STUDY ON A POSITIVE PHOTORESIST WITH HIGH DRY ETCHING
RESISTANCE

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1 INTRODUCTION

Dry etching resistance and thermal stability are required for sub-micron resolved photoresist. Usually, the conventional photoresists used cresol-formaldehyde novolac resin as polymeric binder, and diazonaphthoquinone sulfochloride (NDSC) as sensitive monomer.

The poly(p-hydroxy) styrene (PHS) which has linear molecular structure has higher molecular weight than that of cresol-formaldehyde novolac resin. As a result, the glass transition temperature for PHS shows 140C and above. On the contrary, the glass transition temperature for cresole-formaldehyde resin is in the from 70C to 120C range. PHS shows good photoresist properties in regard to sensitivity and dry etching resistance.

This paper reports a method of improving the resist properties, involving adding four different agents to PHS resist.

2 PN RESIST

The properties of PN resist, which consisted of PHS and NDSC, were investigated. Table 1 shows synthesized binder polymer

for photoresist. There was an average of 18 PHS monomer units. (1, 2)

Table 1 Characteristics for Binder Polymers

Abbr.	PHS	P	M	EB
Mn	2300	1200	1100	720
Unit Structure	$\text{-(CH}_2\text{-CH)}_n\text{-}$	$\text{-CH}_2\text{-}$	$\text{-CH}_2\text{-}$	$\text{-CH}_2\text{-}$

Figure 1 shows ultra violet absorption spectra for PHS and phenol resin. It was clarified that there was no absorption within the 330 to 410nm range. (3)

Fig.1 Ultraviolet Absorption Spectra for Hydroxy Group Containing Polymers

The characteristics were measured for PN resist, sensitivity and contrast, involving various PHS and NDSC ratio. Table 2 shows the PN resist properties. It was found that the PN photoresist sensitivities showed the decrease in the NDSC mole fraction for PHS with a higher PN resist sensitivity. The highest PHS to NDSC sensitivity ratio was 1:0.5 (4).

Table 2 PN photoresist Properties

NDSC Mole Fraction	0.3	0.4	0.5	0.6
Sensitivity (mJ/cm ²)	150	170	280	365
Image Contrast	2.1	1.9	2.9	3.8

3 EB PHOTORESIST

However, PHS has a drawback in regard to adhesion for the substrate. To improve this point, three different polymers, P, M and EB, whose molecular structure was similar to that for PHS, were added to PN photoresist. The photoresist adhesion depended on the additive polymer and the amounts. Test results indicated that adding the EB polymer to PHS improved the adhesion. The most effective adding amounts were 20% and above.

Generally, there are several ways to improve photoresist sensitivity. (6, 7) It was found that adding Benzotriazole (BN; Fig. 2) to PN resist was effective to improve the sensitivity. Table 3 shows the experimental results of adding BN to EB resist. As the BN increased, EB resist sensitivity become higher and higher. EB (20, 3), which showed solid components of 20% EB and 3% BN in PN resist, was increased to 35% in sensitivity for EB (20, 0). The contrast, calculated by Thompson definition, was 3.3.

Abbr.	BN
Molecular Structure

Fig. 2 Molecular Structure of BN Sensitizer

Fig. 3 Characteristics Curve of EB Photoresist

Table 3 Properties of EB Photoresist

EB	(20, 3)	(20, 1)	(20, 0)
BN contents (%)	3	1	0
Sensitivity (mJ/cm ²)	170	215	260
Resolution (μm)	2.0	—	—
Contrast	3.3	—	—

Resist Thickness

1. 24μm

UV Exposure

170mJ/cm²

Developing Time

20sec.

Fig. 4 EB Resist Pattern

Fig. 5 DSC Curves for PHS and EB

Figure 5 shows DSC curves for PHS and EB. Assuming that the dry etching factor for a photoresist, such as AZ-1350, was 1 unit, the dry etching resistivity for EB was calculated as being about 0.8 under the same conditions.

4 CONCLUSION

It was found that PHS, as binder polymer, was adequate for very dry etching resistance photoresist. In order to improve resist properties, adhesion and sensitivity, hydroxy groups containing polymers and benzotiazole, were added to the PN resist. The EB(20,3) resist properties were as follow:

EB (20, 3) RESIST

Glass transition temp.	120C
Sensitivity	170mJ/cm ²
Resolution	2.0um
Contrast	3.3

5 REFERENCE

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