Mechanism of Acid-Catalyzed Crosslinking Reaction with Hydroxyethyl Group and Application to Microlithography

Toshiaki Aoi[‡], JongSoo Lee, Hirohmi Watanabe, Syun'ichi Kondo[‡],
 Nobukazu Miyagawa, Shigeru Takahara and Tsuguo Yamaoka

[‡]*Yoshida-Minami Factory, Fuji Photo Film Co., Ltd., Shizuoka 421-0396, Japan*
Department of Information and Image Sciences, Faculty of Engineering,
Chiba University, Chiba 263-8522, Japan

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1. Introduction

Generally, methacrylate polymers with alicyclic group have been focused on the utility for resist materials used for the light of short wavelength region, such as 193 nm or 248 nm[1-3]. Because these polymers have outstanding transparency in such wavelength. Furthermore, these polymers can be easily prepared with required properties for photoresist, such as a dry etching resistance, an alkaline solubility, an adhesion to Si-wafer, and so on.

We have investigated positive working of 3-components photoresist composing to poly(methacrylate) derivatives, vinyl ether as a crosslinker and photoacid generator (PAG). Then this resist showed sometime not only positive working but also negative working when sufficient condition such as long exposure, high post expose baking (PEB) temperature was given. As the poly(methacrylate) derivatives, terpolymers comprised of benzylmethacrylate (BzMA), methacrylic acid (MAA) and 2-hydroxyethyl methacrylate (HEMA), poly(BzMA-co-MAA-co-HEMA) gave the negative working behavior. The terpolymers were prepared from the purpose that BzMA segment give dry-etching resistance and MAA, HEMA segments give good adhesion with substrate and high solubility to alkaline developer. We found unexpectedly the resist without vinyl ether showed also negative working behavior.

In this paper we investigate the detail of this negative working mechanism and its application to

the photoresist with transparency for short wavelength.

2. Experimental

2.1. Materials

Six kinds of polymers with different polymerization ratio of BzMA, MAA and HEMA were prepared. The physical properties of terpolymers are summarized in Table 1.

Diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a PAG was synthesized according to the literature[4].

Table 1. Physical properties of sp-series polymer

Polymer	Polymerization ratio (mol %)			acid value ^a	average mol weight		T _g (°C)
	BzMA	MAA	HEMA		$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	
sp-1001	63.4	13.7	22.9	38	3.21×10^4	2.04	77
sp-1009	63.2	15.3	19.5	73	2.90×10^4	2.04	85
sp-1021	72.4	19.0	8.6	69	3.20×10^4	1.88	89.4
sp-1039	51.4	18.6	30.0	72	3.07×10^4	1.94	88
sp-1040	79.0	0	21.0	0	3.13×10^4	2.06	90
sp-1042	71.8	28.2	0	105	3.35×10^4	2.01	89.5

^a mg of KOH/g of resin

2.2. Lithographic evaluation

Photopolymer solutions were prepared by dissolving the polymer and 5 wt% PAG in cyclohexanone. Film thicknesses were prepared about 1 μ m by spin coating. The films were prebaked at 120 °C for 5 min and exposed at 365 nm light using high pressure mercury lamp through optical filter, PEB was carried out at 150

°C for 10 min. DN-3C (Fuji Photo Film Co., Ltd.):
H₂O = 1 : 2 (weight ratio) was used as a developer.

3. Results and Discussion

3.1. Photosensitivity

Photosensitivities of these resists using the six kinds of polymers with various polymerization ratio of segments as a base polymer were examined.

Fig. 1. Dependence of sensitivity curves on content of HEMA segment.

Fig. 2. Dependence of sensitivity curves on content of MMA segment.

Fig. 1 shows the dependence of photosensitivity on different HEMA ratio in same MAA ratio. The resist photosensitivity is increased with increase of HEMA ratio. Fig. 2 shows the dependence of photosensitivity on different MAA ratio in same HEMA ratio reversibly. It has a tendency to give increase photosensitivity with decrease of MAA. The resist used of sp-1040, without MAA segment, was even insoluble in the unexposed area due to low acidity. In different development condition the resist film could be observed insolubilization phenomena. On the other hand, one used the sp-1042 without HEMA segment didn't occur insolubilization.

In these results, the insolubilization is concerned with HEMA segment of polymer.

3.2. Reaction of the model compounds

Model compounds with 2-hydroxyethyl group were prepared in order to analyze the mechanism[5].

Fig. 3. ¹H-NMR spectra of a mixture of 2-hydroxy isobutyrate and *p*-toluenesulfonic acid in DMSO-*d*₆ (a) before heating (b) after heating at 150°C for 20 hour.

Fig. 4. ¹³C-NMR spectra of a mixture of 2-hydroxy isobutyrate and *p*-toluenesulfonic acid in DMSO-*d*₆ (a) before heating (b) after heating at 150°C for 20 hour.

It was observed the reaction between 2-hydroxyethyl isobutyrate as the model compound

having HEMA segment and *p*-toluenesulfonic acid instead of DIAS. 2-Hydroxyethyl isobutyrate was reacted with *p*-toluenesulfonic acid in DMSO- d_6 at 150 °C for 20 h and the reactions were monitored by ^1H -NMR and ^{13}C -NMR spectroscopy.

Fig. 3 shows the change of ^1H -NMR spectrum by heating. The peak assignment are based on the labeling system defined in Fig.3. Two methylene peaks of hydroxyethyl group appear at 3.56 and 4.02 ppm, respectively. After reaction for 20 h, these peaks were disappeared and new peak was appeared at 3.78 ppm and peak of hydroxy group at 4.64 ppm decrease and shift to low magnetic field simultaneously.

These changes show that methylene group became equivalent. It means that the product is symmetrical with center of methylene group.

This reaction was also observed by the ^{13}C -NMR spectrum in Fig. 4. Two methylene peaks at 59.0 and 65.6 ppm were changed to one peak at 63.9 ppm.

It was compared the product of model experiment with ethylene glycol diisobutyrate of expected compound. Their peaks were consisted except shift of few peaks in ^1H - and ^{13}C -NMR.

Fig.5. Infrared differential spectrum of 2-hydroxyethyl isobutyrate and ethylene glycol diisobutyrate.

As shown in Fig. 5, IR differential spectrum between 2-hydroxyethyl isobutyrate of reactant and ethylene glycol diisobutyrate of expected compound shows increase in the C-O stretching band of ester around 1125 cm^{-1} and decrease in the O-H stretching band of hydroxy group around 3500 cm^{-1} . Moreover, the C=O stretching band of carbonyl group was shifted from 1714 cm^{-1} to 1743 cm^{-1} .

On the basis of these results, crosslinking reaction is considered to proceed via

transesterification between HEMA segments by acid. The expected mechanism of insolubilization reaction is depicted in scheme 1.

3.3. Reaction in film

The transesterification in film was observed to occur like behavior in solution by IR spectroscopy[6]. Fig. 6 shows a IR differential spectrum between before and after PEB of mixture of sp-1001 and DIAS on Si-wafer. This spectrum change is consistent with behavior in solution. Table 2 shows the IR differential spectra of various polymers. These results show same behavior with the photosensitivity and model reaction.

Fig.6. Infrared differential spectrum of sp-1001 with DIAS before and after post exposure baking.

Table 2. Comparison with IR spectra change before and after post exposure baking.

polymer	$\nu(\text{O-H})_{3500}$	$\nu(\text{C=O})_{1740}$	$\nu(\text{C=O})_{1710}$	$\nu(\text{C-O-C})_{1125}$
poly(BzMA-co-MAA-co-HEMA)	Decrease	Increase	Decrease	Increase
poly(BzMA-co-MAA)	—	Increase	Decrease	—
poly(BzMA-co-HEMA)	Decrease	Increase	Decrease	Increase

3.4. Application to photoresist for short wavelength

This crosslinking reaction can be applied in short wavelength region because this reaction part has little absorption in the region. For application in short wavelength, aromatic group of BzMA is not suitable because of its low transparency, so alicyclic group such as tricyclodecanyl (TCDA) that have a transparency and a dry etching resistance was used instead of BzMA segment.

Scheme 1. Crosslinking mechanism of transesterification.

For the preliminary experiment, the insolubilization of the resist was examined using poly (TCDA-*co*-MAA-*co*-HEMA) and diphenyliodonium trifluoromethanesulfonate (DPI-OTf) as a PAG at the 254 nm. (Fig. 7)

Fig 7. Characteristic curve of poly(TCDA-*co*-MAA-*co*-HEMA) and DPI-OTf

4. Conclusion

In this study, we find out a novel negative working mechanism. The HEMA segments of polymer form crosslinks under acid condition. We

showed that the reaction is a transesterification between HEMA segments. It was examined by the photosensitivity, the model experiment and the IR differential spectrum.

This new crosslinking can be apply to negative resist corresponded to short wavelength light such as 193 nm ArF and 248 nm KrF excimer laser.

References

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