Positive-working Photoimaging Materials Based on Base-amplifying Silicone Resins Having Fluorenlyl Groups

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We reported base-sensitive silicone resins tethering base-amplifying side chains containing fluorenlyl groups as negative-working photopolymers.[1,2] The silicone resins undergo base-catalyzed transformation to form aliphatic primary amino groups covalently attached to a siloxane main chain, leading to the autocatalytic decomposition. We demonstrated that the silicone resins sensitized with a photobase generator (PBG) became insoluble in organic solvents upon UV-irradiation and subsequent post-exposure baking, owing to the photobase-catalyzed hydrolytic condensation of residual ethoxyisilyl units of the resins to form crosslinked networks. Therefore, these function as negative-working photoresists with high sensitivity which stems from autocatalytic formation of amino groups in their side chains to accelerate the base-catalyzed hydrolytic condensation reactions. Most of studies concerning silicone-based chemically amplified photoresists provided negative-tone images based on hydrolytic condensation reaction in a similar manner as above.[3] The progress of base proliferation reaction before hydrolytic condensation reaction in base-amplifying silicone resin may provide a positive-working photoresist with high sensitivity.

We report here that novel base-amplifying silicone resin (1) generating aliphatic secondary amino groups in its side chains, which are relatively strong bases when compared to aliphatic primary amino groups, to enhance the rate of base proliferation reaction [4] of the resin (Scheme 1). This situation would provide a positive-working resist which becomes soluble in an acidic aqueous solution in spite of its crosslinkable alkoxyisilyl units.

The silicone resin 1 (Mw=4800, Mw/Mn=1.1) was obtained by acid-catalyzed hydrolytic polycondensation of the corresponding monomer which was prepared by reacting 3-isocyanatopropytriethoxysilane with 1-(9-fluorenlymethoxy carbonyl)-4-hydroxypiperidine.

Photobase-catalyzed decomposition behavior of a film of 1 was examined by IR absorption spectral measurements. A photopolymer solution was prepared by dissolving 1 (0.10 g / 0.5 mL) and 1,3-bis[(2-nitrobenzyl)oxycarbonyl-4-piperidyl]propane (3) as PBG (10 wt% relative to the resin) in 1-methoxy-2-acetoxypropane. The solution was

![Scheme 1](image)

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spin-coated on silicon wafers and baked at 100 °C for 60 sec to give 0.70 μm-thick films. The films were exposed to 254 nm 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 6 min at 100 °C as shown in Fig. 1. On the other hand, a film of 1 without UV-irradiation decomposed abruptly after prolonged heating for 15 min at 100 °C, illustrating an S-shaped conversion curve. These results indicate obviously that photoinduced base proliferation reaction of 1 proceeds in a film during post-exposure baking (PEB) to give 2 bearing amino groups in its side chains. This means that a positive-working photosresist developable with an aqueous acidic solution is possible when PEB is carried out within 15 min at 100 °C.

Consequently, a thin film of 1 sensitized with PBG was exposed to 254 nm light, followed by heating at 100 °C to be subjected to the development with a 2 wt% aqueous solution of lactic acid and the rinse with water to give photosensitivity curves. As given in Fig. 2, the thin film functions as a positive-tone resist whose photosensitivity is markedly affected by PEB period. Judging from the fact, base-catalyzed hydrolytic condensation of residual ethoxysilyl units of 1 is negligible. An exposure dose was reduced down to 0.3 mJ/cm² when the film was heated at 100 °C for 10 min. This is because the base proliferation reaction of 1 proceeds effectively.

Microphotopatterning was carried out as follows. A thin film consisting of 1 and 10 wt% of 3 as PBG was exposed to 254 nm light through a photomask. Subsequently, the film was baked at 100 °C for 190 sec and developed with a 2 wt% aqueous solution of lactic acid to give positive-tone images. It resolved down to 10 μm line-and-space patterns.

In summary, we developed novel base-amplifying silicone resin. The silicone resin 1 displayed the base proliferation reaction even base-amplifying units are covalently attached to polymer main chains. Furthermore, the resin 1 sensitized with PBG provides positive-working photoresist developable with an aqueous acidic solution.

References