Poly(*N*-phenolicmaleimide) for High-Temperature Stable Near-UV Resist

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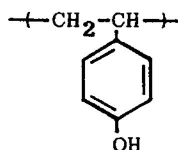
SYNOPSIS

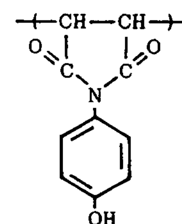
Poly[*N*-(4-hydroxyphenyl)maleimide] (PHPMI) was prepared by the radical polymerization of *N*-(4-acetoxyphenyl)maleimide, followed by transesterification of the acetoxy group. The cyclic maleimide group was responsible for high-temperature stabilities. Thus, a high glass transition temperature of 227°C and a thermal decomposition temperature of 417°C were found. PHPMI sensitized by a diazonaphthoquinone or an aromatic bisazide was prepared and evaluated as a positive or a negative near-UV resist. Microlithographic positive/negative images were obtained that were stable to temperatures higher than 200°C. The developed images showed no pattern deformation induced by swelling during development. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(4-hydroxystyrene) (PHS) is an extremely versatile polymer, useful for high-temperature applications and, more particularly, as positive and negative photoresists for microlithography.[1-7] To date, several advanced integrated circuit (IC) manufacturing techniques such as metal deposition or ion implantation require images that are stable to 200°C and higher. The most widely used novolac-based positive resists are unable to produce good images in this range. PHS-based positive resists have been shown to serve as good replacements for conventional novolac-based resists. Moreover, Eastman Kodak Co. has prepared high-T_g base-soluble copolymers based on *N*-(4-hydroxyphenyl)maleimide (HPMI) and various olefins to serve as better replacements.[8] We also prepared the copolymers of HPMI with silylstyrene for high thermal-resistant and O_2-plasma etching-resistant resists.[9,10] But few studies have been done on the homopolymer of HPMI for photoresist applications. Recently, Fuji Photo Film Co. reported that a positive working photoresist consisting of PHPMI (molecular weight: about 8000), *meta*- and *para*-cresol novolac resin, and a disulfone compound was developed that is sensitive to deep UV regions.[11] In this article, higher molecular weight ($\bar{M}_w$: 34,500) PHPMI with a higher T_g of 227°C compared to 160–180°C for PHS[12] was synthesized. Because the phenolic functionality of PHPMI is expected to inhibit or at least to disrupt its radical polymerization, the polymerization was carried out with *N*-(4-acetoxyphenyl)maleimide rather than with PHPMI, followed by transesterification of the acetoxy group to the desired phenolic derivatives:



PHS



PHPMI

Being applied to lithography, PHPMI was used not only as the positive resist but also as the negative resist under different formulations. The positive re-

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sist function is based upon the photochemistry of diazonaphthoquinone in the base-soluble matrix resin. The negative resist functions by cross-linking a matrix resin via a bisazide that initiates the photocross-linking reaction. Both types of resists are of interest because they are the bases for all commercial near-UV photoresists.

EXPERIMENTAL

Materials

N-(4-Acetoxyphenyl)maleimide (APMI) was prepared as we have described.[9] 2,2′-Azobisisobutyronitrile (AIBN) was reagent grade from Wako Pure Chemical Industries and recrystallized from methanol. Dimethylformamide (DMF) was distilled after dehydration with calcium hydride. Benzophenone–tetradiazonaphthoquinone sulfonate (Bp-*t*-DNS) was obtained from the Industrial Technology Research Institute, Materials Research Lab., Taiwan. 2,6-Bis(*p*-azidobenzylidene)cyclohexanone (BAZ) was purchased from Tokyo Kasei Kogyo Co.

Syntheses

Poly[N-*(4-acetoxyphenyl)maleimide*] *(PAPMI)*

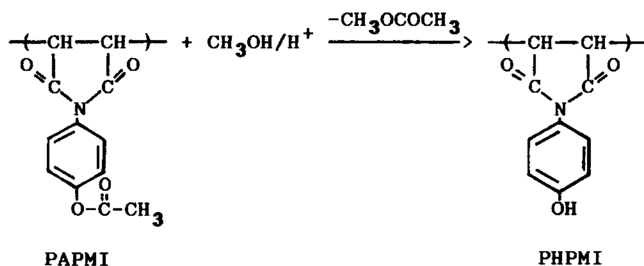
Under a nitrogen atmosphere, a 50 mL polymerization ampule was charged with 6.93 g (0.03 mol) of APMI, 0.035 (0.2 mmol) of AIBN, and 15 mL of DMF. The ampule was chilled by dry ice–acetone and sealed. Polymerization was carried out in a 60°C bath for 24 h. The polymer obtained was isolated by precipitating the viscous polymerization solution into methanol. After drying under vacuum at 60°C for 24 h, 88 wt % of polymer was obtained.

ANAL: Calcd for $C_{12}H_9NO_4$: C, 62.33%; H, 3.89%; N, 6.06%.
Found: C, 62.16%; H, 3.98%; N, 6.03%.

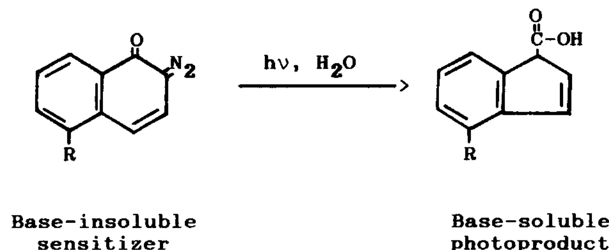
Poly[N-*(4-hydroxyphenyl)maleimide*] *(PHPMI)*

Five grams of the PAPMI polymer and 200 mL of acetone were placed in a 500 mL flask equipped with a condenser and a magnetic stirrer. After the polymer had dissolved, 40 mL of methanol, 50 mL of acetone, and 2.4 g of *p*-toluensulfonic acid were added. Acetone and the methyl acetate that formed were slowly distilled until about 50 mL of residue

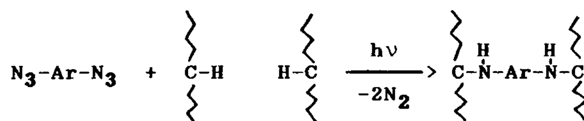
(a)



(b)



(c)



Scheme 1

remained in the flask. The viscous solution was dropped into methanol; after drying, 4.01 g (98 wt %) of polymer was obtained.

ANAL: Calcd. for $C_{10}H_7NO_3$: C, 63.49%; H, 3.70%; N, 7.41%.
Found: C, 63.35%; H, 3.76; N, 7.38%.

Photoresist Processing

Resist Preparation

The positive/negative resist solution was prepared by dissolving 5 wt % of PHPMI and 3 wt % of Bp-*t*-DNS as a base-insoluble sensitizer or BAZ as a cross-linking agent in 92 wt % of THF. The solution was filtered through a 0.5 μm Millipore filter.

Spin Coating and Soft Baked

The resist was spin-coated (4000 rpm) on a 4 in. silicon wafer to yield 1.2–1.4 μm film thickness. The resist film was prebaked in a conventional oven at 60°C for 30 min.

Exposure and Developing

Near-UV exposures (350–450 nm) were carried out using a Canon Contact Aligner PLA-501F. After exposure, the wafer was soaked in 5 wt % tetramethylammonium hydroxide (TMAH) (Hunt Co.) for the positive resist or rinsed in isopropanol for the negative resist with an agitation developer. The film thickness was measured with a Tenco alpha-step instrument.

Measurements of Various Properties

Fourier transform infrared spectra (FTIR) were obtained on a Jasco Model FT/IR 7000 instrument. Elemental analyses were determined using a Perkin-Elmer 2400 instrument. The molecular weight and dispersity of the polymer were measured in THF at 40°C using a Shimadzu Model LC-6A gel permeation chromatography (GPC) equipped with an RI detector (Shimadzu, RID-6A). The GPC measurement was performed using two Styragel columns, G1000H and G3000H, with a flow rate of 1 mL/min. The calibration curve was plotted using monodisperse polystyrene (molecular weight: 500–1,260,000). The average molecular weight was calculated on the basis of the Shimadzu C-R4A GPC Program V 1.1. Thermal analyses were performed on a DuPont TA-2000 thermal analyzer coupled with a 910 DSC module and a DuPont 951 thermogravimetric analyzer. The quality of images was evaluated with a scanning electron microscope (Philips, SEM-515) and a Nikon optical microscope equipped with a Mitsubishi P65UT video copy process.

RESULTS AND DISCUSSION

Preparation of the Polymer

N-(4-Hydroxyphenyl)maleimide (HPMI) could be obtained from transesterification of APMI, but HPMI was difficult to purify and polymerize.[8] It is probably because the phenolic functionality of

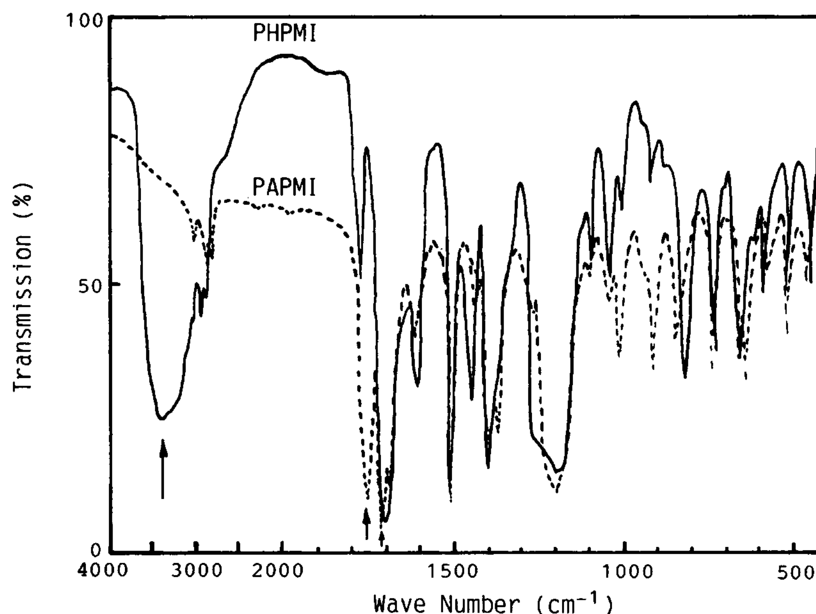


Figure 1 FTIR spectra of (- - -) PAPMI and (——) PHPMI.

HPMI is expected to inhibit or at least to disrupt its free-radical polymerization. Therefore, the polymerization was done with APMI rather than with HPMI. The desired phenolic polymer (PHPMI) was obtained from the prepolymer (PAPMI) by removing the acetoxy group in a transesterification as shown in Scheme I(a). The FTIR spectra of PHPMI has a broad absorption band at 2400–3400 cm^{-1} (—OH), which was not present in PAPMI, as shown in Figure 1. It also shows characteristic cyclic imide absorption bands at 1770 and 1700 cm^{-1}. Removal of the acetoxy groups did not affect the molecular weight distribution of PHPMI. Figure 2 shows the GPC traces of PAPMI and PHPMI. Curve (a) shows PAPMI before transesterification with $\bar{M}_w$ = 41,400 and $\bar{M}_n$ = 21,600 (polydispersity = 1.91), whereas curve (b) shows PHPMI with $\bar{M}_w$ = 34,500 and $\bar{M}_n$ = 18,100 (polydispersity = 1.91).

Polymer Characterization

At first, PAPMI was not soluble in an aqueous base such as sodium hydroxide or TMAH. When the acetoxy was converted to the hydroxy group, PHPMI was readily soluble in the aqueous base. In addition, PHPMI dissolved in a wide range of solvents. The thermal stability and T_g of the polymer were evaluated by thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC), respectively. Figure 3 shows DSC curves of PAPMI and PHPMI in nitrogen at a heating rate of 10°C/min.

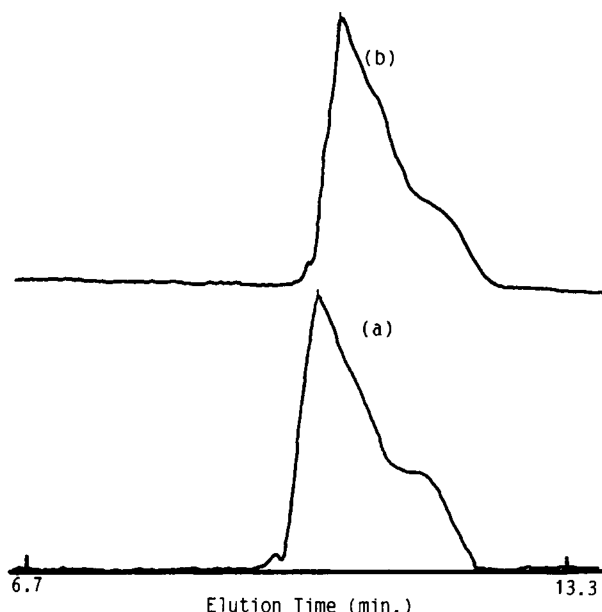


Figure 2 GPC traces of (a) PAPMI and (b) PHPMI (after transesterification).

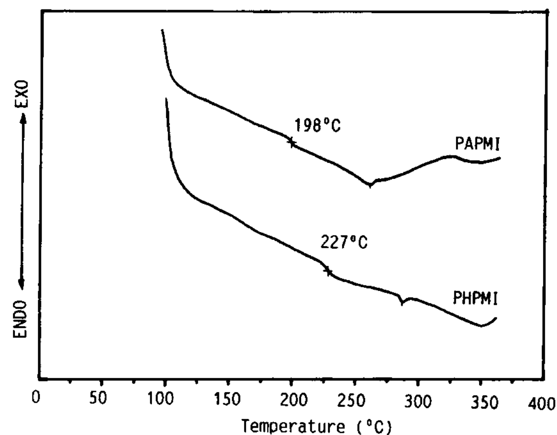


Figure 3 DSC curves of PAPMI and PHPMI.

As expected,[8,9] phenolic PHPMI has a higher T_g of 227°C compared to 198°C for PAPMI. Figure 4 presents the typical TGA curve of the polymer in nitrogen at a heating rate of 20°C/min. PHPMI did not exhibit a weight loss below 360°C. From the traces, the decomposition temperature (where 10% of the weight was lost) and the charcoal of PHPMI were higher than those of PAPMI. The higher values correspond to more rigid phenolic derivatives. After all, the high-temperature stability of PHPMI is attributed to the chain-stiffening effect of the cyclic maleimide structure.

Lithographic Characteristics

PHPMI was rendered insoluble through the addition of a base-insoluble sensitizer like a diazonaphthoquinone sulfonate (DNS). After being exposed to irradiation, the DNS brings about a carbene formation that undergoes a Wolff rearrangement to form a ketene followed by hydrolysis to a base-sol-

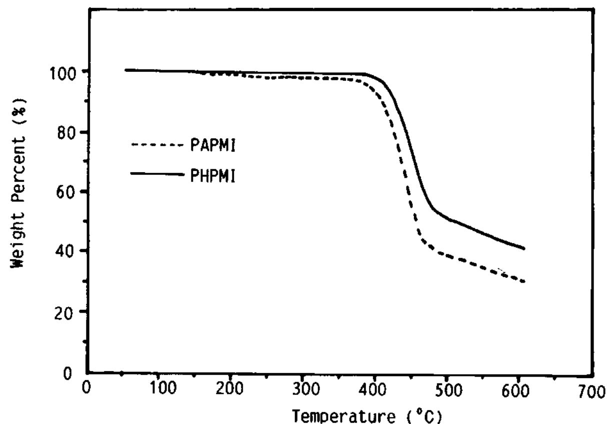


Figure 4 TGA diagrams of the polymers.

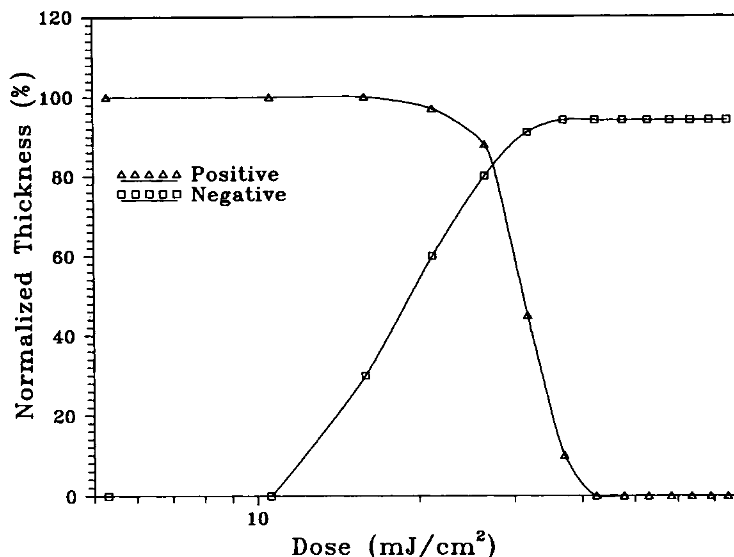
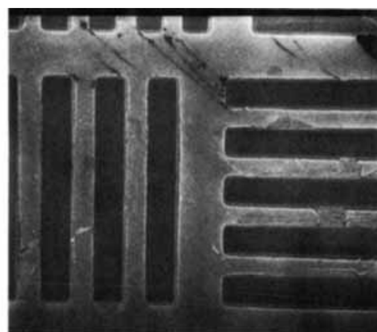


Figure 5 The exposured response curves of the resists.

uble indencarboxylic acid[13] that no longer inhibits dissolution of PHPMI in the aqueous base, thereby facilitating development of a positive image as shown in Scheme I(b). In the case of the negative resist, the insolubilization by aromatic bisazides is supposed to be due to insertion of reactive nitrens formed upon irradiation in carbon hydrogen bonds of the polymer,[14] as shown in Scheme I(c). The above photochemical reactions are old but interesting because they are the bases for all commercial positive or negative near-UV photoresists. As prepared, PHPMI itself is not sensitive to near-UV irradiation. Incorporation of a photosensitizer does affect to the near-UV regions.

The exposure response curve of the prepared resist is shown in Figure 5, which indicates that the positive resist was able to produce high-contrast images ($\gamma = 5.17$) at a dose of 39.2 mJ/cm^2 and that the negative resist produced images ($\gamma = 2.16$) at a dose of 30.8 mJ/cm^2. These resist films were exposed for various exposure times at a fixed intensity (10.6 mW/cm^2) without any mask. For examining the resolution of the prepared resists, the Toppan Printing Co. resolution mask was used. It is noted that novolac- or phenolic-based resists usually show no pattern deformation induced by swelling during development. Our prepared positive or negative resist also shows the same phenomenon as shown in Figure 6. The line space and width of patterns is 1.4 μm. In addition, the developed image patterns possessed an excellent thermal durability, i.e., images could be aged without deformation at 200°C for 30 min. However, image profiles that are stable to 200°C and above are desired for several advanced

(a) Positive images



(b) Negative images

Figure 6 SEM of (a) the positive and (b) the negative image patterns. The line space and width is 1.4 μm.

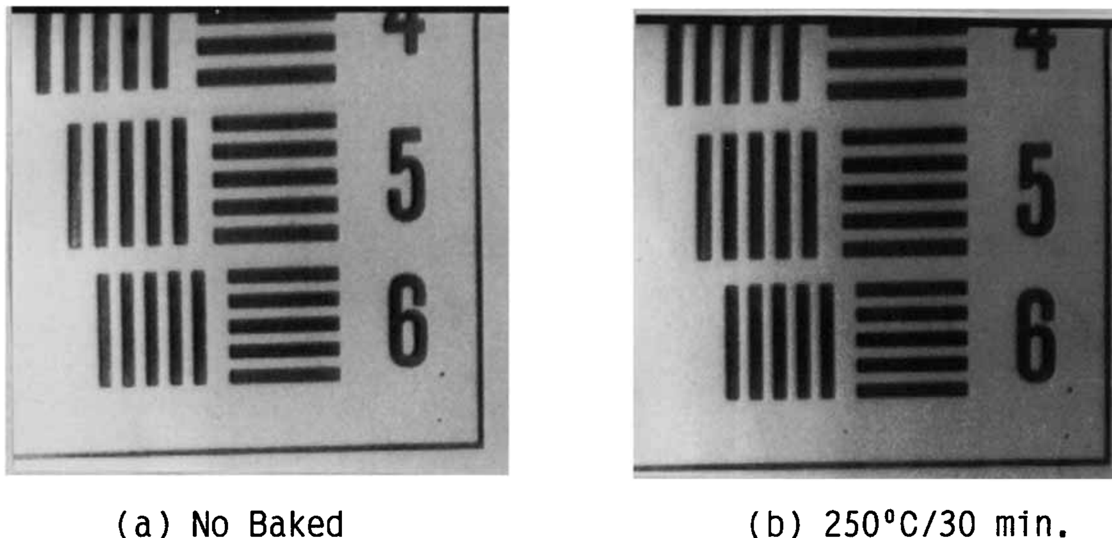


Figure 7 Microphotographs of the negative images before and after being postbaked (×100).

processes used in IC manufacturing. The best of the widely used commercial novolac-based resists is unable to perform very well in this region. Moreover, the developed negative images were stable even at 250°C for 30 min, as shown in Figure 7. This advantage indicates that photocross-linking increases the rigidity of the polymer matrix.

CONCLUSION

Poly(*N*-(4-hydroxyphenyl)maleimide) (PHPMI) sensitized by a diazonaphthoquinone or an aromatic bisazide was prepared and evaluated as a positive or a negative near-UV resist. The chain-stiffening effect of the maleimide was responsible for high-temperature stabilities. Microlithographic images were stable to temperatures higher than 200°C. The greater thermal durability of the developed negative images is due to the photocross-linking of the polymer matrix.

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