Novel Resist Materials Using Acid Amplifiers. Part II

Soh Noguchi¹, Koji Arimitsu¹, Kunihiro Ichimura¹, Kazuaki Kudo²,
 Takeshi Ohfuji³ and Masaru Sasago³

¹Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

²Institute of Industrial Science, University of Tokyo,
 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan

³Association of Super-Advanced Electronics Technologies,
 292 Yoshida-cho, Totsuka-ku, Yokohama 244, Japan

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We reported the concept of acid proliferation reactions involving autocatalytic acidolytic reactions initiated by a photogenerated acid species to enhance the photosensitivity of chemically amplified photoimaging materials.[1-4] The key compound in this novel processes is an acid amplifier which is subjected to the thermal decomposition catalyzed by an acid to release acid molecules. We have developed so far *cis*-1-phenyl-2-(*p*-toluenesulfonyloxy)-1-cyclohexanol(1) as an acid amplifier. This type of a diol monotosylate decomposes acidolytically to lead to an autocatalytic reaction. Decomposition products were identified with cyclopentyl phenyl ketone and 2-phenylcyclohexanone as pinacol-rearrangement products and *p*-toluenesulfonic acid (Scheme 1).[5]

Ternary components of a photoacid generator, a phenolic resin and a dissolution inhibitor are comprised in a chemically amplified photoresist system.[6,7] The role of the dissolution inhibitor is based on a considerable modification of its chemical structure as a result of an acidolytic reaction. In this context, we have expected that the decomposition ketonic compounds derived from the diol monotosylate acts as a dissolution inhibitor in a phenolic resin because of the disappearance of OH residue. We report here that the addition of the diol monotosylate in a Novolak resin provides a novel negative-working photoresist.

We prepared solutions of a Novolak resin, 2mol% of [4-(phenylthio)-phenyl] diphenylsulfonium hexafluoroantimonate (DTS) and the diol monotosylate in variant

Scheme 1

Figure 1. The characteristic curve of films of the novel resist material containing ($\diamond$)0, ($\bullet$)5, ($\square$)10 and ($\blacktriangle$)15mol% of 1, respectively.

concentrations in propylene glycol 1-monomethyl ether 2-acetate. Films of 0.3 μm thickness were spin-cast on silicon wafers and irradiated with 313 nm light, followed by heat treatment at 110°C for 30 sec. to give rise to the acid-catalyzed reaction. After development of the film with a 7wt% of tetramethylammonium hydroxide aqueous solution for 2 min., residual thickness was measured to give photosensitivity characteristics. As summarized in **Figure 1**, the combination of the tosylate with the phenolic resin provides a negative-working photoimaging material. This fact indicates obviously that the photoproducts suppress effectively the solubility of the resin in the alkaline solution. There seems to be an optimal load of the tosylate for the photoimage formation. In a 5mol% load, the photosensitivity is rather low because much exposure doses are required to produce a critical amount of hydrophobic photoproducts.

On the other hand, the 15mol% load results in the insufficient dissolution of films which are unexposed or exposed to UV light of a dose of 1 mJ/cm^2 or less. This arises from the decrease in the solubility of the resin owing to the insolubility of the tosylate in an alkaline solution. Consequently, reasonable photosensitivity characteristics is obtained when the material contains 10mol% of the tosylate. The photosensitivity is higher than that of a ternary chemically amplified photoresist,[6,7] though the latter is a positive-working photoresist.

In summary, a novel negative-working photoresist has been developed by using the acid amplifier which modify the solubility of the phenolic resin after the acidlytical reaction, though further optimization is needed to apply this system to microlithography.

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