A Chemically Amplified, Negative-type Photosensitive Poly(phenylene ether ketone) (PEK) Resist Based on Ketal-protected PEK and a Photoacid Generator

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A novel chemically amplified photosensitive poly(phenylene ether ketone) (PEK) based on ketal-protected PEK as a precursor polymer and diphenylidonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a PAG has been developed to remedy warpage of thinner silicon wafers. This resist does not require high thermal treatment after development. The 8-μm negative pattern was obtained on 1.5-μm thick film consisting of ketal-protected PEK (90 wt %) and DIAS (10 wt %).

Photosensitive polyimides (PSPIs) and polybenzoxazoles (PSPBOs) have been widely applied as practical packaging and/or insulating materials in microelectronics. For instance, buffer coatings, passivation layers, α particle barriers, interlayer insulations, and wafer scale packages, are used in industrial manufacturing, including integrated circuits (ICs), and multichip packages (MCPs). Advances in the outstanding properties of polyimides (PIs) and polybenzoxazoles (PBOs) as thermally stable polymers, along with expanded sources of monomers, have established that PSPIs and PSPBOs can function over a much broader range.[1,2] PI and PBO films are mostly formed by thermal treatment of their precursors, such as poly(amic acid)s and poly(*o*-hydroxy amide)s, respectively, up to 350 °C after casting the solution on a substrate. Such a thermal imidization process recently addressed another aspect to be considered and claims to be an improvement toward low-temperature cyclization to remedy warpage of thinner silicon wafers.

Poly(phenylene ether ketone)s (PEK)s have valuable characteristics, including excellent resistance to solvents, high melting points, and useful properties at temperatures exceeding 250 °C.[3] However, the lack of solubility and high melting points limit their polymerizations and processing. To resolve these problems, there have been several reports describing amorphous precursor polymers containing *t*-butyl-substituted monomers[4] or monomers with carbonyl groups protected by ketimines,[5] ketals,[6] and thioketals.[7] In previous papers, we reported that alkyl-substituted PEK functions as negative-type photosensitive polymer with good sensitivity and contrast for 300–400-nm UV radiation.[8,9] These photosensitive polymers do not require high thermal treatment. It is also important to develop another type of photopatterning process to expand the application of photosensitive PEK.

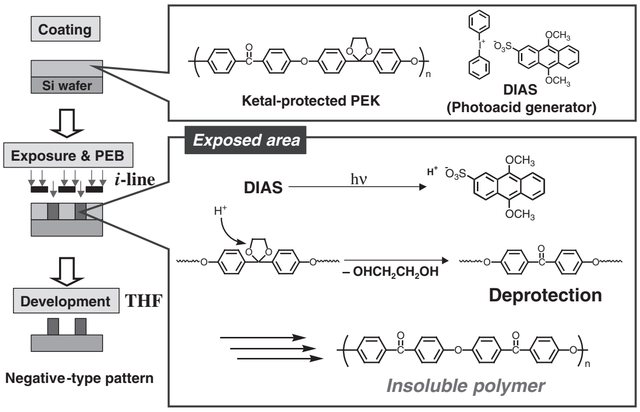

Figure 1. Patterning process of CAPEK.

Here we report a chemically amplified PEK resist (CAPEK) based on ketal-protected PEK from 4,4′-difluorobenzophenone and a cyclic ketal of 4,4′-dihydroxybenzophenone [2,2-bis(4-hydroxyphenyl)-1,3-dioxolane] as a precursor polymer and diphenylidonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a photoacid generator (PAG). The photopatterning process of this CAPEK is shown in Figure 1. The coated film is exposed to the *i*-line through a printed photomask to generate a strong acid as an acid catalyst from DIAS. Upon post-exposure baking (PEB) treatment of the CAPEK film, the strong acid catalyzes the deprotection of cyclic ketal groups to form PEK. The solubility of the resulting PEK is lower than that of ketal-protected PEK, thus a negative-type pattern is obtained after development.

Ketal-protected PEK was prepared by nucleophilic aromatic substitution with 4,4′-difluorobenzophenone and 2,2-bis(4-hydroxyphenyl)-1,3-dioxolane, giving a white and flaky polymer with M_n of 21000 and PDI of 1.74.[6] The obtained polymer was soluble in conventional organic solvents such as chloroform, tetrahydrofuran (THF), and tetrachloroethane. The glass transition temperature (T_g) of ketal-protected PEK measured by differential scanning calorimetry (DSC) was 160 °C.

To clarify the deprotection behavior of the exposed area, 1.0-μm thick polymer films were obtained by spin-casting from tetrachloroethane solutions on silicon wafers. These films were prebaked at 100 °C for 5 min, and then exposed to *i*-line irradiation while changing the dose, followed by PEB at a temperature of 120–190 °C for 5 min. The exposed films were developed with THF at room temperature. The progress of the reaction was monitored by using IR spectroscopy. Figure 2 shows the FT-IR spectra of a ketal-protected PEK resist on 1.0-μm thick films, measured after (a) and before (b) PEB at 150 °C for 10 min after 200 mJ cm^{-2} of *i*-line exposure, respectively. After PEB, the absorption at 1083 cm^{-1}, assigned to the ketal bond, disappears. This result indicates that the deprotection reaction successfully proceeds by PEB in the film state and is complete after PEB at 150 °C for 10 min.

To follow the degree of deprotection, the absorption intensities on FT-IR spectra at 1083 cm^{-1} (A_{1083}), characteristic carbonyl groups at 1650 cm^{-1} (A_{1650}), and aromatic C=C stretchings at 1500 cm^{-1} (A_{1500}) using the 1.0-μm thick films were measured. The decrease in A_{1083} reveals a decrease in the ketal

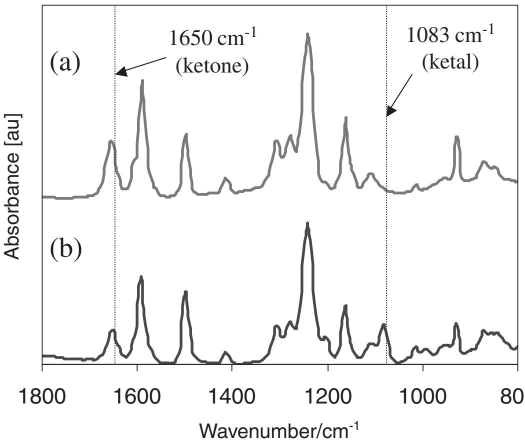

Figure 2. FT-IR spectra of CAPEK films from ketal-protected PEK and DIAS on silicon wafers. (a) The fully deprotected CAPEK film baked at 150 °C for 10 min after *i*-line exposure at 200 mJ cm^{-2}. (b) The fully protected CAPEK film before PEB.

groups due to the acid-catalyzed deprotection reaction. At the same time, the increase in A_{1650} indicates an increase in the ketone formation. The degrees of deprotection of the ketal groups and the formation of ketone groups were determined using the two following eqs 1 and 2:

$$\text{Deprotection (\%)} =$$

$$\frac{A_{1083}/A_{1500}(\text{samp}) - A_{1083}/A_{1500}(\text{ket})}{A_{1083}/A_{1500}(\text{init}) - A_{1083}/A_{1500}(\text{ket})} \times 100 \qquad (1)$$

$$\frac{A_{1650}/A_{1500}(\text{samp}) - A_{1650}/A_{1500}(\text{init})}{A_{1650}/A_{1500}(\text{ket}) - A_{1650}/A_{1500}(\text{init})} \times 100 \qquad (2)$$

The three kinds of subscripts following A_{1083}/A_{1500} and A_{1650}/A_{1500} in the two equations indicate states of the polymer film; e.g., (samp) is the polymer sampled at each baking time after exposure (0–5 min); (ket) is fully a deprotected polymer after exposure and baking for 10 min at 150 °C; (init) means initially prebaked at 100 °C for 5 min. The results are shown in Figure 3. The deprotection reaction smoothly occurs as the PEB time is increased from 0 to 5 min at 150 °C. The deprotection starts right after PEB treatment, reaches around 80% after 1 min of PEB, and is complete after 4 min of PEB time.

After optimizing the patterning condition, resist film consisting of ketal-protected PEK (90 wt %) and DIAS (10 wt %) was formulated. Figure 4 shows an SEM image after *i*-line exposure at 100 mJ cm^{-2}, postbaked at 150 °C for 5 min, and followed by developing with THF. γ-Butyrolactone, cyclohexanone, and cyclopentanone can be also used as a developer.

A clear 8-µm negative contact-printed pattern was obtained on the 1.5-µm thick film.

In summary, a new photopatterning process for PEK, based on ketal-protected PEK as a precursor polymer and DIAS as a PAG, has been developed. The 8-µm negative pattern was obtained on 1.5-µm thick films consisting of ketal-protected PEK (90 wt %) and DIAS (10 wt %). This method does not require high thermal treatment after development and will be useful to remedy warpage of thinner silicon wafers.

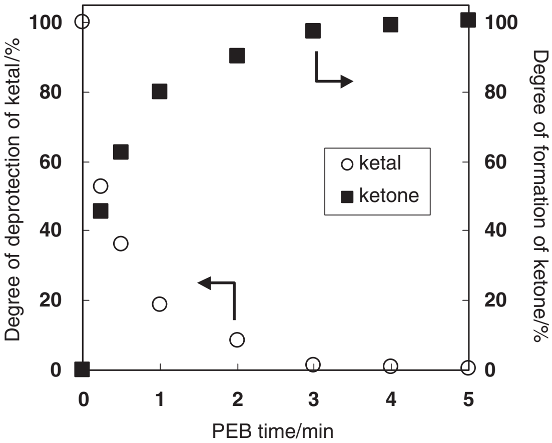

Figure 3. Effect of PEB time at 150 °C PEB treatment on the degrees of deprotection and formation of ketone. The open circle and square dots indicate the degrees of deprotection of the ketal groups and the formation of ketone groups, respectively.

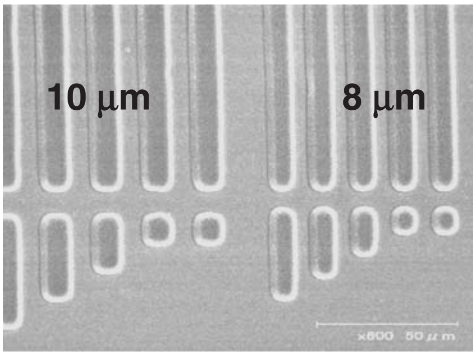

Figure 4. SEM image of the negative-type CAPEK pattern.

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