CBR (CONTRAST BOOSTED RESISTS) USING HALOMETHYLARYL KETONE AS A BASE-LABILE WATER-REPELLENT COMPOUND

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In recent years, contrast enhanced resists using base-labile compounds, such as phenolphthalein [1, 2, 3] or acetoxybenzene [4] derivatives have been reported. All of these contrast enhanced resists have been positive resists. We previously reported a new contrast enhancement method [5] which can be applied to both negative and positive resists. The resists made using this method are called contrast boosted resists (CBRs) and they consist of a phenolic resin, a photoactive compound, and a base-labile water-repellent compound. The patterning process of a negative CBR is shown in Fig. 1. The CBR offers high resolution because the photochemically induced solubility difference between the exposed and unexposed regions is enhanced by the base-labile water-repellent compound. In the exposed region, the photochemically produced hydrophobic compounds and the added water-repellent compound work together to retard permeability of the base developer penetrating into the resist. Thus, the exposed region of the CBR is completely insolubilized in the base developer. On the other hand, the base developer permeates into the unexposed region of the CBR and converts the water-repellent compound into hydrophilic compounds that do not inhibit dissolution in phenolic resin. Therefore, CBRs exhibit a large dissolution rate contrast compared to conventional resists.

To find base-labile water-repellent compounds suitable for CBRs, the halomethylaryl ketones listed in Table 1 were evaluated as the base-labile water-repellent compounds. A halomethylaryl ketone was doped into a conventional negative resist composed of 4,4'-diazido-3,3'-dimethoxybiphenyl (DMDA) and m,p-cresol novolak resin (DMDA/novolak=10/100; in weight ratio). The sensitivity curves of the resists consisting of DMDA, a halomethylaryl ketone, and an m,p-cresol novolak resin (DMDA/halomethylaryl ketone/ novolak= 10/20/100; in weight ratio) are shown in Fig. 2. The resist doped with TBAB gave the highest resist contrast, and followed by BBAB and BAB.

The contrast enhancement of the resist using TBAB can be explained as follows. When the resist is exposed to UV light (i-line: 365 nm), DMDA crosslinks the novolak resin. The crosslinked novolak resin and TBAB work together to retard the permeability of the base developer penetrating the resist in the exposed region. Then, the exposed region is completely

Fig. 1 Patterning process of negative CBR

Fig. 3 Second-order rate plots of halomethylaryl ketones with base in ethanol

Table 1 Base-labile water-repellent compounds evaluated

Compound	Name	Chemical Structure
Bromoacetyl benzene	BAB	<chem>BrCC(=O)c1ccccc1</chem>
p-Bis(bromoacetyl) benzene	p-BBAB	<chem>BrCC(=O)c1ccc(cc1)C(=O)CCBr</chem>
m-Bis(bromoacetyl) benzene	m-BBAB	<chem>BrCC(=O)c1cccc(c1)C(=O)CCBr</chem>
1,3,5-Tris(bromoacetyl) benzene	TBAB	<chem>BrCC(=O)c1cc(C(=O)CCBr)cc(C(=O)CCBr)c1</chem>
1,3,5-Tris(dibromoacetyl) benzene	TDBAB	<chem>BrC(=O)CCBrC(=O)c1cc(C(=O)CCBr)cc(C(=O)CCBr)c1</chem>
1,3,5-Tris(chloroacetyl) benzene	TCAB	<chem>ClCC(=O)c1cc(C(=O)CCCl)cc(C(=O)CCCl)c1</chem>

Fig. 2 Sensitivity curves of negative CBRs using halomethylaryl ketones with a different number of bromoacetyl groups on the benzene ring (i-line exposure)

CBR: DMDA/Halomethylaryl ketone/
Novolak= 10/20/100

Conventional: DMDA/Novolak = 100/10

insolubilized in the base developer. On the other hand, the base developer permeates easily into the unexposed region and reacts with TBAB to produce 1,3,5-tris(hydroxyacetyl)benzene (THAB), which does not inhibit dissolution in novolak resin. Therefore, the resist doped with TBAB has higher contrast than the conventional resist.

The degree of contrast enhancement depends on both the number of bromoacetyl groups on the aromatic rings and the number of halogen atoms on acetyl groups as can be seen in Fig. 2. This indicates that the large water-repellent/hydrophilicity change and the reactivity of halomethylaryl ketones with the base give rise to a large contrast enhancement in the resist. To evaluate the reactivity of the halomethylaryl ketones with the base developer, the second-order rate plots of the halomethylaryl ketones with a base are shown in Fig. 3. The reaction rate was obtained by measuring the decay of the UV absorption of halomethylaryl ketones in basic ethanol after adding a base. The rate constant of the TBAB is the largest among the halomethylaryl ketones evaluated and that of BBAB was next largest. This result indicates that the reaction rate of halomethylaryl ketone plays an important role in the contrast enhancement of CBRs.

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