Syntheses and Characterization of Photocrosslinkable Poly(amic acid-*co*-urea)s with Diazoresin

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ABSTRACT: To improve the transparency, flexibility, and solubility of polyimide, and to fabricate a negative working photoresist, polyamic acid, polyurea, and poly(amic acidco-urea) in various contents were synthesized. Photosensitive diazoresin was synthesized and was used as the photocrosslinking agent. Characteristics of the polymers were identified by using IR, EA, DSC, TGA, and UV. From dissolution capabilities and thermal properties of the polymers, we chose the most suitable polymer PA25 as the main resin of the negative photoresist. The mixture of the polymer and diazo resin can be used as a negative photoresist. Optical characteristics of the polymer and diazo resin were evaluated by UV spectrophotometer. It was found that the polymer and diazo resin showed different absorption wavelengths under UV exposure. Characteristics of the negative photoresist were investigated by using *i*-line lithography. A contact printing exposure technique was used in this investigation. Dissolution rate and resolution capability of the photoresist containing various amounts of diazo resin were evaluated. The optimal prebaking time, postbaking time, and SEM patterns of the negative photoresist were also investigated. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2401-2407. 1998

Key words: poly(amic acid-co-urea); photosensitized diazoresin; photocrosslinking

INTRODUCTION

In the microelectronics industry, there has been growing interest in developing a technology employing an organic polymer as an insulator for multilevel interconnections. The demands on these polymers include excellent thermal stabilities, electrical and mechanical properties, etc. Polyimides have been widely used as an organic polymer capable of satisfying the above demands.

In microelectronic device applications, the polyimide is coated on a substrate and patterned to produce the via holes.¹⁻⁴ This is accomplished by photolithographic methods; the polyimide is etched by using photopatterned resists as an etch-

ing mask. However, some problems still remain; for example, this process contains a large number of processing steps, and undercutting caused by lowering of patterning accuracy may occur when the polyimide is etched by hydrazine and so on.

Positive-type polyimides, which can be made soluble by UV irradiation, have been investigated since Kubota et al.⁵ first reported an *o*-nitrobenzyl-type polyimide precursor. Khanna et al.⁶ developed hydroxy polyimides and polybenzoxazole precursors containing the hexafluoroisopropylidene-linking group, and the polymers containing *o*-naphthoquinonediazide (NQD) showed imageable properties similar to cresol novolak resin and NQD.^{7,8} On the other hand, most photoreactive polyimides described in published works so far are of the negative type, which shows resistivity to solvent because of its light-induced crosslinking structure.^{9–11} However, the flexibility and the

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Polyamic acid



Polyurea



Poly(amic acid-co-urea)



adhesion between polyimide and substrate such as silicon wafer are not always satisfactory. An approach to increase the flexibility and to enhance the bonding strength between polymer and substrate is to introduce a siloxane-containing moiety into the main chain of a polyimide.^{12,13}

In this work, to improve the transparency, flexibility, and solubility, and to fabricate a negative photoresist, polyamic acid, polyurea, and poly-(amic acid-*co*-urea) in various contents were synthesized. From dissolution capabilities and thermal properties of the polymers we chose one of the most suitable polymers as main resin in the photoresist. Diazo resin was used as a photocrosslinking agent. Optical characteristics of the polymer and diazo resin were evaluated. Dissolution rate and resolution capability of the photoresist containing various amount of diazo resin were estimated. Effects of prebaking time, postbaking time, and scanning electron microscope (SEM) patterns of the resist were also investigated.

EXPERIMENTAL

Materials and Measurements

A commercially available diazo resin was obtained from Shinco Technical Research Co. and used as the photocrosslinking agent. The UV-visible spectra of films of the photoresist on quartz substrates were measured with a Jasco UV/VIS 7850 double-beam spectrometer. The photoresist was exposed with a Karl Suss MJB-3 aligner. After exposure, the photoresist were developed with a 15-s immersion in developer $(DMSO/H_2O)$ = 10/1, wt/wt). Dissolution rate is defined as the changes of photoresist film thickness per development time. The film thickness was measured with a Tencor Instrument alpha step-200 film thickness monitor. 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 Nicolet FTIR-550 spectrometer, respectively. Elemental analyses were calculated with a Heraeus CHN-O rapid elemental analyzer.

Preparation of Polyamic Acid

4,4'-Diaminodiphenyl ether (40 g) was dissolved in 270 mL *N*,*N*-dimethyl acetamide. 1,2,4,5-Ben-

Polymer ^a		Molar Ratio		$\eta \; (dL/g)^{\rm b}$	Yield (%)
	ODA	TDI	PMDA		
PA	4	0	4	0.37	90.4
PA75	4	1	3	0.36	89.6
PA50	4	2	2	0.46	89.2
PA25	4	3	1	0.53	90.1
PU	4	4	0	0.49	88.9

 Table I Results of Polymerization

^a PA: Polyamic acid; PU: Polyurea; PA75, PA50, PA25: Poly(amic acid-co-urea) contains 75, 50, and 25% of PA in molar ratio, respectively.

 $^{\rm b}$ Inherent viscosity measured at a concentration of 0.5 g/dL in DMAC at 30°C.

	Solvent								
Polymer	H_2SO_4	HMAC	NMP	DMF	DMSO	Ру	CHCl_3	$\mathrm{C_6H_{12}}$	
$\rm PA^{a}$	++	+h	++	++	++	++		c	
PA75	++	++	++	++	++	-h			
PA50	++	++	++	++	++	-h			
PA25	++	++	++	++	++	$-\mathbf{h}$			
PU	++	++	++		++				
PI^b	++								
PI75	++								
PI50	++	+h	+h	+h	+h				
PI25	++	++	++	++	++	$-\mathbf{h}$			
PU	++	++	++		++				

Table II Solubility of Polymers in Various Solvents before and after Cyclization

^a Before cyclization.

^b After cyclization.

(++): soluble at room temperature, (+h): soluble on heating, (-h): partial soluble on heating, (--): insoluble.

zenetetra carboxylic dianhydride (43.6 g) was added five times for 30 min. The mixture was stirred at 25° C for 2 h. The resultant polyamic acid solution was poured into a large amount of methanol to precipitate the polyamic acid (PA). A light yellow polyamic acid powder was obtained. The polymer PA was dried at 50°C *in vacuo* for 20 h.

Preparation of Polyurea

4,4'-Diaminodiphenyl ether (30 g) was dissolved in 200 mL N,N-dimethyl acetamide. Toluene 2,4diisocyanate (26.5 g) in 70 mL of N,N-dimethyl acetamide was added dropwised for 30 min. The mixture was stirred at 25°C for 1 h. After that, a mixture of methanol (15 mL) and N,N-dimethyl acetamide (25 mL) was added and then stirred for a further 1 hour. The resultant polyurea solution was poured into a large amount of methanol to precipitate the polyurea (PU). The polymer structures are shown in Scheme 1.

Preparation of Poly(amic acid-co-urea)

4,4'-Diaminodiphenyl ether (a mol) was dissolved in N,N-dimethyl acetamide at 25°C. Toluene 2,4diisocyanate (b mol) in N,N-dimethyl acetamide was added dropwised for 20 min. The mixture was stirred at 25°C for 1 h. After that, 1,2,4,5-benzenetetra carboxlic dianhydride (c mol) was added in five times for 30 min. The mixture was stirred at 25°C for a further 2 h. The resultant polyamic acid solution was poured into a large amount of methanol to precipitate the polyamic acid (PA). A light yellow poly(amic acid-co-urea) powder was obtained. The copolymer was dried at 50°C *in vacuo* for 20 h. Three kinds of copoymers (PA75, PA50, and PA25) were prepared. PA75 means 75 mol % of polyamic acid were included in the copolymer.

Synthesis of Diazoresin

4-Aminodiphenylamine (18.4 g, 0.1 mol) was dissolved in 5 wt % aqueous hydrochloric acid (300

Table IIIResults of Thermal Analysis ofPolymers before and after Cyclization

Polymer	$\begin{array}{c}T_w\\ (^{\rm o}{\rm C})^{\rm a}\end{array}$	$\begin{array}{c}T_m\\(^{\rm o}{\rm C})^{\rm b}\end{array}$	$T_{10\%} (^{\circ}\mathrm{C})^{\mathrm{c}}$	$R_{750} \ (\%)^{ m d}$
PA	119.7	198.1	229.2	42.9
PA75	125.5	206.6	245.7	22.9
PA50	124.6	218.5	277.8	25.5
PA25	126.2	231.5	286.8	24.9
PU		244.6	288.9	2.3
PI	_		571.9	24.7
PI75	_		328.1	15.7
PI50			309.7	34.4
PI25			291.1	21.1
PU	_	_	289.1	2.3

^a Dehydration temperature.

^b Melting point.

 $^{\rm c}$ Temperature at which 10% weight loss was recorded by means of TGA with a heating rate of 20°C/min.

^d Residual weight at 750°C from TGA chart.



Figure 1 UV spectra of (a) Diazo resin, and (b) Polymer matrix PA25.

mL). The solution was then cooled to below 0°C with an ice bath. Sodium nitrite 6.9 g (0.1 mol) was added dropwise to the aqueous solution under stirring. The mixture was then stirred for another 30 min. Fast addition of sodium nitrite causes temperature increases and lead to a low conversion of the product. To precipitate the water-soluble diazonium salt, 6.8 g (0.05 mol) of zinc

chloride was added to the reaction mixture. After rapid stirring, the reaction mixture was kept at below 10°C for 30 min. The crystallized 4-diazodiphenylamine chloride zinc chloride was filtered off, washed with ether, and dried under vacuum.



Figure 2 Effect of prebaking at 90°C on the UV spectra of diazo resin. Curves 1–5: prebaking with various time (1: 0 min.; 2: 10 min.; 3: 15 min.; 4: 20 min.; 5: 30 min). Curve 6: fully exposed after prebaked at 90°C for 30 min.



Figure 3 Exposure characteristic curve for the system of PA25 and 10 wt % of Diazo resin.

The double salt can be purified by recrystallization from isopropanol/water (3 : 1 v/v) mixture. IR : 2168, 1578 cm⁻¹ (N=N, Ar-N stretch). UV: $\lambda_{\text{max}} = 400$ nm (Bleachable).

 $\rm C_6H_5NHC_6H_4N_2Cl$ \cdot 1/2ZnCl_2 (299.83) Calcd. C 48.07 H 3.36 N 14.01; found C 47.72 H 3.47 N 13.81.

Photosensitivity

Photosensitive solution was obtained by dissolving polyamic acid (PA25, 0.8 g) and diazoresin (0.08 g) in 10 mL of dimethyl sulfoxide (DMSO). The solution was filtered using a 5- μ m filter and then spin coated onto a silicon wafer, then dried at 90°C for 15 min. One micron-thick PA25 films on a silicon wafer were exposed to 365 nm radiation using a filtered superhigh-pressure mercury lamp. Exposed films were developed in DMSO/ H₂O = 10/1 (wt/wt) at 30°C for 25 s, and subsequently rinsed with distilled water. After that, the film was postbaked at 150°C for 20 min to cyclize the polyimide ring. Disolution rate and resolution capability of the photosensitive polymers were evaluated.

Measurements

The infrared spectra were recorded on a Nicolet Magna-IR 550 spectrometer and UV-visible spectra on a Jasco UV/VIS 7850 spectrophotometer. The NMR spectra were obtained on a Bruker AC-200 high-resolution ¹H FT-NMR spectrometer. Viscosity measurements were carried out by using an Ostwald viscometer at 30°C. Thermal analyses were performed on a Du Pont DSC-910 at a heating rate of 10°C/min for differential scanning calorimeter (DSC) under nitrogen and a Perkin–Elmer TGA-7 at a heating rate of 10°C/min for thermogravimetric analyses (TGA). Resolution patterns were evaluated by a JEOL JSM-35 scanning microscope and JEOL JAX-840 electron probe microanalyzer. The film thickness was measured on a Tencor Instruments alpha step 200. Elemental analyses were calculated with a Heraeus CHN—O rapid elemental analyzer.

RESULTS AND DISCUSSION

Preparation and Characterization of Polymers

Because water in the solvent will react with 1,2,4,5-benzenetetra-carboxylic anhydride and toluene 2,4-diisocyanate, solvents used in this investigation were all dehydrated. Preparation of polyamic acid, polyurea, and poly(amic acid-courea) in various contents were carried out at 25°C in anhydrous N.N-dimethyl acetamide. The polymer structures are shown in Scheme 1. The results of the polymerization are summarized in Table I. The structure of polyamic acid, polyimide, and copolymers were confirmed by means of infrared spectroscopy and elemental analyses. The IR spectra exhibited characteristic absorptions at 1720, 1540, and 3300 cm^{-1} due to carbonyl (-COOH, -CONH-), and NH stretching vibrations, respectively. Elemental analyses also



Figure 4 Effects of content of diazo resin on dissolution rate. (\bullet): Unexposed resists; (\blacksquare): Exposed resists with 800 mJ/cm under 365 nm.



(a)







Figure 5 Scanning electron micrograph of the pattern from PA25 containing diazoresin.

supported the formation of the expected structure.

Solubility of polymers in various solvents before and after cyclization are shown in Table II. The results in Table II show that the solubility of copolymers after cyclization increase with increasing the content of polyurea unit. It was also found that increasing the content of polyurea unit increases the flexibility and the transmittance of polymer films.

Thermal Properties of Polymers

DSC on a powder sample was performed, and the results are shown in Table III. The polymers exhibited an endotherm at 110 to 127° C and a second endothermic peak at 200 to 250° C. The IR spectrum after the thermal treatment showed strong imide carbonyl absorptions at 1780 and 1725 cm^{-1} . On the basis of these studies, the first endotherm around 127° C and the second endothermic peak at around 250° C are assigned to the cyclization temperature and the melting temperature of the polymers, respectively. TGA curves of polymers before and after cyclization were also evaluated. The results are summarized in Table III. Polyimide shows better thermal stability than other copolymers.

Lithographic Evaluation

Figure 1 shows the UV spectra of diazo resin and PA25 copolymer. The results suggest that UV light of 365 nm (i-line) is available. After preliminary optimization studies involving the loading of PA25, prebaking and postbaking temperature, developer, and developing temperature, we formulated a photosensitive poly(imide-co-urea) precursor system consisting of PA25 and 10 wt % of diazoresin. The polymer solution was spin coated on a silicon wafer and then prebaked at 90°C for 15 min. The polymer film (ca. 1 μ m thick) containing 10 wt % of diazo resin were exposed to 365 nm UV irradiation, developed with DMSO/H₂O = 10/1 (wt/wt) at 30°C for 25 s and then rinsed with deionic water. After development, the film was postbaked at 150°C for 20 min.

To investigate the effect of prebaking on the diazo resin, UV spectra of diazo resin with various prebaking time were estimated. As can be seen in Figure 2, diazo resin shows good thermal stability at 90°C and high UV-light sensitivity. The prebaking time of 15 min at 90°C was selected in this investigation.

The exposure characteristic curve for the system of PA25 and 10 wt % of diazo resin was estimated. As shown in Figure 3, the sensitivity is about 800 mJ/cm². The effect of content of diazo resin on dissolution rate was also investigated. The results are summarized in Figure 4. The optimal resolution capability (R_p/R_o) of the negative photoresist is achieved at 10 wt % content of diazo resin under the UV exposure of 800 mJ/cm². As shown in Figure 4, 15 wt % of diazo resin content leads to decreasing of the resolution capability. The result suggests that UV irradiation of 800 mJ/cm² is not sufficient for the system.

In Figure 5 are presented scanning electron micrographs of negative images contact-printed in PA25 by postbaking at 150° C for 20 min after exposure to 800 mJ/cm².

CONCLUSION

Three kinds of poly(amic acid-co-urea) with various contents of amic acid were synthesized. The solubility of copolymers after cyclization increased with increasing the content of the polyurea unit. Polyimide shows better thermal stability than other copolymers. From the thermal properties and dissolution capabilities of the copolymers, PA25 with 25 mol % of amic acid was selected as the main resin of the negative working photoresist. The sensitivity of the system of PA25 with 10 wt % of diazo resin is about 800 mJ/cm². The optimal resolution capability (R_p/R_o) of the

negative photoresist is achieved at 10 wt % of diazo resin under the UV exposure of 800 mJ/cm².

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