scanning calorimeter, Perkin-Elmer TGA-7 thermogravimetric analyzer, and JASCO FTIR spectrometer, respectively. Elemental analyses were calculated with a Heraeus CHN-O rapid elemental analyzer.

Preparation of Copolymers

Poly(TBMA-*co*-AA-*co*-NBA) (1) and poly(TBMA-*co*-HEMA) (3) were obtained by the copolymerization of monomers in tetrahydrofuran (THF) in the presence of 1 wt % AIBN at 60°C for 12 h. After complete the reaction, copolymers were precipitated from a large amount of water/methanol (1 : 1 in volume) solution, and then washed with distilled water completely.

Functionalization of Poly(TBMA-*co*-AA-*co*-NBA)

Poly(TBMA-*co*-AA-*co*-NBA) (1) (27.8 g), hydroquinone (0.5 g), and triphenyl phosphine (0.5 g) were dissolved in 40 mL of THF. Glycidyl methacrylate (21.3 g) was added to the mixture dropwise, and then reacted at 65°C for 24 h. The polymer structures are shown in Scheme 1. After complete the reaction, the functionalized copolymer was precipitated from an excess water/methanol solution. A white copolymer (2) powder was obtained, and dried at 28°C in vacua for 1 h. The functionalized copolymers were stocked in refrigerator prior to use.

Functionalization of Poly(TBMA-*co*-HEMA)

Poly(TBMA-*co*-HEMA) (3) (20.1 g), and *N,N*-dimethyl aniline (12.1 g) were dissolved in 40 mL of THF. Acryloyl chloride (13.6 g) was added to the mixture dropwise, and then reacted at 40°C for 24 h. The polymer structures are shown in Scheme 1. After completing the reaction, an excess distilled water was added to decompose the excess amount of acryloyl chloride. The functionalized copolymer was precipitated from a large amount of water/methanol solution. A white copolymer (4) powder was obtained, and dried at 28°C in vacua for 1 h. The functionalized copolymers were stocked in refrigerator prior to use.

Exposure Method

Photosensitive solution was obtained by dissolving functionalized copolymers (1 g), photo-acid

Table II Thermal Properties of Poly(TBMA-*co*-HEMA)

Copolymers	$T_{d,5\%}$[a] (°C)	T_{d2} (°C)	T_{d3} (°C)	Char Yield at 550°C
Poly(TBMA-*co*-HEMA)	198.7	226.3	442.3	0.7%
Functionalized Copolymer[b]	238.2	264.1	457.0	4.5%
Crosslinked polymer[c]	264.6	284.5	473.1	5.5%

[a] Initial degrading temperature at 5% weight loss.
[b] Functionalized poly(TBMA-*co*-HEMA), before crosslinking.
[c] Functionalized copolymer crosslinked at 140°C for 30 min.

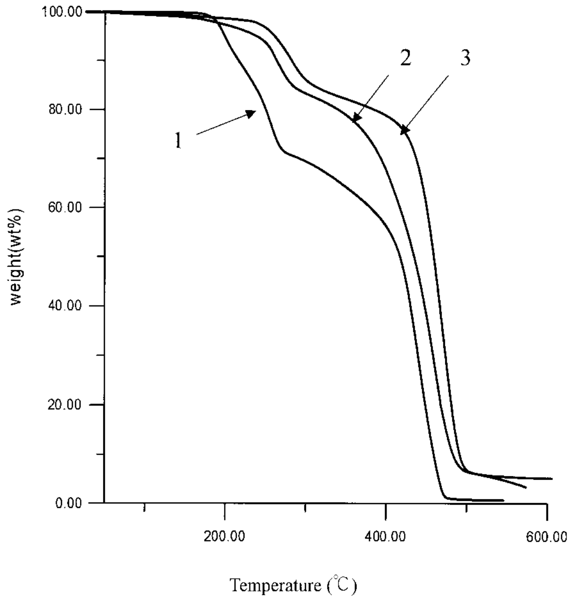


Figure 1 TGA curves of (1) poly(TBMA-*co*-HEMA), (2) functionalized poly(TBMA-*co*-HEMA) before, and (3) after crosslinking.

generator (0.1 g), and AIBN (0.2 g) in 10 mL of THF. The photosensitive solution was filtered with a 0.45 μm filter, and then spin coated onto a silicon wafer plate by 1000 rpm for 10 s, and then 2500 rpm for 20 s. Prebaked at 80°C for 3 min. The photoresist was exposed with a Karl Suss MJB-3 aligner. After exposure, and postexposure bake (PEB) the photoresist were developed with a 30-s immersion in 10 wt % sodium carbonate developer. The residual positive image was then treated at 140°C for 30 min. The thermal treatment lead the residual pattern of the photoresist to crosslink and increase its physical properties.

RESULTS AND DISCUSSION

Preparation and functionalization of poly(TBMA-*co*-AA-*co*-NBA) and poly(TBMA-*co*-HEMA) are shown in Schemes 1 and 2, respectively. The acid-cleavable *tert*-butyl groups and crosslinakable unsaturated double bounds were introduced onto the copolymer pendant side. From the film transparency and flexibility of copolymers, the feed monomer ratio of 1/1/0.5 for poly(TBMA-*co*-AA-*co*-NBA) and 1/2 for poly(TBMA-*co*-HEMA) was selected in this investigation. Thermal properties of the copolymers were analyzed by using TGA

Table III Effects of EGDMA on Thermal Properties of Copolymers[a]

EGDMA (wt %)	$T_{d,5\%}$[b] (°C)	T_{d2} (°C)	T_{d3} (°C)	Char Yield at 550°C
0%	250.0	280.5	473.1	5.5%
10%	272.9	282.7	483.2	5.5%
25%	274.5	283.0	473.7	5.6%

[a] Functionalized poly(TBMA-*co*-HEMA) crosslinked at 140°C for 30 min.

[b] Initial degrading temperature at 5% weight loss.

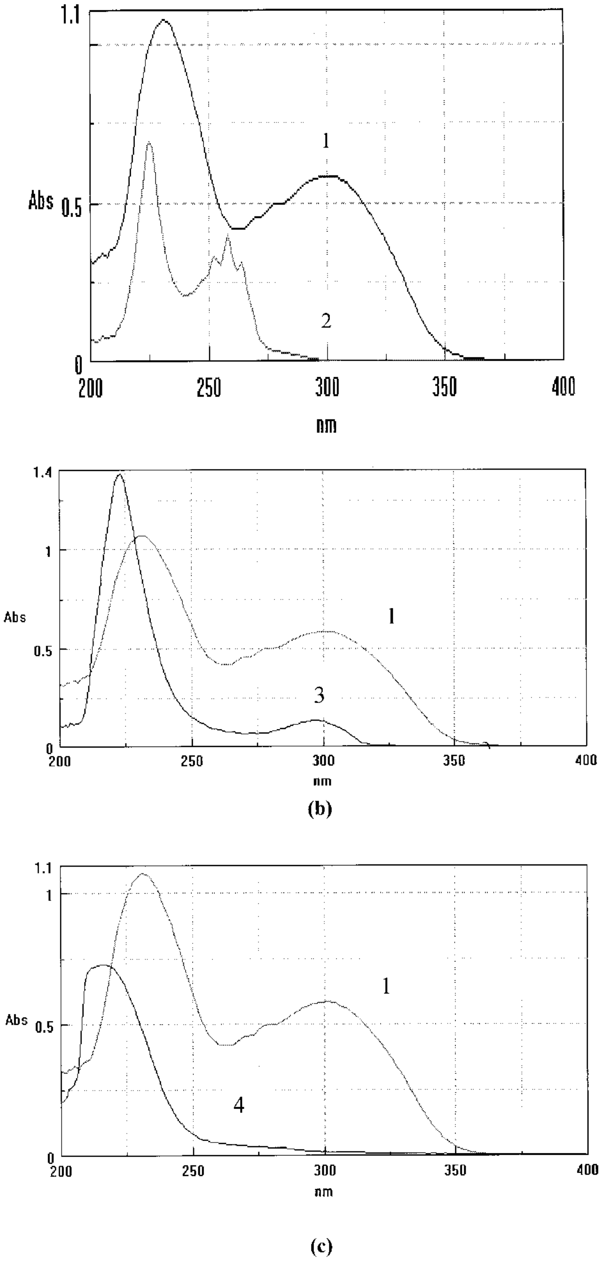


Figure 2 UV spectra of (a) PAG(1)/DCPO(2), (b) PAG(1)/functionalized poly(TBMA-*co*-AA-*co*-NBA)(3), (c) PAG(1)/functionalized poly(TBMA-*co*-HEMA)(4).

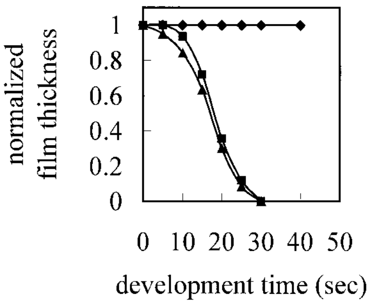


Figure 3 Development rate curves of functionalized poly(TBMA-*co*-HEMA) with various conditions in 10 wt % Na_2CO_3 developer. (◆): Unexposed, PEB at 110°C for 5 min; (■): Exposed 120 s, PEB at 100°C for 5 min; (▲): Exposed 120 s, PEB at 110°C for 5 min.

method and the results are summarized in Tables I and II. As shown in the tables, the thermal properties of both copolymers were improved by the functionalization and crosslinking treatment. $T_{d5\%}$, T_2, and T_3 represent the initial degrading temperature of copolymers at 5% weight loss, the degrading temperature at the second stage, and at the third stage, respectively. Table I shows only a small crosslinking effect, and the thermal stability observed in Table II are all greater than those observed in Table I. The results suggest that the degree of crosslinking in poly(TBMA-*co*-HEMA) is greater than that of poly(TBMA-*co*-AA-*co*-NBA).

Figure 1 shows the comparison of TGA curves of poly(TBMA-*co*-HEMA) before and after functionalization and crosslinking. The thermal properties are improved obviously after functionalization and crosslinking treatment. The results suggest that the thermal resistance of residual image of positive photoresist will be improved by using the copolymers as binder resins.

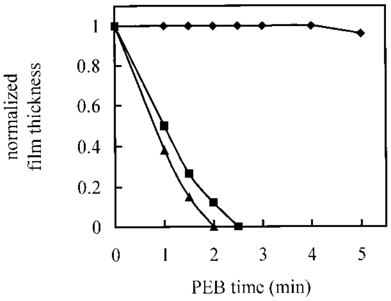


Figure 4 Dependence of normalized film thickness on PEB time in 10 wt % Na_2CO_3 developer for 30 s. Exposed 90 s and PEB at, (◆): 80°C; (■): 100°C; (▲): 110°C.

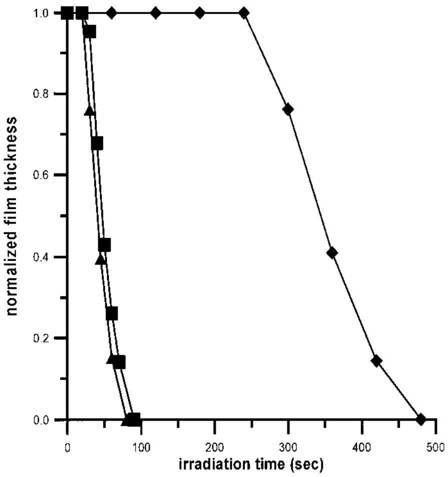
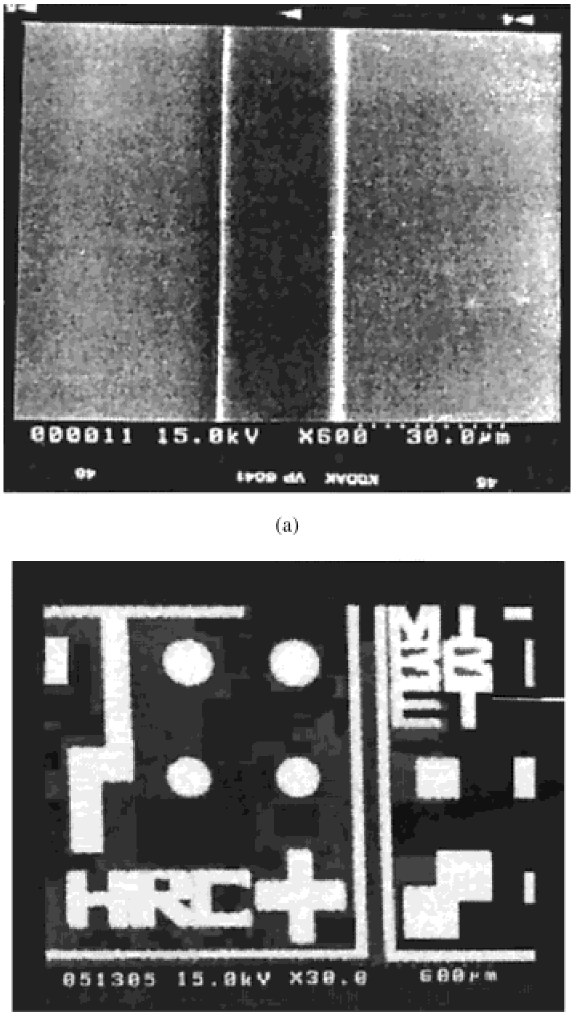


Figure 5 Dependence of normalized film thickness on UV irradiation in 10 wt % Na_2CO_3 developer for 30 s. PEB for 5 min at (◆): 80°C; (■): 100°C; (▲): 110°C.

Table III shows the effect of crosslinking agent of ethyleneglycol dimethacrylate (EGDMA) on the thermal properties of copolymers. Adding of crosslinking agent may increase the degree of crosslinking and lead to the increasing of thermal stability of the copolymers. The amount of 10 wt % of EGDMA seems suitable for the poly(TBMA-*co*-HEMA).

From the thermal stability, dicumyl peroxide (DCPO) was selected as the thermal initiator for the crosslinking reaction of pendant unsaturated groups. Figure 2 shows the UV spectra of photoacid generator, DCPO, and copolymers used in this investigation, respectively. From the results, the wavelength of 250 to 300 nm is suitable for the photoresist. The thermal stability of photoacid generator (PAG) was investigated. As shown in Figure 3 (curve 1), the PAG is stable at the postexposure backing (PEB) temperature 110°C for 5 min. The photoacid cleavage reaction of the binder copolymer was not occurred without any UV irradiation. Curves 2 and 3 show the exposure curve of photoresist comprising copoly(TBMA-*co*-HEMA) with various PEB conditions. Higher temperature seems good for the proceeding of acid cleavage reaction in the PEB stage.

The results of the dependence of normalized film thickness on PEB time are shown in Figure 4. After completing the exposure and PEB treatment, the resist was developed in 10 wt % sodium carbonate for 30 s. As shown in the figure, the acid-catalyzed cleavage reaction of the resist binder polymer accelerated with the increasing of PEB time. The PEB condition of 80°C seems not



(a)

(b)

Figure 6 SEM photographs of resist patterns.

suitable for the exposure condition of 90-s UV irradiation.

A short UV irradiation may release not enough acid to proceed the cleavage reaction at the lower PEB temperature. As can be seen in Figure 5, the sensitivity and the contrast of the photoresist are all improved at the higher PEB temperature. The results consist with those observed in Figure 4. At higher PEB temperatures, the acid-catalyzed cleavage reaction of the pendant *tert*-butyl groups will be accelerated effectively. The lithographic evaluation of the positive tone photoresist with poly(TBMA-*co*-HEMA) as a binder resin was also investigated. Figure 6(a) and (b) shows the scanning electron micrograph (SEM) of the patterns; a 15-μm pattern resolution was achieved. The acrylic copolymers synthesized in this investigation containing no aromatic ring, which can be used as deep-UV imageable materials.

CONCLUSION

The functionalized poly(TBMA-*co*-HEMA) having pendant unsaturated double bound groups can be used as a resin binder for the deep-UV positive tone photoresist. The thermal properties of the residual image photoresist can be improved by PEB treatment. The acid-catalyzed cleavage reaction will be accelerated at a higher PEB temperature. Photoresist comprised of poly(TBMA-*co*-HEMA) having pendant unsaturated groups containing no aromatic rings can be used as deep-UV imageable materials.

REFERENCES

1. Ershov, V. V.; Nikiforov, G. A.; De Jonge, C. Quinonediazide; Elsevier: New York, 1981, p. 261.
2. Kosbar, L. L.; Frank, C. W.; Pease, R. F. W.; Hutchinson, J. ACS Symp Series 1993, 527, 245.
3. Ahne, H.; Rubner, R.; Kuhn, E. Eur. Pat. Disclosure, EP0023626 (1980).
4. Rubner, R.; Hammerschmid, A.; Leuschner, R.; Ahne, H. Polymers for Microelectronics—PME'89; VCH publishers: New York; Kodansha Scientific Ltd.: Tokyo, 1989, p. 789.
5. Grishina, A. D.; Vannikov, A. V.; Khazova, G. O.; Teodoradze, M. G.; Koltsov, Y. I. J Photochem Photobiol A Chem 1998, 114, 159.
6. Dinaburg, M. S. Photosensitive Diazo Compounds; The Focal Library: London, 1964.
7. Nader, A. E.; Imai, K.; Craig, J. D. Polym Eng Sci 1992, 32, 1613.
8. Allen, R.; Foster, M.; Yen, Y. T. J Electrochem Soc 1980, 127, 1379.
9. Hiraoka, H.; Pacansky, J. J Electrochem Soc 1981, 128, 2645.
10. Liu, J. H.; Lee, S. Y.; Tsai, F. R. J Appl Polym Sci 1998, 70, 2401.
11. Liu, J. H.; Tsai, F. R.; Tsai, T. Y. Polym Adv Technol 2000, 11, 228.