

COPOLYMERS OF CHLOROETHYL METHACRYLATE, GLYCIDYL METHACRYLATE, AND METHYL METHACRYLATE AS SYNCHROTRON RADIATION x-RAY PHOTORESISTS*

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Abstract The copolymers of chloroethyl methacrylate (CMA), glycidyl methacrylate (GMA), and methyl methacrylate (MMA) were synthesized in benzene solution. Their breadths of the molecular weight distributions are 2.1 and 2.3, respectively. The thermal stability of P(GMA-CMA) is superior to that of P(CMA-MMA). The resolutions of P(CMA-MMA) and P(GMA-CMA) photoresists were found to be $0.1\sim 0.16\mu\text{m}$ and $0.17\sim 0.2\mu\text{m}$, respectively.

Keywords Copolymer; X-ray Photoresists; Submicron; Resolution

INTRODUCTION

X-ray lithography by synchrotron radiation is a promising technique for very high resolution replication of submicron patterns. X-ray photoresists used in very large scale integrated (VLSI) fabrication has high resolution and good adhesion. Shi^[1] reported the design of X-ray photoresists. Maydan^[2] described the recent advances in X-ray lithography combined with reactive sputter etching process techniques as applied to the fabrication of devices with $0.7\mu\text{m}$ effective channel length. Bernstein^[3] studied new high-contrast developers for poly (methyl methacrylate) photoresist. When PMMA is used for large scale integrated (LSI) fabrication, however, it has

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certain deficiencies such as low sensitivity, poor adhesion and poor thermal stability. The sensitivity can be improved by copolymerization with highly radiation susceptible groups. Acrylonitrile^[4] and isobutylene^[5] were incorporated into PMMA. On the other hand, polymers of methacrylic esters containing halogens^[6] were reported to yield a more highly sensitive yet less thermostable positive electron photoresist than PMMA.

To obtain higher sensitivity and thermal stability polymers incorporated with methacrylic acid and methacryloyl chloride were synthesized and evaluated^[7].

To obtain higher sensitivity, adhesion, and thermal stability than methacrylic esters such as PMMA, copolymers of glycidyl methacrylate with chloroethyl methacrylate [P(GMA-CMA)] and copolymer of chloroethyl methacrylate with methyl methacrylate [P(CMA-MMA)] were synthesized. These copolymers molecular side chains contain active glycidyl group and chlorine atom, therefore, their photoresist properties were improved. The P(GMA-CMA) and P(CMA-MMA) will form intermolecular cross-linking after heating, and the copolymers' molecular main chains were degraded after radiation. Therefore, these photoresists were called the positive photoresists. The good performances of P(GMA-CMA) and P(CMA-MMA) in this study are their high-resolution, high-sensitivity, good adhesion, and thermostability.

EXPERIMENTAL

Materials

MA and MMA were obtained from the Shanghai First Chemical Reagent Factory. MMA was vacuum-distilled before use.

Synthesis of monomers

To a 1000 mL three-necked flask equipped with a mechanical stirrer, reflux condenser with calcium chloride drying tube, and thermometer and containing 350 mL of epichlorohydrin, 60 g of potassium methacrylate, 1.8 g of tetraammonium chloride, and 1 g of hydroquinone. The reaction mixture is heated at about 97°C under vigorous stirring and then same temperature reflowed for 3 h. The crude reactant was purified by vacuum distillation (b.p. 70~72°C/1.3 Pa) Glycidyl methacrylate (GMA) was obtained.

To a 500 mL three-necked flask equipped with a mechanical stirrer and thermometer and containing 84 mL of methacrylic acid, 67 mL of ethylene chlorohydrin, 1 g of hydroquinone, 3 mL of 95~98% sulfuric acid, and 120 mL of toluene. The reaction mixture is heated at 105°C for 2.5 h was cooled to room temperature and

then 250 mL of 10% Na_2CO_3 aqueous solution was added in reactant under stirring. The neutralized product was separated and then oil layer was washed by a saturated aqueous solution of sodium chloride. The oil layer was dried with dehydrated sodium sulfate and purified by vacuum distillation (b.p. $81\sim 84^\circ\text{C}/5.6\text{ Pa}$). Chloroethyl methacrylate (CMA) was obtained. GMA and CMA were synthesized according to the procedure described by Shi, et al.^[8] and the yields were 88% and 81%, respectively.

Preparation of polymers

The copolymers of GMA with CMA and CMA with MMA were synthesized in solution polymerization in a nitrogen atmosphere at 60°C by using 2,2'-azobisisobutyronitrile (AIBN) as the initiator and benzene as the solvent according to the method described by Talyor, et al.^[9]. Finally, the fractionated polymers were obtained.

Characterization of polymer

The molecular weight of polymers were determined by Waters 150-C Gel Permeation Chromatograph. ^1H NMR spectra were obtained on a EM-360, 60 MHz NMR spectrometer. Thermal decomposition temperatures were determined with a Rigaku TG-DTA-30 differential thermal analyzer. The thickness of the photoresist film was measured by a Model 6JA interference microscope.

Photoresist films and exposure

Photoresist films were spin-coated on a SiO_2 surfaces supported on Si wafers. The films were baked at 80°C for 30 min and their thickness was measured with photointerference method.

Exposure was performed under 5×10^{-6} torr environment in a lithography station of Hefei National Synchrotron Radiation Laboratory (HENSRL).

RESULTS AND DISCUSSION

Molecular weight and distribution of the polymers

The effect of the ratio $\overline{M}_w/\overline{M}_n$ on photoresist properties is important^[9]. The molecular weights and polydispersities of the fractionated polymers are listed in Table 1.

Table 1 Molecular weights and polydispersities of fractionated polymers

Copolymer	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
P(GMA-CMA)	33.50	16.00	2.1
P(CMA-MMA)	31.60	13.60	2.3

Copolymer composition

The ^1H -NMR spectra of P(GMA-CMA) and P(CMA-MMA) are shown in Fig.1. According to the ratio of each absorption peak area in Fig.1(a) and 1(b), the molar ratios of GMA-CMA and CMA-MMA in the copolymer were calculated, and they are 0.49:0.51 and 0.51:0.49, respectively.

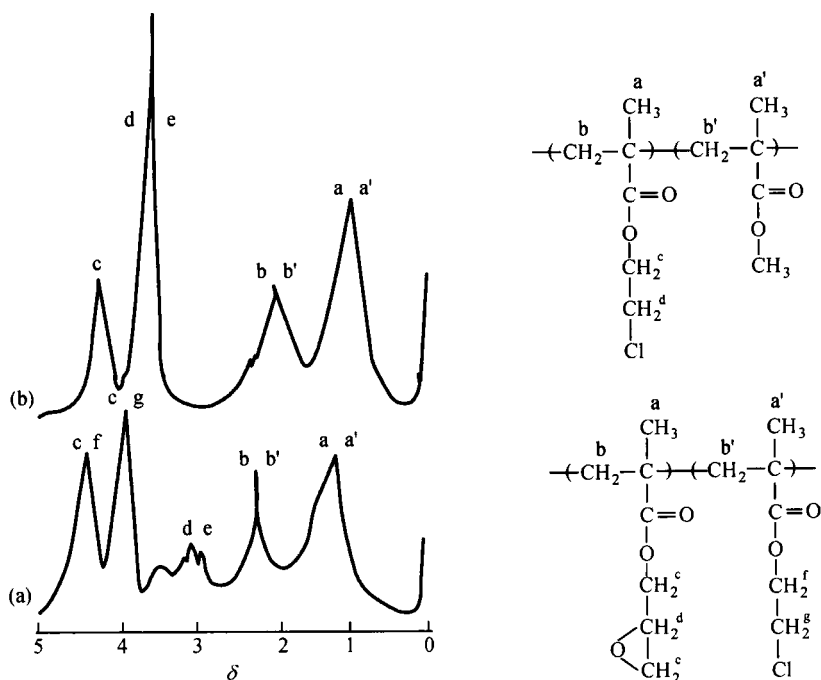


Fig.1 ^1H -NMR spectra of copolymers
(a) P(GMA-CMA); (b) P(CMA-MMA)

Thermal decomposition

Fig.2 shows the TGA curves of the copolymers. From Fig.2, it can be seen that the thermal decomposition temperatures of P(GMA-CMA) and P(CMA-MMA) are 345°C and 295°C , respectively.

Sensitivity of photoresist

The sensitivity curves of P(CMA-MMA) and P(GMA-CMA) are shown in Fig.3.

The sensitivities of P(CMA-MMA) and P(GMA-CMA) developed in methyl-isobutyl-ketone (MIBK): isopropyl alcohol (IPA)=3:1(v/v) for 30 seconds are 1100 mA min and 4300 mA min, respectively. The sensitivity of P(CMA-MMA) is about 4 times larger than that of P(GMA-CMA).

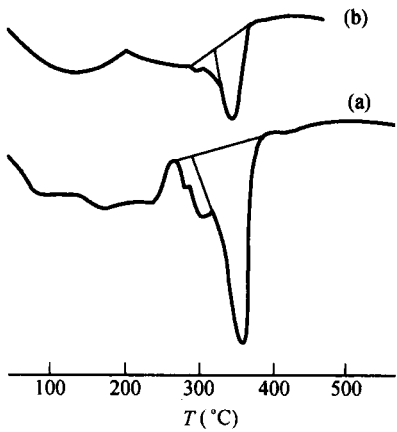


Fig.2 TGA curves for copolymers
(a) P(GMA-CMA); (b) P(CMA-MMA)

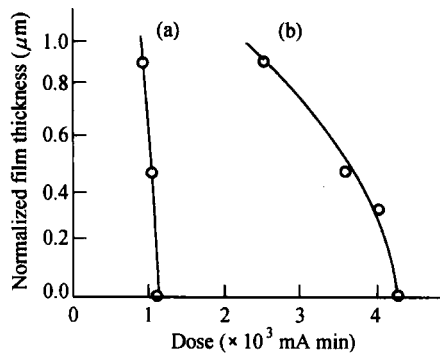


Fig.3 Typical sensitivity curves of P(CMA-MMA) and P(GMA-CMA) developed in MIBK: IPA=3:1 at 25°C
(a) P(CMA-MMA); (b) P(GMA-CMA)

Lithography results

Fig.4 shows the scanning electron micrograph of replicated patterns in P(CMA-MMA) and P(GMA-CMA) photoresists. From Fig.4(a) and 4(b), it can be seen that the line width of P(CMA-MMA) is 0.6 μm and 0.1~0.16 μm , respectively. From Fig.4(c) and 4(d), it can be seen that the line width of P(GMA-CMA) is 0.3 μm and 0.17~0.2 μm , respectively. When Fig.4(b) is compared with Fig.4(d), it can be seen that the high resolutions of P(CMA-MMA) and P(GMA-CMA) photoresists achieve the submicron scale.

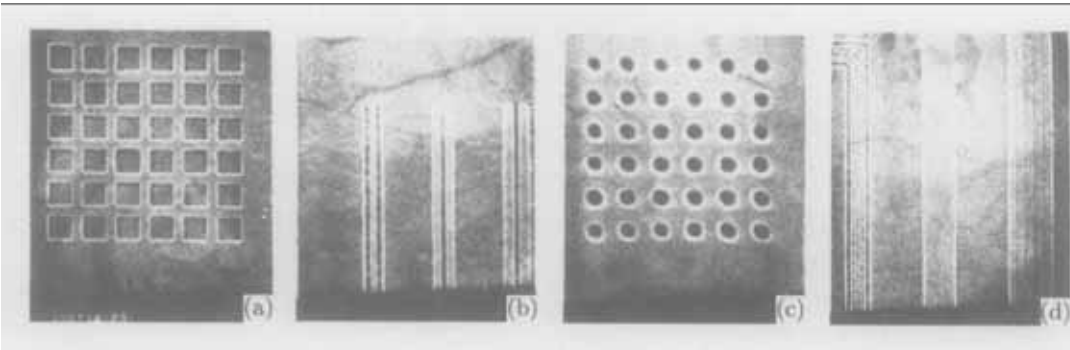


Fig.4 Scanning electron micrographs of replicated patterns for P(CMA-MMA) and P(GMA-MMA)
(a) (b) photoresist: P(CMA-MMA); thickness: 0.6 μm ; Dose: 3500 mA min; Developing time: 30 s; Developing temperature: room temperature; (c) (d) photoresist: P(GMA-CMA); thickness: 0.4 μm ; Dose: 2700 mA min; Developing time: 30 s; developing temperature: room temperature

CONCLUSIONS

The breadths of the molecular weight distributions of P(CMA-MMA) and P(GMA-CMA) are 2.1 to 2.3.

The thermal decomposition temperature of P(CMA-MMA) and P(GMA-CMA) are 295°C and 345°C, respectively.

The resolutions of P(CMA-MMA) and P(GMA-CMA) photoresists are submicron scale.

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