Visible-Light-Sensitive Photopolymer Systems Using Diol Monosulfonate as Acid Amplifiers

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We have proposed a new concept of acid proliferation reactions which involves the acid-catalyzed decomposition of an organic compound to release another strong acid, leading to the autocatalytic decomposition. On the bases of this concept, we have so far studied on photoresist materials using these acid amplifiers for UV light sensitive systems to improve this photosensitivity.[1-5] Chemically amplified photoresists for visible laser direct imaging were reported.[6,7] This material consists of a photoacid generator, a sensitizer dye and an acid-labile polymer. In this system, the formation of acid from a photoacid generator sensitized by a dye results in the acid-catalyzed

deprotection of acid-labile polymer, providing positive-working photoresists.

In this work, we adopt this system and aimed at the development a novel visible-light-sensitive photopolymer using acid amplifiers to improve the photosensitivity (Fig. 1).

A film of poly(*tert*-butyl methacrylate) (PT-BMA) containing 10 wt% of diphenyliodonium triflate (DPITf) as a photoacid generator, 2 wt% of 9,10-bis(phenylethynyl)anthracene (BPEA) or 1,8-dimethoxy-9,10-bis(phenylethynyl)anthracene as a sensitizer dye and 10-20 wt% of *cis*-3-(*p*-toluenesulfonyloxy)-2-pinanol (**1**) as an acid amplifier was made by spin-coating onto a silicon wafer and baking at 110 °C on a

Fig. 1. Visible-light-sensitive photopolymer system

Fig. 2 Sensitivity curves of PTBMA films containing 10 wt% DPITf and 2 wt% BPEA in the absence of (O) and in the presence of 10 wt% (Δ), 15 wt% (◆) and 20 wt% of 1 (▼) upon 436 nm irradiation.

hot stage to give a film of 2.5-3.0 μm in thickness. The films were exposed subsequently to 436 nm light using a Hg-Xe lamp or 488 nm light using an Ar laser, followed by heating at 110 $^{\circ}\text{C}$ for 90 sec to give rise to the acid-catalyzed reaction. The film thickness was measured to give photosensitivity characteristics.

Fig. 2 shows photosensitivity characteristics of the photopolymer systems. The new materials containing the acid amplifier have high photosensitivity when compared to the material in the absence of the acid amplifier. Furthermore the sensitivity and the contrast became higher as the concentration of 1 was increased.

These results indicate that photogenerated acidic species from DPITf initiate the decomposition of the acid amplifier, leading to the proliferation of acidic species, followed by the acid-catalyzed deprotection of PTBMA.

In summary, we developed new visible-light-sensitive photopolymer systems using an acid amplifier. These materials show high photosensitivity, due to the proliferation of acidic species generated from the acid amplifier.

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