Characteristics of Silicone Resins as Base Amplifiers and Their Applications to Photopatterning

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We reported a novel concept of base proliferation reactions to enhance the photosensitivity of photopolymers utilizing base-catalyzed reactions.[1-3] The concept involves the base-catalyzed decomposition of a compound termed as a base amplifier which releases newborn amine molecules, leading to its autocatalytic decomposition. Based on the concept, we designed novel siloxane oligomers (Mw = 1300-3300) bearing base-amplifying units as a base resin for photoresist formulations.[4] We demonstrated that the oligomers undergo base-catalyzed transformations to generate amino groups in their side chains to give rise to the autocatalytic decomposition. This leads to the solubility change of siloxane oligomers. The other option of the siloxane skeleton as an oligomer main chain is expected to enhance plasma-etching resistance.[5] We showed that the siloxane oligomers sensitized with a photobase generator (PBG) provide positive- and negative-working photoresists with high sensitivity. The sensitivity enhancement stems from base proliferation reactions of the siloxane oligomers, which are induced by a tiny amount of photogenerated amine molecules. However, the siloxane oligomers are not suitable for a base resin of photoresists because a solution of a photoresist with low Mw is hardly spin-coated to give films with appropriate thickness. We report here the synthesis and photosensitivity characteristics of novel copolymers (1) of a dialkoxysilane having a base-amplifying unit and tetraethoxysilane (TEOS) to obtain base-amplifying silicone resins with high Mw (Scheme 1).

The copolymer 1 was obtained by acid-catalyzed hydrolytic copolycondensation of TEOS and 9-fluorenyl[N-(3-methyl-diethoxy-silyl)propyl]carbamate as a base-amplifying alkoxyasilane. The molecular weight of 1 increased up to Mw = 18000 with increasing the amount of water in hydrolytic copolycondensation. ²⁹Si-NMR spectra of 1 (Mw = 18000 and 6000) showed m : n = 5.4 : 1.0 and 1.6 : 1.0, respectively.

Base-catalyzed decomposition behavior of a film of 1 (Mw = 18000, m : n = 5.4 : 1.0) was examined by IR absorption spectral measurements. A photoresist solution was prepared by dissolving 1 (0.10 g / 1 mL) and 1,3-bis[(2-nitrobenzyl)oxy carbonyl]-4-piperidyl]propane (2)[6] as a PBG (10 wt% relative to the polymer) in chloroform. The solution was spin-coated on
silicon wafers and baked at 100 °C for 60 sec to give 1.0 μm-thick films. The films were exposed to UV light and heated at 100 °C to be subjected to IR absorption measurements. A film of 1 with initial UV irradiation decomposed completely after heating for 9 min at 100 °C. On the other hand, a film of 1 without UV irradiation decomposed abruptly after prolonged heating for 190 min at 100 °C. These results indicate unequivocally that photobase-catalyzed decomposition of 1 proceeds autocatalytically to form amino groups in the side chains.

The base-amplifying silicone resin 1 becomes insoluble in organic solvents in the presence of PBG upon UV irradiation and subsequent post-exposure baking, owing to the photobase-catalyzed hydrolytic condensation of ethoxy silyl units of 1 to give rise to crosslinking, which functions as a negative-working photoresist. To determine photosensitivity, a thin film of 1 (Mw = 18000, m : n = 5.4 : 1.0) sensitized with 1,3-bis[(2-nitro-4,5′-dimethoxybenzyl)oxy]carbonyl-4-piperidyl]propane (3) as PBG was exposed to 365 nm light and heated at 100 °C for 50 min or 130 °C for 14 min. The film was developed with acetone to obtain photosensitivity curves, which are shown in Fig. 1. The sensitivity is defined as the irradiation energy required for the reduction of normalized film thickness by 0.5. The sensitivity increased with increasing the heating temperature after UV irradiation. An exposure dose was reduced down to 2.5 mJ/cm² when the film was heated at 130 °C for 14 min. This is because the base proliferation reaction of 1 proceeds effectively at a higher temperature during postbaking, resulting in the enhancement of base-catalyzed hydrolytic condensation of ethoxy silyl groups of 1. This sensitivity is much higher than that of conventional chemically amplified resists relying on base-catalyzed reactions.

Microphotopatterning was carried out as follows. A resist film consisting of 1 (Mw=6000, m:n=1.6:1.0) and 10 wt% of 3 as PBG was exposed to 365 nm light through a photomask. Subsequently, the film was baked at 130 °C for 150 sec and developed with acetone for 10 sec. Fig. 2 shows negative-tone images obtained from the resist comprising 1 and 3. It resolved down to 4-10 μm line-and-space (L&S) patterns.

In summary, we developed novel base-amplifying silicone resins with higher Mw which undergo base-catalyzed transformation to form amino groups in their side chains. The combination of the silicone resins with PBG provides negative-working photoresists with high sensitivity.

![Photoresist Image](image-url)

**Fig. 1** Photosensitivity curves of films of 1 sensitized with 10 wt% of 3 heated at 100 °C for 50 min (●) and 130 °C for 14 min (○).

![Photomask Image](image-url)

**Fig. 2** Microphotograph of lines and spaces of a film of 1 sensitized with 10 wt% of 3.

**References**