A Novel Positive Resist for Deep UV Lithography
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Mechanism of the positive resist

The mechanism of the positive resist involves the acid catalytic hydrolysis of silylated phenol group. A novel positive resist consists of poly(p-trimethylsilyloxystyrene) and photosensitive acid precursor.

On exposure, acid is released from the precursor, which catalytically deblocks the silyl group to convert the polymer to alkaline soluble poly(p-hydroxystyrene).

Results and discussion

Preparation of poly(p-trimethylsiloxystyrene)

Poly(p-hydroxystyrene) (Mw=7500) was reacted with trimethylchlorosilane in purified dioxane with the aid of imidazole catalysis at 20°C for 24 hours. The reacted solution was poured into an excess amount of iced water to precipitate the silylated polymer. The precipitated polymer was filtrated and dried rapidly in vacuo. Characterization of the polymer was carried out with $^1$H NMR and IR spectrum, and indicated that almost 100 percent silylation was successfully accomplished.

Fig.1 shows the transmittance spectrum of 1 μm thick film of the polymer. The transmittance at 248 nm is 64 percent which is much more transparent compared with novolak resin.
Acid precursor

A variety of acid precursor involving diazonium salts, triphenylsulfonium salts and trichloromethyl-s-triazine derivatives can act as the sensitizer for this polymer. However, the new acid precursor gave most successful results for resist characteristics.

The new acid precursor, p-nitrobenzyl-9,10-diethoxyanthracene-2-sulfonate (NBAS) is photochemically decomposed to give p-nitrosobenzaldehyde and 9,10-diethoxyanthracene-2-sulfonic acid. The latter is strongly acidic and deblocks the silyl group of the polymer.

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\begin{align*}
\text{Scheme 2. Photoreaction of p-nitrobenzyl-9,10-diethoxyanthracene-2-sulfonate}
\end{align*}
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Resist characteristics

The polymer 1.0 g was dissolved in diethylene glycol dimethyl ether and 0.1 g of NBAS was added to prepare the resist solution.

Unlike novolak type resist where the insolvibility in the unexposed areas are brought about by the solubility inhibition of 0-naphthoquinonediazide sulfonic ester, the advantage of this positive resist is that the polymer is completely insoluble in the alkaline developer unless it is exposed to light. The high solubility contrast on the exposed and the unexposed area is expected to give the high resolution. The solution was spin-coated on a wafer to form 1 μm thick layer, exposed with deep UV light shorter than 300 nm, and developed in 1 % water solution of TMAH. Fig. 2 shows the exposure characteristic curve for this photoresist. Fig. 3 and Fig. 4 show the SEM photographs. It can be seen that 0.65 μm L&S is reproduced with high aspect ratio.

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\begin{align*}
\text{Fig. 2. Sensitivity curves of the resist for deep UV} \\
\text{Fig. 3. SEM photograph of 1.0 μm L&S} \\
\text{Fig. 4. SEM photograph of 0.65 μm L&S}
\end{align*}
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