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# Factors affecting photosensitivity enhancement of chemically amplified photoresists by an acid amplifier

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The acid proliferation reaction of *tert*-butyl 2-methyl-2-(tosyloxymethyl)acetoacetate to liberate the corresponding sulfonic acid by the action of a tiny amount of photogenerated acid was investigated in positive- and negative-working chemically amplified photoresists. The addition of the acetoacetate as an acid amplifier to the photoresists resulted in a marked improvement in contrast, while the level of photosensitivity enhancement was relatively small for both types of photoresists, showing that the inconspicuous enhancement of photosensitivity is due to the suppression of the diffusion of acidic species in polymer films. The marked improvement of photosensitivity was achieved by the fabrication of novel double-layered photoresists doped with the acid amplifier.

Since the proposal of the concept of chemically amplified (CA) photoresists to improve resist performances,[1] numerous kinds of CA photoresists have been investigated, aiming predominantly at developing high performance photoresists for next generation microphotopatterning. Basically, they consist of a photoacid generator (PAG) and acid-labile molecules which are attached to a polymer backbone or mixed physically with a matrix polymer so that photogenerated acidic species catalyze acidolytic reactions in the polymer solid, leading to marked solubility alteration.[2] It is worthy of note that CA photoresists exhibit dual solubility characteristics since exposed areas are insoluble in less polar organic solvents. Ternary systems comprising a base polymer, a PAG and an acid-labile crosslinking agent are also available to provide negative-working photoresists.[3] A photogenerated acid leads to the acid-catalyzed crosslinking reaction of the polymer, which becomes insoluble in any solvent.

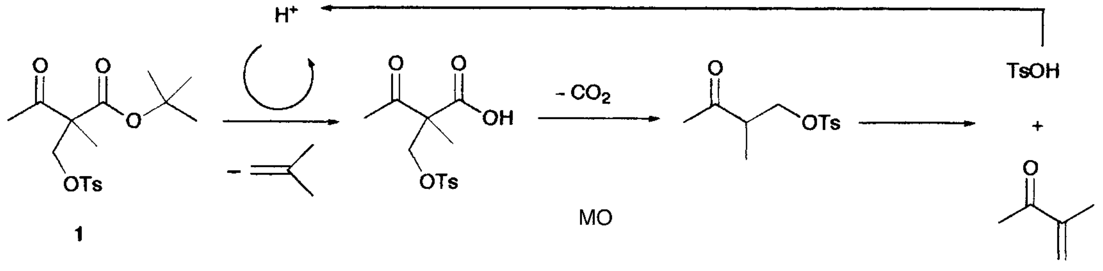
We have recently proposed a novel concept of acid-proliferation to enhance the photosensitivity characteristics of CA photoresists.[4] The acid proliferation involves the autocatalytic acid-catalyzed decomposition of an acid amplifier which releases a strong acidic species, leading to the acidolytic chain reaction. *tert*-Butyl 2-methyl-2-(tosyloxymethyl)acetoacetate (**1**) was designed as the acid amplifier.[4a] It was revealed that **1** undergoes deprotection of the *tert*-butyl ester by toluene-*p*-sulfonic acid (TsOH), followed by decarboxylation and the subsequent liberation of another TsOH in solution at an elevated temperature (Scheme 1), giving rise to a non-linear increase in the concentration of TsOH. We have also examined the autocatalytic process of **1** in polymer films to apply to CA photoresist systems. β-Sulfonyloxyketals,[5] 1,2-diol monosulfonates,[6] 1,4-diol disulfonates,[7] a trioxane derivative[8] and benzyl sulfonates[9] have been developed as acid amplifiers.

As described in our previous paper, though the addition of **1** enhances the photosensitivity of a CA photoresist consisting of poly{4-[(*tert*-butoxycarbonyl)oxy]styrene} (PBOCST) doped with a PAG, the level of photosensitivity enhancement was not so prominent, when compared with the non-linear chemistry in solution.[4b] We report here the effect of the addition of **1** to positive- as well as negative-working CA photoresists on their photosensitivity characteristics in order to obtain further insight into the role of the acid amplifier in the photoresists. It was found that photosensitivity is markedly improved when double-layered films are fabricated to separate photoacid generation and acid proliferation reaction or photoacid-catalyzed acid proliferation and acid-catalyzed alteration to accelerate the diffusion of acidic molecules in films.

## Experimental

### Materials

Diphenyl-(4-phenylthiophenyl)sulfonium hexafluoroantimonate (DPS-$SbF_6$) and triphenylsulfonium triflate (TPS-Tf) were donated by Midori Chemicals Co., Ltd. Novolak resin was a gift from Toppan Printing Co., Ltd. Polystyrene and 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate



**Scheme 1** Autocatalytic fragmentation of **1**.

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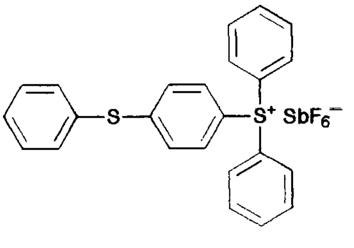
(EEC) were purchased from Scientific Polymer Products, Inc. and Aldrich Chemical Co. Inc., respectively. PBOCST,[10] poly[4-(2-hydroxy-2-propyl)styrene] (PHPS),[11] poly{4-[(cyclohexyloxycarbonyl)oxy]styrene-*co*-4-hydroxystyrene} (PCOCST),[12] α-tosyloxymethylated benzoin (TMB)[13] and the *tert*-butyl acetoacetate containing a tosyloxy group (**1**)[4b] were prepared according to the literature. Properties of the polymers used here are listed in Table 1. The chemical structures of PAGs and acid-labile polymers are shown. An aqueous solution of tetramethylammonium hydroxide (TMAH) (10%) was available from Tokyo Kasei Kogyo Co., Ltd.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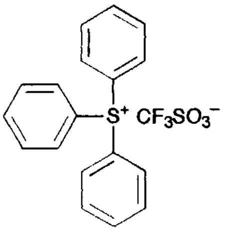
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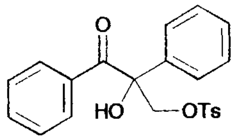
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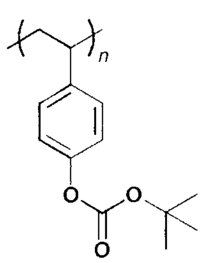
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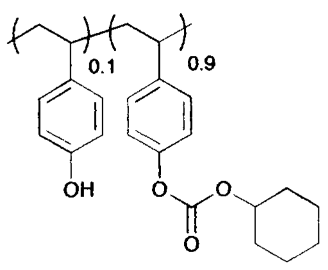
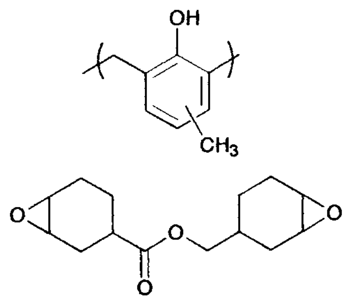
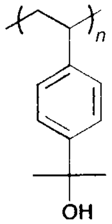

PCOCST


Novolak resin / EEC


PHPS

### Preparation of photosensitive polymer films

A conventional single-layered film was prepared by spin-coating of a solution of 1-methoxy-2-acetoxypropane (MAP) dissolving an acid-labile polymer, DPS-SbF$_6$ and **1**. Mixing ratios of a polymer, DPS-SbF$_6$ and **1** by weight were 100:5.5:0.1–10 for PBOCST and PCOCST, 100:11:0.1–10 for the Novolak resin–EEC system and 100:7.5:0.13–13 for PHPS, respectively. Spin-cast films on silicon wafers were *ca.* 0.21–0.24 μm in thickness and pre-baked at 100 °C for 1 min to be subjected to spectral analysis and photosensitivity determination.

A double-layered type-I consisting of a photoacid generating layer and an acid-labile polymer layer containing **1**, as illustrated in Scheme 2, was fabricated as follows. A solution of PBOCST and **1** (100:0.1–10 by weight) in MAP was spin-cast on a silicon wafer, followed by over-coating with a solution of a Novolak resin and TPS-Tf (100:3.5 by weight) in propan-2-ol. A double-layered type-II comprising a phototriggered acid proliferating layer and an acid-catalyzed curable polymer layer, as shown in Scheme 2, was fabricated as follows. A polymer solution for the upper layer was prepared by dissolving polystyrene, TMB as a PAG and **1** in a ratio of 100:3.6:0.1–10 by weight in toluene while a solution for the lower layer was prepared by dissolving a Novolak resin and EEC in a mixing ratio of 100:25 by weight in MAP. A solution of a Novolak resin and EEC in MAP was spin-cast on a silicon wafer to give a thin film, which was covered with a thin film consisting of polystyrene, TMB as a PAG and **1** in a ratio of 100:3.6:0.1–10 by weight by spin-coating of a toluene solution of the components.

Table 1 Properties of polymers employed in this study

| Polymer | $M_w \times 10^{-5}$ | $M_w/M_n$ | $T_g$/°C |
|---|---|---|---|
| PBOCST | 1.2 | 1.6 | 121 |
| PCOCST | 0.41 | 4.9 | 107 |
| Novolak resin | | | 72 |
| PHPS | 5.5 | 2.4 | 100 |
| Polystyrene | 2.8 | — | 100 |

### Physical measurements

Film thickness was measured with a DEKTAK$^3$ST (ULVAC Japan), whereas IR spectra were taken on a JASCO FT/IR-300. Photoirradiation was carried out by a San-ei Supercure-202S Hg–Xe lamp.

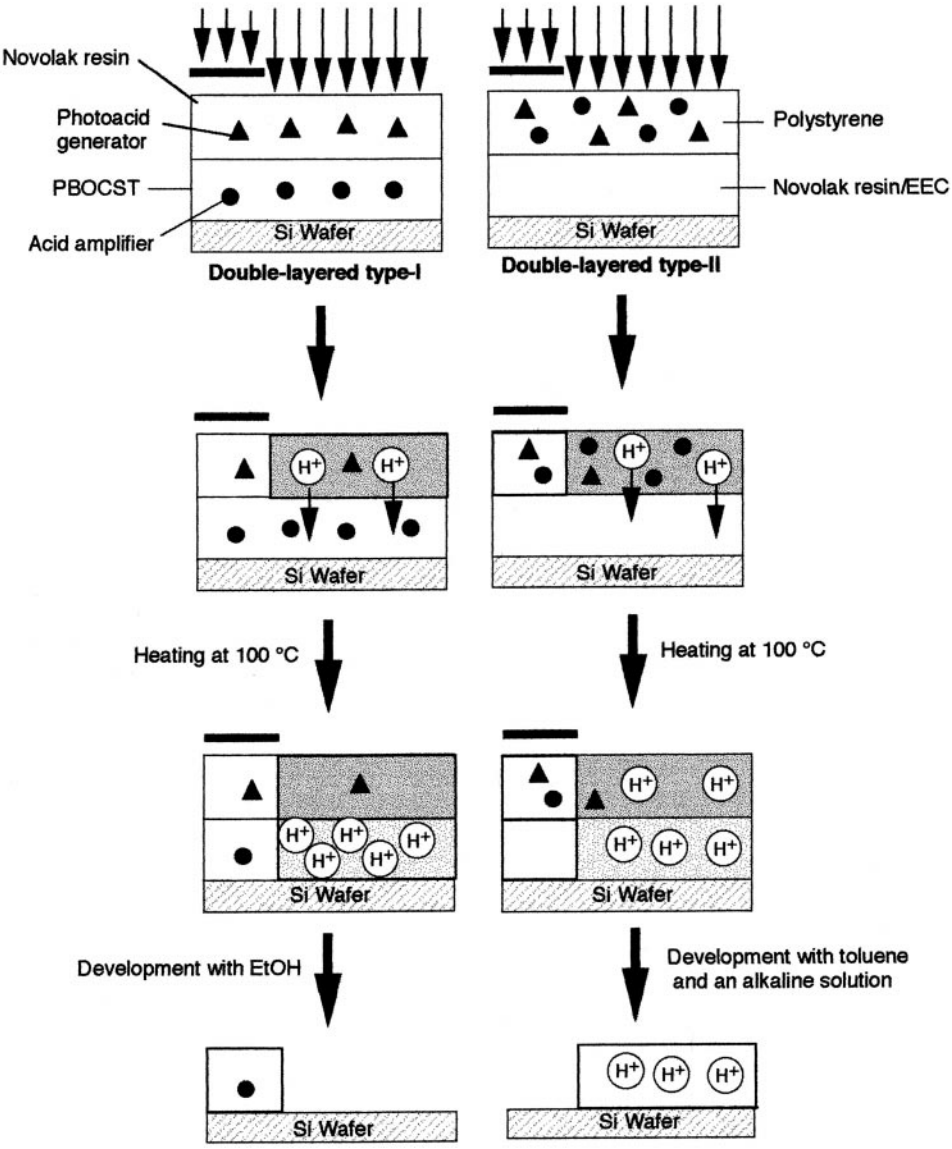
### Photosensitivity determination

**Single-layered type.** A spin-cast film on a silicon wafer was exposed to 313 nm light from a San-ei Supercure-202S Hg–Xe lamp through a combination of color filters (UV-33 and UV-D35, Toshiba) and a quartz cell filled with an aqueous alkaline $K_2CrO_4$ solution. Subsequently, the film was baked at 100 °C for a few min on a hot stage, dipped in a developing solvent and followed by measurement of the residual film thickness to give photosensitivity curves. The conditions for the photosensitivity determination are listed in Table 2.

**Double-layered type-I.** A solution of PBOCST containing **1** was spin-coated on a silicon wafer and pre-baked at 100 °C for 1 min to give a 0.27 μm-thick film. Subsequently, a solution of Novolak resin containing TPS-Tf was spin-cast on the film and pre-baked at 100 °C for 1 min to give a 0.35 μm-thick film. Total thickness of the double-layered type-I was 0.62 μm. The layer was irradiated with a Hg–Xe lamp without any filter, baked at 100 °C on a hot plate and developed under the conditions described in Table 2. Residual film thickness was measured to give photosensitivity curves.

Table 2 Conditions for the evaluation of photosensitivity

| Base polymer | Length of pre-bake at 100 °C/min | Length of post-bake at 100 °C/min | Developer |
|---|---|---|---|
| PBOCST | 1 | 6 | 3 wt% TMAH |
| PCOCST | 1 | 6 | Toluene |
| PHPS | 1 | 6 | Propan-2-ol |
| Novolak resin | 1 | 5 | 4 wt% TMAH |
| Double-layered type-I | 1 | 8 | Ethanol |
| Double-layered type-II | 1 | 5 | Toluene, followed by 3 wt% TMAH |



**Scheme 2** Imaging processes of double-layered systems.

**Double-layered type-II.** A solution containing Novolak resin and EEC as a crosslinking reagent was spin-coated on a silicon wafer, followed by pre-baking at 100 °C for 1 min to give a 0.24 µm-thick film. A solution of polystyrene, TMB and **1** was spin-coated on the film and pre-baked at 100 °C for 1 min to give a 0.50 µm-thick film. Total film thickness of double-layered type-II was 0.74 µm. The layer was irradiated in a way similar to the double-layered type-I. The conditions for the photosensitivity determination are described in Table 2.

## Results

### Single-layered films

In order to reveal the effect of an acid amplifier on photosensitivity characteristics, thin films of conventional CA photoresists were exposed to UV light in the absence or in the presence of the acid amplifier **1**. PBOCST, PCOCST, PHPS and Novolak resin were employed as a base resin in this work, taking notice of the followings. PBOCST has been extensively applied to CA photoresists, so that the comparison of the present work with reported results is conveniently achieved. PCOCST possesses cyclohexyloxycarbonyl (c-HOC) residues exhibiting a slower rate of acidolytic deprotection when compared with t-Boc of PBOCST. Our motivation was based on the anticipation that the effect of **1** may be more remarkable in PCOCST films than in PBOCST films. This is because the autocatalytic fragmentation of **1** may occur much faster than the deprotection of c-HOC in the presence of DPS-$SbF_6$. PHPS was used because of the fact that both acidolytic reactions, which are the acidolytic reaction of a polymer and the acid proliferation reaction of **1**, can be traced separately by monitoring the IR absorption bands of OH for PHPS and of C=O for **1**, respectively. Novolak resin doped with EEC was employed to gain information about the effect of photocrosslinking on photosensitivity of negative-working photoresists because the diffusion process of catalytic acidic species plays a crucial role in acid proliferation reaction in polymer solids. The compound **1** was used here as an acid amplifier because of the reasonable thermal stability and the capability to liberate a strong acid.[4b]

The evaluation of the additive effect of **1** on the photosensitivity characteristics was performed for CA photoresists derived from the above polymers containing DPS-$SbF_6$ as a PAG. Thin films of the photoresist were illuminated with 313 nm light and developed with an appropriate developer after post-exposure baking. Fig. 1 shows photosensitivity curves of the PBOCST films. A film in the absence of **1** was completely soluble at an exposure dose of 8.4 mJ $cm^{-2}$. This situation was not much modified by the addition of 0.1 wt% of **1**. The addition of 1 wt% of **1** resulted in the reduction of

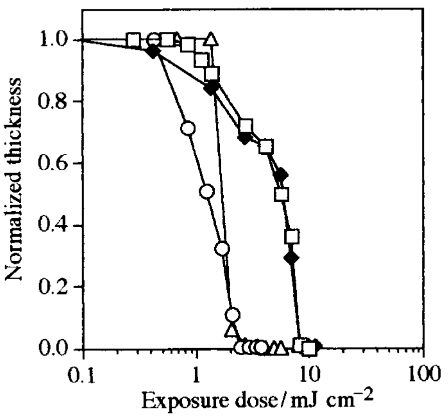


**Fig. 1** Photosensitivity curves of films of PBOCST containing 5.5 wt% of DPS-SbF$_6$ as a photoacid generator in the absence (□) and in the presence of 0.1 wt% (◆), 1 wt% (○) and 10 wt% (△) of **1**.

exposure doses down to 2.5 mJ cm$^{-2}$, which was required for the thorough dissolution of the film in an alkaline solution. A 10 wt% loading of **1** gave rise to no further reduction of the minimum exposure dose needed for the dissolution of a film, though the contrast defined as the gradient of the photosensitivity curve was markedly enhanced by a factor of 4. This situation did not change when TPS-Tf[14] or TMB[13] was used as a PAG instead of DPS-SbF$_6$. This means that the additive effect of **1** on the photosensitivity enhancement is independent of the kind of PAGs. The addition of **1** to the other polymer films also resulted in the significant enhancement of the contrast, whereas photosensitivity was not much improved, as in the PBOCST system. These results are summarized in Table 3.

In order to follow the acidolytic reaction of a polymer and the acid proliferation reaction of **1** in polymer films, a thin film of PHPS containing 7.5 wt% of DPS-SbF$_6$ and 13 wt% of **1** was spin-coated on a silicon wafer, followed by pre-baking at 100 °C to be subjected to IR absorption spectral measurements. The film was irradiated with 313 nm light of a 9.7 mJ cm$^{-2}$ dose and post-baked at 100 °C. IR spectra of a photoirradiated PHPS film were recorded before and after post-exposure baking. On prolonged heating, the broad absorption band at *ca.* 3400 cm$^{-1}$ due to alcoholic OH disappeared abruptly, supporting the acidolytic dehydration of the tertiary alcohol residues. On the other hand, the disappearance of $\nu_{C=O}$ due to the ester group of **1** at 1719 cm$^{-1}$ occurred slowly. This situation is visualized by plotting peak areas of $\nu_{OH}$ of PHPS and $\nu_{C=O}$ of **1** as a function of heating period. As seen in Fig. 2, the acid-catalyzed dehydration of PHPS is completed within 50 s, whereas the acid-catalyzed decomposition of **1** is accomplished after *ca.* 300 s. This means that the acidolytic dehydration of tertiary alcohol residues of PHPS takes place much faster than the acid-catalyzed decomposition of **1**.

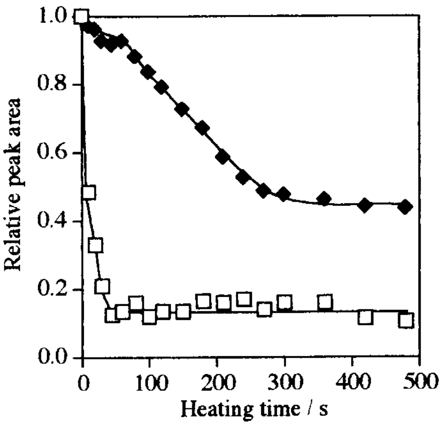


**Fig. 2** Time courses of the consumption of 13 wt% of **1** (◆) and dehydration of PHPS (□) in a film.

## Double-layered films

As described above, the addition of **1** to CA photoresists results in low levels of photosensitivity enhancement. The following two possibilities should be considered. One of these is the suppression of diffusion of photogenerated acidic molecules in a polymer film. If the diffusion range of photogenerated acids is too small, the acid proliferation reaction of **1** is not initiated effectively. The other possibility comes from the competition of two acid-catalyzed reactions; the acidolytic reaction of an acid-labile polymer and the acid proliferation reaction of **1**. If the latter proceeds more slowly than the former, essentially no acceleration of the acidolytic transformation of the polymer takes place. These considerations led us to the idea that the enhancement of photosensitivity can be achieved efficiently when photoacid generation and acid-catalyzed reaction occur in two separated polymer layers or when the acid proliferation reaction and the acidolytic reaction of an acid-labile polymer occur in two separated polymer layers. The former is to enhance the diffusion of photogenerated acids, while the latter is to avoid the competition of the two acid-catalyzed reactions.

Two types of double-layered systems were fabricated, as sketched in Scheme 2. The first one, referred to as type-I, is composed of an acid photogenerating layer and an acid-sensitive layer. The PAG and the acid amplifier are separated into two layers so that this system may involve the enhancement of diffusion of photogenerated acids induced by a concentration gradient of the acid. A lower layer was prepared by spin-coating a solution of PBOCST containing **1** on a silicon wafer. A propan-2-ol solution of Novolak resin containing TPS-Tf was spin-cast on the acid-sensitive layer. Novolak resin is employed here because of its good solubility in propan-2-ol which is a poor solvent for PBOCST, so that the mixing of two polymeric layers is minimized. An alternative double-layered film, type-II, consisting of the combination of a layer for the acid proliferation and an acid-sensitive layer was fabricated to suppress the competition of two acid-catalyzed reactions involving the acidolytic reaction of an acid-labile polymer and the acid proliferation reaction of **1**. A solution of Novolak resin and the crosslinking reagent, EEC, was spin-cast on a silicon wafer to form a lower layer, followed by spin-coating of a toluene solution of polystyrene (PSt) containing TMB and **1** on the first layer. Novolak resin was used here not only because of its good solubility in an alkaline solution, but also because of its high acid-crosslinkability with EEC. PSt was employed as a polymer matrix on account of the inertness to acidic species

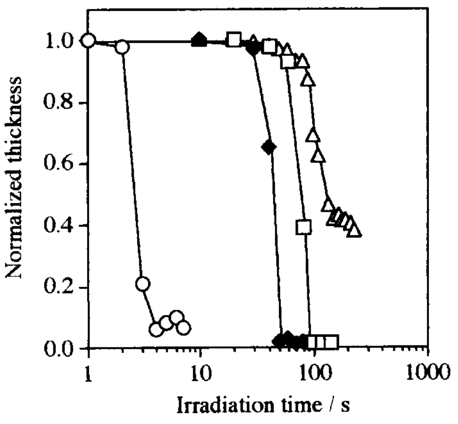


**Fig. 3** Photosensitivity curves of films of double-layered type-I containing 3.5 wt% of TPS-Tf as a photoacid generator in the presence of 0.1 wt% (□), 1 wt% (◆) and 10 wt% (○) of **1** and single-layered type containing 3.5 wt% of TPS-Tf in the absence of **1** (△).

**Table 3** Photosensitivity enhancement of CA photoresists by the acid amplifier **1**

| Base polymer | Conc. of **1** (wt%) | Sensitivity[c] /mJ cm$^{-2}$ | γ-Value | Remarks |
|---|---|---|---|---|
| PBOCST[a] | 0 | 8.4 | 1.9 | Fig. 1 |
| | 0.1 | 8.4 | 1.9 | Fig. 1 |
| | 1 | 2.5 | 1.5 | Fig. 1 |
| | 10 | 2.1 | 6.7 | Fig. 1 |
| PCOCST[b] | 0 | 24 | 1.7 | — |
| | 0.1 | 22 | 1.7 | — |
| | 1 | 14 | 5.0 | — |
| | 10 | 14 | 5.0 | — |
| PHPS[b] | 0 | 0.62 | 2.3 | — |
| | 0.13 | 0.56 | 2.3 | — |
| | 1.3 | 0.45 | 1.7 | — |
| | 13 | 0.40 | 1.4 | — |
| Novolak resin[b] | 0 | 2.6 | 1.6 | — |
| | 0.1 | 2.2 | 1.3 | — |
| | 1 | 1.4 | 1.5 | — |
| | 10 | 1.8 | 3.6 | — |

[a]Positive-working. [b]Though phenolic hydroxy residues of the polymer were formed, the alkaline development failed in this case, so that the exposed films were developed with toluene and evaluated as a negative-working photoresist. [c]Sensitivity is defined as the exposure dose required for the complete dissolution for a positive-working photoresist and as the exposure dose required for the reduction of normalized film thickness by half for a negative-working photoresist.

and the good solubility in toluene which is a poor solvent for Novolak resin, so that the mixing of two polymeric layers is minimized. TMB was used as a nonionic PAG on account of the good solubility in toluene as a casting solvent for the second layer. Photoimaging procedures of both systems are illustrated in Scheme 2.

The double-layered type-I provides a positive-working photoresist due to the deprotection of PBOCST. After imagewise exposure to UV light to generate an acidic species, the double-layered film was heated at 100 °C to cause the diffusion of acidic molecules generated in the upper layer into the lower layer of PBOCST containing **1**. Development was made by using ethanol because both Novolak resin and deprotected PBOCST dissolve in the alcoholic solvent. Photosensitivity curves of the type-I systems are shown in Fig. 3. The addition of **1** gave rise to considerable improvement of photosensitivity when compared with a single-layered PBOCST film. A double-layered film containing 10 wt% of **1** exhibits about 50 times as high a photosensitivity as a single-layered PBOCST film which is a conventional CA photoresist material, as listed in Table 4.

**Table 4** Photosensitivity enhancement of double-layered systems by **1**

| Base polymer | Conc. of **1** (wt%) | Sensitivity[c] /s | γ-Value | Remarks |
|---|---|---|---|---|
| Double-layered type-I[a] | 0 (single-layered) | 200[d] | 2.5 | Fig. 3 |
| | 0.1 | 100 | 5.0 | Fig. 3 |
| | 1 | 50 | 5.0 | Fig. 3 |
| | 10 | 4[d] | 3.3 | Fig. 3 |
| Double-layered type-II[b] | 0 (single-layered) | 82 | 2.5 | Fig. 4 |
| | 0 | 50 | 5.0 | Fig. 4 |
| | 0.1 | 39 | 5.0 | Fig. 4 |
| | 1 | 7 | 1.0 | Fig. 4 |
| | 10 | 5 | 1.0 | Fig. 4 |

[a]Positive-working. [b]Negative-working. [c]Sensitivity is defined as the irradiation time required for the complete dissolution for a positive-working photoresist and as the irradiation time required for the reduction of normalized film thickness by half for a negative-working photoresist. [d]Irradiation time is estimated by extrapolation.

The double-layered type-II provides a negative-working photoresist owing to cationic crosslinking of EEC (Scheme 2). A double-layered film was exposed to UV light to generate acidic species in the upper PSt layer and subsequently subjected to post-exposure baking to accelerate both the acid proliferation in the upper PSt layer and the diffusion of acid molecules into the lower Novolak layer to result in acid-catalyzed crosslinking of the Novolak resin. Development was made by rinsing with toluene to remove the PSt layer and subsequently with an alkaline solution to dissolve Novolak resin. Photosensitivity curves of the double-layered type-II are presented in Fig. 4. The addition of **1** to the type-II also resulted in considerable improvement of photosensitivity even in the presence of 1 wt% of **1**. The negative-working double-layered system containing **1** shows 16 times as high a photosensitivity as a single-layered type without the acid amplifier, as summarized in Table 4.

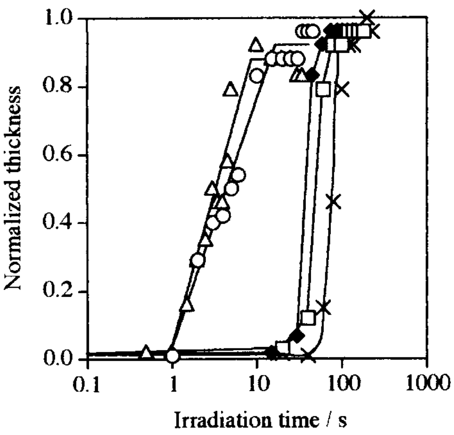


**Fig. 4** Photosensitivity curves of films of double-layered type-II containing 3.6 wt% of TMB as a photoacid generator in the absence (□) and in the presence of 0.1 wt% (◆), 1 wt% (○) and 10 wt% (△) of **1** and single-layered type containing 3.6 wt% of TMB as a photoacid generator in the absence of **1** (×).

## Discussion

Despite of our expectation that the addition of **1** to CA photoresists brings about a marked acceleration of acidolytic reactions of polymers, the improvement of photosensitivity is not so remarkable. The following two possibilities should be considered.

The first possibility is the suppression of the acid diffusion in a polymer film due to the homogeneously distributed photogenerated acidic species in irradiated areas of a photosensitive polymer film. It is well known that the driving force for the diffusion of molecules in solid matrices is due to the gradient of their concentration. If the acid diffusion is suppressed, the acid proliferation reaction of **1** can not proceed effectively in a polymer film. This assumption was proved to be reasonable by fabricating a novel double-layered system, type-I, which provides positive-working photoresist (Scheme 2). The addition of **1** to the system resulted in the marked enhancement of photosensitivity as shown in Table 4. In this system, the photoacid generation is performed in a layer which contains no acid-sensitive substance, so that photoimage formation requires efficient diffusion of photogenerated acidic species into the acid-sensitive layer upon post-exposure baking. There have been reports on the diffusion behavior of acidic molecules in polymer solids in conjunction with the elucidation of working mechanism of CA photoresists on the basis of Fick's law. For example, diffusion lengths of photogenerated acids in single-layered films of partially blocked poly[*p*-(vinyl)phenol] are estimated to be 23 nm for toluene-*p*-sulfonic acid and 46 nm for trifluoromethanesulfonic acid upon heating at 90 °C for 1 min, respectively.[15] On the other hand, the diffusion range of acid species photogenerated in a Novolak resin film into another fresh acid-labile polymer film is markedly influenced by the size of acidic species and comes to 500 nm for methanesulfonic acid upon heating at 100 °C for 1 min.[16] This value is one order of magnitude greater than the diffusion length in a single-layered film. In other words, the diffusion of acidic species is much accelerated in a double-layered film because of the difference in acid concentration between two layers. This situation suggests that the marked improvement of photosensitivity observed in the type-I photosensitive system arises essentially from the double-layered structure, leading to the enhancement of diffusion of photogenerated acid molecules. As a result, the acid proliferation reaction of **1** takes place more effectively in the acid-sensitive layer. This consideration has led us to the assumption that the reason why the single-layered system exhibits no marked improvement of photosensitivity even in the presence of **1** stems from the homogeneously distributed photogenerated acidic species in the polymer layer.

The second possibility is that acid species are captured by some kinds of proton acceptors embedded in polymer matrices. As discussed in the previous paper, solvent molecules having proton acceptor site(s) such as dioxane and methanol suppress critically the autocatalytic fragmentation of **1**.[4b] In PBOCST and PCOCST films, there are many trapping sites capable of protonation by strong acids, including alkoxycarbonyloxy side chains and even phenolic OH groups as deprotected residues. A pronounced example supporting this assumption is the Novolak resin–EEC system. The acid amplifier **1** does not bring about marked enhancement of photosensitivity of this kind of negative-working photoresist. This system involves trapping sites such as epoxides, aliphatic OH, ether, ester and phenolic OH residues. In particular, oxygen atoms of aliphatic ethers and aliphatic OH act as an effective quencher because the $\mathrm{p}K_\mathrm{a}$ of a conjugated acid of ether is *ca.* −3.59[17] and that of an aliphatic OH is *ca.* −2.1,[18] whereas ester groups have a $\mathrm{p}K_\mathrm{a}$ of the order of *ca.* −6.0.[19]

Concerning the effect of the basicity of polymer residues in acid proliferation reactions, IR spectral measurements of the PHPS system gave us novel information. As presented in Fig. 2, the dehydration of the polymer and the disappearance of **1** are both monitored by following the corresponding characteristic absorption bands. In this system, the addition of **1** gives rise to no improvement of photosensitivity although acid proliferation seems to occur, as being judged from the appearance of a sigmoidal time conversion curve of the decomposition of **1**. Unequivocally, no addition effect of **1** arises from the fact that the dehydration reaction of tertiary alcohol residues of PHPS proceeds much faster than the acid-catalyzed decomposition of **1** to result in the acid proliferation. That is, the dehydration rate of tertiary alcohol of PHPS is far larger than the rate of acid-catalyzed decomposition of **1**, so that the additive effect of **1** is completely hidden. This is because of a large difference (about 4 pH units) in $\mathrm{p}K_\mathrm{a}$ values of conjugated acids between the OH groups of the polymer and ester groups of **1**. Though there is no data on the basicity of carbonate residues, it is safe to say that the basicity of the carbonate residues of acid-labile PBOCST is somewhat stronger than that of the ester group of **1** because of the electron-donating effect of an oxygen atom in the carbonate group. It follows that the deprotection of PBOCST takes place relatively faster than the dealkylation of **1**. This is the reason why the improvement of photosensitivity is observed in this system though the extent of the improvement is not so large.

These considerations concerning the second assumption are proved to be reasonable by the fabrication of a novel double-layered system, type-II, which provides a negative-working photoresist (Scheme 2). The addition of **1** to the system gave rise to a marked improvement in photosensitivity as shown in Table 4. In this system, the enhancement of photosensitivity reflects directly the autocatalytic decomposition of **1** which occurs efficiently in a PSt film because the polymer has no trapping site of strong acids. That is to say, this system can avoid the competition of two acid-catalyzed reactions; the acidolytic reaction of an acid-labile polymer and the acid proliferation reaction of **1**. The high photosensitivity of this system is also thanks to the accelerated diffusion of photogenerated and proliferated acid molecules into the acid-sensitive layer in a way similar to the type-I system.

These double-layered materials, type-I and type-II, provide novel photopolymer systems exhibiting remarkably high photosensitivity and have potential values for practical applications though the resolution power should be reduced because of the involvement of the diffusion process of catalytic acids.

In addition, it should be mentioned that the addition of **1** to single-layered systems, PBOCST, PCOCST and Novolak resin–EEC systems, results in a marked improvement in the contrast which is usually defined as the gradient of the photosensitivity curve. This is a bonus for the application of the present system to microphotolithography. In fact, it has been recently disclosed that the other type of an acid amplifier, *cis*-1-phenyl-1-hydroxy-2-*p*-tosyloxycyclohexane, displays a remarkable improvement of profiles of a photopatterned CA photoresist which is subjected to 193 nm lithography.[20] The appearance of T-topping is suppressed so that the resolution is much increased. This is probably due to non-linear increase of acidic species as a result of the acid proliferation reaction.

## Conclusion

The acid proliferation reaction of **1** was thoroughly investigated in positive- and negative-working CA photoresists. The addition of **1** to the photoresists resulted in marked improvement of contrast whereas the photosensitivity was not much improved for both types of photoresists. The suppression of additive effect of **1** on the photosensitivity results from the two following factors. First, the diffusion of photogenerated acidic species occurs less effectively because acid molecules are homogeneously distributed in photoirradiated areas. Second, it is due to the retardation of the acid proliferation reaction since acidic species are trapped at basic sites embedded in polymer solids. To overcome these problems, we have proposed novel types of CA photopolymer systems consisting of two layers, which are double-layered type-I and type-II. Type-I is composed of an acid photogenerating layer and an acid-sensitive layer, while type-II is composed of an acid proliferation layer and an acid-sensitive layer. Both double-layered systems, exhibiting much improved photosensitivity, were developed by an appropriate choice of acid-labile polymers and by the addition of **1**. The photosensitivity of these types of materials is one order magnitude greater than that of conventional CA photoresists.

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