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European Polymer Journal 38 (2002) 1761–1768

EUROPEAN POLYMER JOURNAL

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Preparation of trimethylsilyl group containing copolymer for negative-type photoresists that enable stripped by an alkaline solution

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Received 12 September 2001; received in revised form 10 January 2002; accepted 7 February 2002

Abstract

A series of four trimethylsilyl group containing copolymers were synthesized using the solution free-radical copolymerization with azobisisobutyronitrile (AIBN) in 1,4-dioxane at 60 °C. The photoresists were prepared by dissolving copolymer, one of two kind photosensitizer (dimethylaminoethyl methacrylate and diethylaminoethyl methacrylate) and Michler's ketone in tetrahydrofuran (THF). The cyclic maleimide group was responsible for the high thermal stabilities. After irradiation by a deep-ultraviolet light and development with mixed solvent (methyl isobutyl ketone: 2-propanol = 1:3), the developed patterns showed negative images and exhibited good adhesion to the silicon wafer without using any adhesion promoter. The resolution of the resists was at least 1.75 μm and the oxygen plasma etching rate was 1/6 of hard-baked HPR-204, which can be also used as the top-imaging layer of a bilayer resist for microlithographic application. These photoresists can be stripped by week alkaline solution such as sodium carbonate solution (0.01 wt.%) after exposure. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Photoresist; Trimethylsilyl group; Oxygen plasma etching; Alkaline solution

1. Introduction

Polymers have been increasingly used in many areas of electronics in recent years. One of the main applications of polymers in electronics is as lithographic resists in integrated circuit fabrication. When the resist is exposed to high-energy radiation such as ultraviolet (UV) light, electron-beam (EB) or X-rays, certain chemical reactions take place in the exposed area, resulting in a change in its solubility. Utilizing the solubility difference between the exposed and unexposed area, a pattern can be developed by using developer. The main requirements of lithographic resists are high sensitivity, high resolution, high thermal stability, good adhesion to the substrate, and an adequate wet and dry-etching resistance [1,2].

The increasing density of very large-scale integrated circuits is imposing stricter demands on the optical lithographic process [3]. Line width required are shrinking to the submicron range. However, it would be very difficult to obtain such fine patterns on wafers having stepped topography using a conventional single layer process [4]. A bilevel system was suggested in order to simplify the above process. However, silicon-containing polymer was demonstrated to possess high resistance to oxygen reaction ion etching (O_2-RIE). Small amounts of silicon (about 10%) can drastically lower the etching rates of organic polymers [5]. Electron spectroscopy for chemical analysis (ESCA) reveals that oxygen plasma converts silicon into silicon oxide or silicon dioxide. On the other problem, resist pattern will collapse during the resist development process. Resist pattern collapse occurs while the rinse liquid is being

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PII: S0014-3057(02)00073-3

dried off [6]. The source of resist pattern collapse is the surface tension of the rinse liquid. The force increases with decreasing space width in the resist pattern [6,7]. To avoid the resist pattern collapse problem, dry-developable resist systems, such as trilayer resists, silicon-containing resists, and top surface imaging process were proposed. However, the trilayer resists process and top surface imaging processes are cumbersome. There are a significant number of processing steps, and large capital investment is required.

But silicon-containing resists are considerably harder to stripping, because their adhesion is good with silicon wafers. Here one approach is to boil the slices in concentrated sulfuric acid for about 20 min, followed by mechanical agitation. Often a 1:1 mixture of hot sulfuric acid and hydrogen peroxide is used, at a somewhat lower working temperature. The most common removal technique for negative photoresists consists of using hot chlorinated hydrocarbons to swell the polymer, together with acid to loosen its adhesion to the substrate. Solvent mixtures of trichlorethylene, methylene chloride, and dichlorobenzene, combined with formic acid or phenol, are used in the form of proprietary mixture for this purpose [8]. However, these organic solvents will destroy our environment seriously, the stripping method using aqueous solvents must be useful.

Our laboratory has developed near-UV photoresists using diazonaphthoquinone sulfonate as a dissolution inhibitor [9–13]. The deep-UV photoresists are made using photosensitive copolymers with the *p*-nitrobenzyl group [14], and the former contains the silyl group with the *o*-nitrobenzyl cholate as a dissolution inhibitor [15–17]. These photoresists show excellent thermal properties and outstanding oxygen reactive ion etching resistance.

This paper illustrates photoresists made using copolymers containing the trimethylsilyl group with dimethylaminoethyl methacrylate or diethylaminoethyl methacrylate as the photosensitizer. The resulting photoresists could be used as the top-imaging layer in a bilayer resist process and can be stripped by weak alkaline solution. This is available in reduce environmental contamination.

2. Experimental

2.1. Materials

Maleic anhydride, sodium acetate, Michler's ketone, acetic anhydride and *p*-aminobenzoic acid (*p*-ABA) were used without further purification. *N,N'*-azobisisobutyronitrile (AIBN) was recrystallized from methanol before use. Dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, allyltrimethylsilane and vinyltrimethylsilane were purified by distillation under reduced pressure. Organic solvents were purified using standard methods before use. *N*-(4-carboxyphenyl) maleimide (CPMI) was synthesized by reacting of maleic anhydride with *p*-ABA in presence of dimethylformamide (DMF) as described [18].

2.2. Measurement

Fourier transform infrared (FT-IR) spectra were obtained on a JASCO Model FT/IR 7000 instrument. ^{1}H NMR spectra were recorded on a BEUKER AM-400 spectrometer in DMSO-d_6 (dimethylsulfoxide, DMSO) without tetramethylsilane (TMS). Using a Perkin–Elmer 2400 instrument performed elemental analyses. The molecular weight distribution was determined with gel permeation chromatography using a water-40 column and tetrahydrofuran (THF) as solvent. The thermal analyses were performed on a Perkin–Elmer DSC 7 and thermalgravimetry analysis (TGA) instrument (DuPont) 2960-SDT. All experiments were conducted under a constant dry nitrogen flow of 20 ml/min (DSC) or 150 ml/min (TGA) and a heating rate of 20 °C/min. Adhesion tests were performed according to ASTM-D3359-95b. The oxygen plasma etching resistance of several polymer films was evaluated by using a Mega Strip 6 (Drytek Inc.) at RF power level of 1300 W and a chamber pressure of 0.4 Torr.

2.2.1. Copolymerization of poly(N-(4-carboxyphenyl)-maleimide-co-allyltrimethylsilane) (I) and poly(N-(4-carboxyphenyl)maleimide-co-vinyltrimethylsilane) (II)

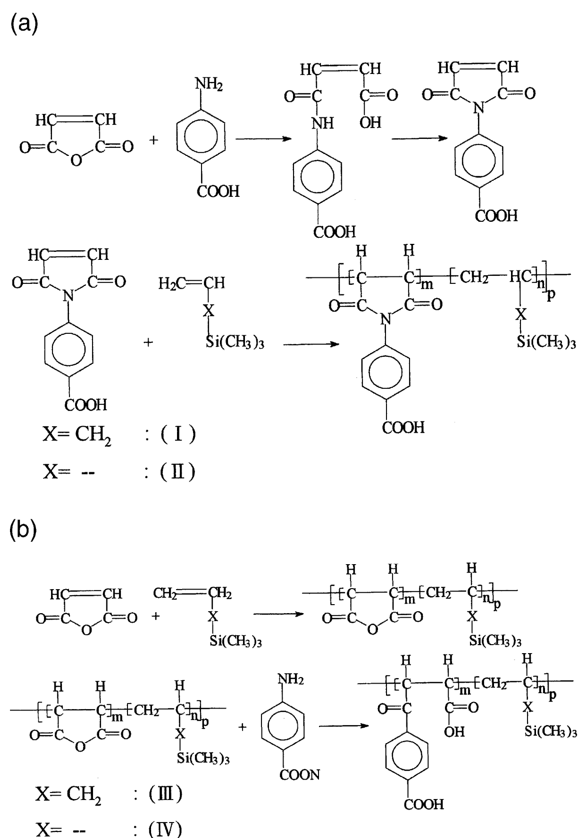
The synthesis of the copolymers was carried out as shown in Scheme 1a.

Under a nitrogen atmosphere, a 50 ml polymerization ampoule charged allyltrimethylsilane (1.14 g, 0.01 mol), CPMI (2.31 g, 0.01 mol) and AIBN (0.0164 g, 0.1 mmol) in 1,4-dioxane (20 ml). The polymerization mixture was then degassed with the freeze–thaw technique. The inlet of ampoule was sealed with a gas-oxygen mixture under a nitrogen atmosphere at low pressure, and then transferred to a thermostat oil-bath at 60 °C for 24 h. The copolymer was obtained by precipitation into a large amount on methanol. The precipitated polymer was purified twice by reprecipitation for the methylene dichloride/methanol system then dried in a vacuum at 60 °C for 24 h, the copolymer (I) of 2.29 g (66.6 wt.%) was obtained. IR (KBr), 1700 cm^{-1}, 1770 cm^{-1} (C=O), 1250 cm^{-1} (C–Si), ^{1}H-NMR(DMSO-d_6), 7.71–7.90 δ (the protons of aromatic), 0 δ(t-Me-Si).

The copolymer (II) was synthesized in the same way.

2.2.2. Synthesis of poly(N-(4-carboxyphenyl)maleamic acid-co-allyltrimethylsilane) (III) and poly(N-(4-carboxyphenyl)maleamic acid-co-vinyltrimethylsilane) (IV)

The synthesis of the copolymers was carried out as shown in Scheme 1b.



Scheme 1. Preparation of photoresists using copolymers.

Under a nitrogen atmosphere, a 50 ml polymerization ampoule charged Allyltrimethylsilane (1.14 g, 0.01 mol), maleic andydride (0.98 g, 0.01 mol) and AIBN (0.0164 g, 0.1 mmol) in 1,4-dioxane. (20 ml) Polymers were synthesized using free-radical polymerization using AIBN as initiator. The polymerization mixture was then degassed by the freeze–thaw technique and sealed under a nitrogen atmosphere at low pressure. The ampoule was then transferred to a thermostatic oil-bath at 60 °C for 24 h. The poly(maleic andydride-co-allyltrimethylsilane) (PMAAT) was obtained by precipitation into a large amount on hexane. The precipitation polymer was purified twice by reprecipiation for the hexane/isopropanol system then dried in a vacuum at 60 °C for 24 h, the copolymer (PMAAT) of 1.89 g (89.05 wt.%) was obtained. IR (KBr), 1780 cm^{-1}, 1850 cm^{-1} (C=O), 1250 cm^{-1} (C–Si), ^{1}H-NMR(DMSO-d_6), 0 δ (t-Me-Si).

To a well-stirred solution of *p*-ABA (0.3 mol) in 60 ml DMF under nitrogen atmosphere, PMAAT (0.32 mol) in 40 ml DMF was gradually added to the above mixture. The mixture was stirred at room temperature for 5 h, poured into a large amount of water to precipitate the crude copolymer (III). The precipitated polymer was purified twice by reprecipiation for the methylene dichloride/methanol system then dried in a vacuum at 60 °C for 24 h. yield: 76%.

IR (KBr), 1700 cm^{-1} (C=O), 1250 cm^{-1} (C–Si), ^{1}H-NMR(DMSO-d_6), 0 δ (t-Me-Si), 7.54–7.86 δ (the protons of aromatic), 10.61 δ (=NH).

The copolymer (IV) was synthesized in the same way as above.

The polymerization result and elemental analyses of copolymers are summarized in Table 1.

2.3. Photoresist processing and O_2 plasma etching resistance testing

The photoresists were prepared by dissolving the copolymer, one of two kind photosensitive (dimethylaminoethyl methacrylate and diethylaminoethyl

Table 1
Polymerization result and elemental analysis results for copolymer

Copolymer	C (%)	H (%)	N (%)	Si (%)	$(m/n)^a$	T_d (°C)	M_w ($\times 10^3$)	M_n ($\times 10^3$)	Polydispersity
I									
Found	61.62	6.30	4.25	8.34	0.98	308	18.17	8.30	2.18
Anal	61.87	6.10	4.24	8.89	–				
II									
Found	60.57	6.50	4.47	8.58	0.96	330	12.98	6.57	1.97
Anal	60.74	5.73	4.43	8.89	–				
III									
Found	58.52	6.68	3.94	8.28	1.02	210	85.73	56.47	1.51
Anal	58.60	6.36	4.01	8.06	–				
IV									
Found	57.31	6.26	4.17	8.35	1.05	226	75.18	52.94	1.42
Anal	56.47	6.02	3.59	8.40	–				

[a] The values of m/n was determined by elemental analyses.

Table 2
The Composition of the prepared photoresists

Photoresist code	Copolymer (g)	Solvent (ml)	Photosensitive[a]	Micher's ketone (g)
PRI1	I (1.4)	20	Dimethylaminoethyl methacrylate (1:2)	0.07
PRI2	I (1.4)	20	Diethylaminoethyl methacrylate (1:2)	0.07
PRII1	II (1.4)	20	Dimethylaminoethyl methacrylate (1:2)	0.07
PRII2	II (1.4)	20	Diethylaminoethyl methacrylate (1:2)	0.07
PRIII1	III (1.4)	20	Dimethylaminoethyl methacrylate (1:1)	0.07
PRIII2	III (1.4)	20	Diethylaminoethyl methacrylate (1:1)	0.07
PRIV1	IV (1.4)	20	Dimethylaminoethyl methacrylate (1:1)	0.07
PRIV2	IV (1.4)	20	Diethylaminoethyl methacrylate (1:1)	0.07

[a] Mole ratio to copolymer.

methacrylate) and Michler's ketone as photoinitiator which can be chosen according to full spectrum of a Hg lamp activity [19] in THF. Table 2 shows the composition of the photoresists and their prepared conditions. The solutions were filtered through a 0.25 μm millipore filter before spin coating onto silicon wafers.

Resist films were prepared by spin coating resist solutions on to 4″ silicon wafers using a conventional spinner and were prebaked in a conventional oven at 90 °C for 3 min. Film thickness was measured with a stylus instrument (Alpha Step 200). The films were exposed with a Hg–Xe lamp filter combination (ORIEL). The exposure was carried out by the contact technique using a Toppan resolution mask as a photomask. After exposure, the resist films were postexposure baked in a conventional oven at 110 °C for 15 min. After post-exposure backed, the wafers were soaked in a special solution (methyl isobutyl ketone (MIBK):2-propanol (IPA) = 1:3) for 5 s before being rinsed with hexane for 10 s. The developed films were baked in a conventional oven at 130 °C for 30 min. Oxygen plasma etching resistance of several polymer films was evaluated with using a Mega Strip 6, RF level power 1300 W, and chamber pressure of 0.4 mmHg.

3. Results and discussion

3.1. Copolymer preparation and characterization

Various trimethylsilyl groups were introduced to improve dry-etching resistance. Thermal behaviors of the copolymers were evaluated by means of DSC and TGA. In DSC curve, there is no distinct glass transition temperature (T_g) observed. Well-defined melting points (T_m) of these copolymers were not found, probably due to their low crystalline. But the TGA curve for the copolymers shown in Fig. 1 indicate that the decomposition temperature T_d (where 10% of the weight was lost) of those copolymers are higher than 200 °C mean that they have good thermal stability in photoresist process. Moreover, the T_d of copolymers (I) and (II) can be found

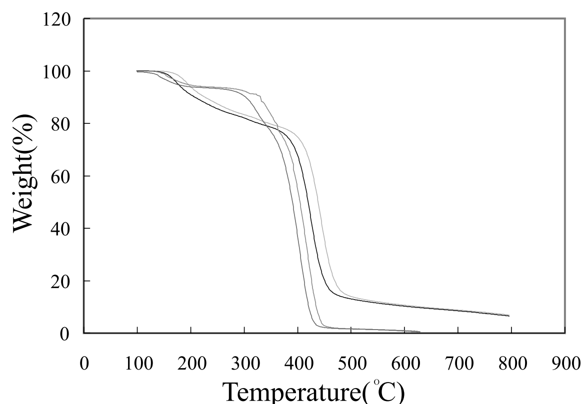


Fig. 1. TGA diagrams of copolymer.

to be higher than that of copolymers (III) and (IV), which might be due to the chain-stiffening effect of the maleimide structure. The polymerization result and elemental analyses of copolymers are summarized in Table 2. It shows that the composition of the copolymers were close to an alternating structure.

The FT-IR spectrum of the monomer showed a vinyl absorption at 1600 cm^{-1}, which after polymerization disappeared completely, and the band appearing at 1250 cm^{-1} is the absorption of the C–Si structure. The ^{1}H-NMR spectra of copolymer (III) and copolymer (IV) are compared in Fig. 2. The ^{1}H-NMR spectrums of copolymers showed a trimethylsilyl group at 0–0.04 ppm, aromatic protons at 7.16–8.03 ppm and —COOH protons at 12.99–13.04 ppm.

Since solubility is one of the important requirements for a photoresist, the solubility of the copolymers in various organic solvents was tested. These copolymers were easily soluble in polar aprotic solvent, namely dimethylacetamide, DMF, DMSO, THF, 1,4-dioxane etc., and alkaline solvents such as sodium hydroxide, sodium hydrogen carbonate and sodium carbonate. They were insoluble in chlorinate solvents such as chloroform and methylene dichloride.

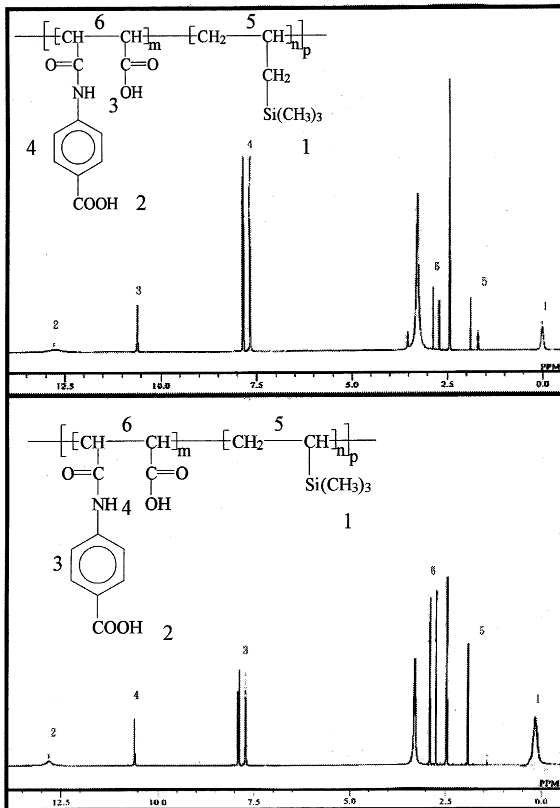


Fig. 2. The ^{1}H-NMR spectra of copolymer (I) and copolymer (II) (without TMS).

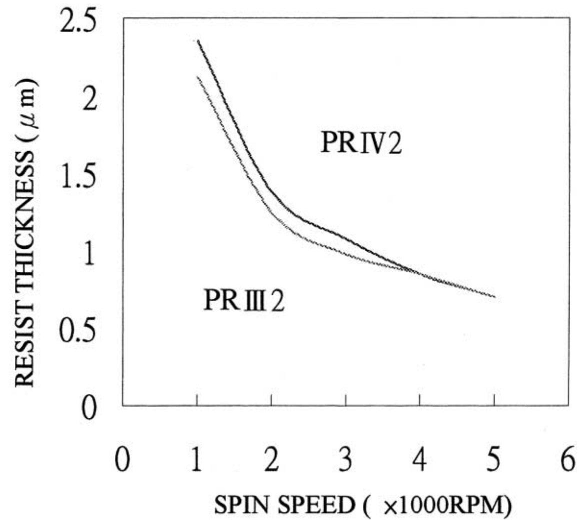


Fig. 3. Coating resist thickness vs spin speed.

3.2. Photoresist's characteristics

The spin coating condition has an important effect on the spin coating film thickness that it will affect on the resist's characteristics. The resist coating thickness curves of PRIV2 and PRIII2 are shown in Fig. 3. When the optimum coating conditions (spin speed is about 3800 rpm for 30 s) are used, coating uniformity within 50 Å and 1 μm film thickness can be achieved across a four in wafer.

All of the prepared resists had good adhesion to the silicon wafer without using any adhesion promoter. The exposure response curves of the resists that using diethylaminoethyl methacrylate as photosensitive (Fig. 4) by using a mixed solvent (MIBK:IPA = 1:3) as the developer show that the normalized film thickness of the resist increases with the increase in the dose; i.e., they are negative-type resists. Table 3 shows the characteristics of the photoresists. It can see there is a good contrast present. Beside, the radiation response and sensitivities

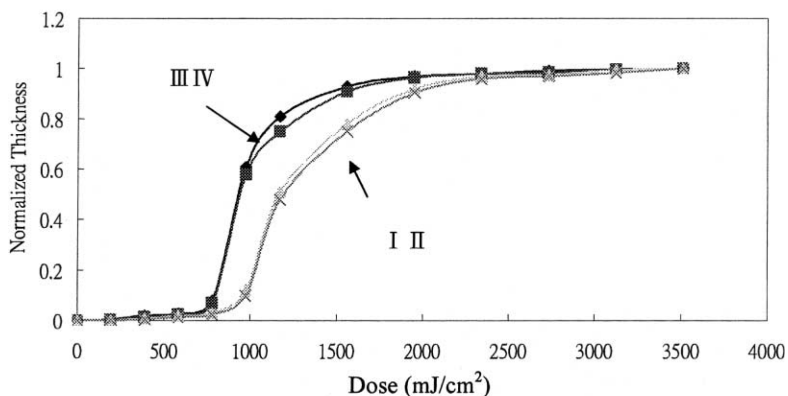


Fig. 4. Plot of the normalized thickness vs dose for 248 nm exposure of copolymer/diethylaminoethyl methacrylate, PEB condition: 110 °C for 15 min.

Table 3
The characteristics and oxygen plasma etching results of photoresists

Code	Sensitivity ($D_g^{0.5}$) (mJ/cm^2)	Contrast ratio (γ_n)	Si content (wt.%)	Etching rate (Å/min)	Etching selectivity[a]
PRI1	1040	5.8	8.34	76	1:5.52
PRI2	1010	5.8	8.34	76	1:5.52
PRII1	1180	5.7	8.58	70	1:6.00
PRII2	1130	5.6	8.58	70	1:6.00
PRIII1	920	6.9	8.28	84	1:5.00
PRIII2	910	6.8	8.28	84	1:5.00
PRIV1	960	6.4	8.35	80	1:5.25
PRIV2	920	6.2	8.35	80	1:5.25
Novolac resin (Hunt. HPR-204)	–	–	–	420[b]	–

[a] The etching rate compared to HPR-204.
[b] Ref. [9].

of resists containing copolymer (III) or copolymer (IV) is faster than that of resists containing copolymer (I) or copolymer (II). Certain factors such as the dissolution parameter, molecular weight and polydispersity do influence sensitivity and contrast. Fig. 5 shows the pattern of PRIII2, with the line width of the pattern at 1.75 μm.

3.3. Oxygen plasma etching resistance

The oxygen plasma etching rates of the Si-containing resists and HPR-204 (Hunt Co., its matrix is believed to be a novolac-type resin, baked at 200 °C for 30 min as a coating on silicon wafer) was investigated. The oxygen plasma etching results of the resists were examined and compared with HPR-204 as shown in Table 3. The HPR-204 (Hunt Co., Novolac resin) has a constant etching rate of about 420 Å/min [9]. The effects of some factors as polymer structure and molecular weight do not influence the etching rate much. It is concluded that most effective factor for increasing etching resistance is to increasing the silicon content [19]. ESCA revealed that the oxygen plasma converted the silyl group into silicon oxide or silicon dioxide [20]. Therefore, it is concluded that an increase in the silicone content is the most effective factor in the increase of etching resistance.

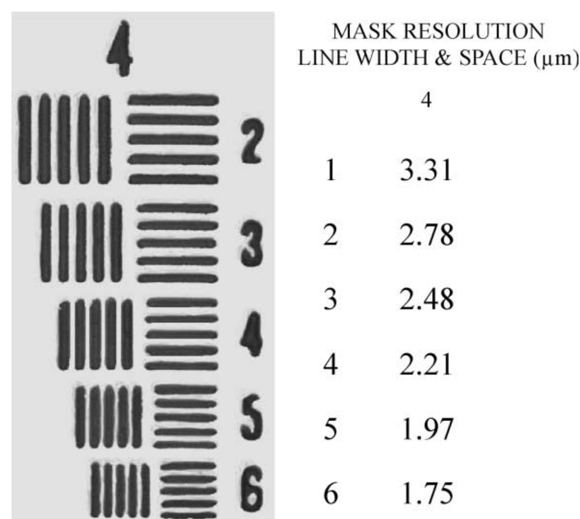


Fig. 5. Microphotography of the image pattern based on PRIII2 after developed.

3.4. The mechanism of stripping by weak alkaline solution

An earlier paper [21] showed that when an amine is added to a polyamic acid, this polymer can form a polymer–polymer complex with itself; i.e., without the need to add a second polymer. Such complex formation of a polymer, with itself, occurs rarely. Normally, two different polymers are involved. For example, when a solution of poly(methacrylic acid) is added to a solution of poly(methacrylamine), hydrogen bonds will be formed between the —COOH and —$CONH_2$ groups. If favorable conditions are chosen, ladder-like structures with cooperative hydrogen bonding, between the two polymers, are formed. This causes strong contraction of the polymer coils and complex is usually insoluble. On the basis of this principle, we modified a series containing acid group of polymers to form a negative photoresist by neutralizing with dimethylaminoethyl methacrylate or diethylaminoethyl methacrylate. After exposure, they will form a complex with electrostatic bonding through the —COOH · NR_2— groups. Exposed areas are insoluble in a suitable developer and patterns can be made.

But when we went to strip the photoresist film, a weak alkaline solution such as sodium carbonate (0.01 wt.%)

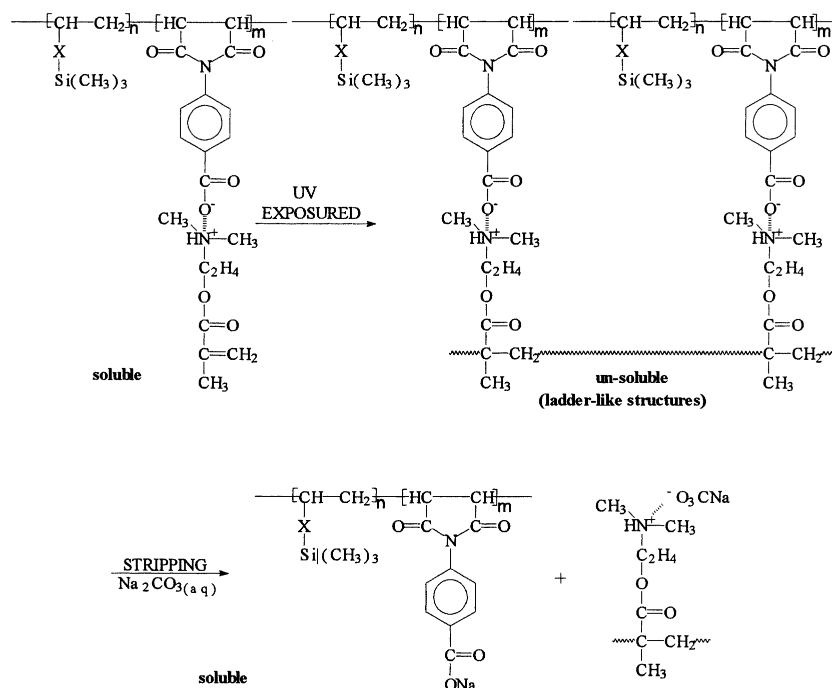


Fig. 6. The proposed mechanism of negative-type photoresist formed by UV crosslinking to produce a ladder-like structures and stripping by sodium carbonate solution.

is added to the system. The ladder-like structure will be destroyed when neutralized to make exposed areas become soluble in a weak alkaline solution. Especially, We used containing sodium ion of weak alkaline solution such as sodium carbonate (0.01 wt.%), polymer will form sodium salt structure to dissolve easier. The mechanism of stripping is shown in Fig. 6.

4. Conclusion

Four of trimethylsilyl groups containing copolymers were synthesized and the photoresists were prepared by dissolving copolymer, one of two kind photosensititives and Michler's ketone in THF. The T_d of copolymers (I) and (II) can be found to be higher than that of copolymers (III) and (IV), which may be due to the chain-stiffening effect of the maleimide structure. All of the prepared resists had good adhesion to the silicon wafer without using an adhesion promoter. Moreover, resists showed good resistance to the oxygen plasma etching, and the etching selectivity was about 1:6, compared to hard-baked HPR-204. The resists have good contrast value (3.9–5.6), and provide the line/space resolution of 1.75 μm. These photoresists can be stripped by weak alkaline solution such as sodium carbonate solution (0.01 wt.%) after been exposured.

Acknowledgements

The authors express their appreciation to Dr. T.S. Lin, the president of Tatung University for his encouragement. Thanks are due to the National Science Council for its' financial support under contract number NSC 89-2218-E-036-012.

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