Positive-Working DUV Resist Based on Terpene Derivatives as Cross-linker

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1. Introduction
A chemically amplified positive working resist used for processing of the Large Scale Integrated circuit of semiconductor devices has been demanded high sensitivity and high resolution. After the concept of chemically amplified resist was proposed [1-2], positive working resist using protecting group such as t-butoxycarbonyl, tetrahydropyranyl or alkoxyethyl is main current in microlithography [3-4]. Yamaoka and co-workers have been studying cross-linking type positive working resist using vinyl ether cross-linker [5-11]. Thermal cross-linking reaction between polymer and vinyl ether cross-linker can make acetal bonding. The acetal bond is easily de-cross-linked by photochemically-generated acid. This positive working resist with vinyl ether cross-linker has a high sensitivity. Furthermore, the vinyl ether cross-linker can be freely used in any polymer which has carboxyl group or phenol group, for example, novolak resign, poly(p-hydroxy styrene), poly(acrylic acid) and so forth.

Chemically amplified resist using acid-catalyzed reaction needs acid diffusion in exposed area for achievement of high sensitivity. However, the acid diffusion from exposed area to un-exposed area give a problem for high resolution. The cross-linked structure between polymer and vinyl ether cross-linker is expected to control the acid diffusion.

Vinyl ether cross-linker with 4,4'-isopropylidenebisbenzenol structure has been used so far, however, this type has a big problem in the view of the pollution of the environment. Therefore, we tried here to introduce terpene structure to vinyl ether cross-linker. Terpene is a natural product which is extracted from plants.

In this paper, we investigate that a new type of vinyl ether cross-linker using terpene derivatives and the application to the photolithography materials.

2. Experimental
2.1. Materials
Terpene derivatives, 4-isopropyl-1-methyl-1,3-bis[4-(2-vinyloxyethoxy)phenyl]cyclohexane (BPT-DEVE) and 4-isopropyl-1-methyl-1,3-bis[4-(2-vinyloxyethoxy)cyclohexyl]cyclohexane (BCT-DEVE) (Fig. 1) were synthesized in this study.

Fig. 1. Chemical structure of vinyl ether compounds

These were readily synthesized by the reaction of 1,3-bis(4-hydroxyphenyl)-4-isopropyl-1-methylec lohexane or 1,3-bis(4-hydroxy cyclohexyl)-4-isopropyl-1-methylecloc hexane with 2-chloroethyl vinyl ether in dimethyl sulfoxide (DMSO) [12].

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Poly(tricyclodecyl acrylate-co-methacrylic acid) was synthesized as a base polymer. (Mw: 16000, Mw/Mn: 1.65) Triphenylsulfonium trifluoromethanesulfonate (TPS-OTf) was obtained from Midori Chemicals Co. 2,2-bis(4-(2-vinylxyetoxy)phenyl)propane (BPA-DEVE) was synthesized according to our previous paper. Poly(methyl methacrylate) was purchased from Aldrich Chemical Company, Inc. Poly(vinylalcohol) (PVA; 80% saponified) and novolak resin for measurement of acid diffusion was obtained from Nippon Synthetic Chemical Industry Co., Ltd. and Daicel Chemical Industries Ltd., respectively.

3. Results and Discussion
3.1. Cross-linking and De-cross-linking reaction in film
It is known that vinyl ether compound reacts easily with phenol or carboxyl group of polymer by heating. Thus, an acetal structure is made between hydroxyl group of polymer and vinyl group of vinyl ether compound. The dissolution rate in an alkaline aqueous solution is decreased with the increase of molecular weight and change of polarity.

Upon the exposure and post-exposure baking (PEB), generated acid from photo-acid generator (PAG) and subsequent heating cut off the acetal bonding. As a result, dissolution rate in exposed area is increased. In this exposed area came terpolymer structure before pre-bake (PB) and decomposition compounds such as alcohol compound and aldehyde are formed and the polarity is changed. This thermal cross-linking and acid-catalyzed de-cross-linking reaction is depicted in Fig. 2.

![Fig. 2. Concept of thermal cross-linking and acid-catalyzed de-cross-linking reaction in film.](image)

Fig. 3 shows differential IR spectra of poly(TCDA-co-MAA) with BPT-DEVE and TPS-OTf on NaCl plate. As shown in Fig. 3 (a), upon PB the peaks of carboxyl group of polymer at 3500 cm\(^{-1}\) and vinyl group of vinyl ether cross-linker at 1616 cm\(^{-1}\) were decreased. As well, the peaks at 1039 cm\(^{-1}\) and 1134 cm\(^{-1}\) of acetal bond appeared.

After exposure of the film to 254 nm light and followed by PEB, the peaks of acetal bond are reduced as show in Fig. 3 (b). The -OH group of polymer at 3500 cm\(^{-1}\) was increased. It suggests that de-cross-link took place between polymer and cross-linker. This change of IR spectra consistent with the concept of Fig. 2.

3.2. VUV-UV absorption spectra of vinyl ether cross-linkers
Fig. 4 shows VUV-UV absorption spectra of poly(methyl methacrylate) (PMMA) containing vinyl ether cross-linkers. BPA-DEVE and BPT-DEVE have a low absorption in DUV region. Therefore, BPT-DEVE can use vinyl ether cross-linkers as DUV lithography material.

Materials of photoresist for VUV lithography are restricted with structure of compound from strong absorption of benzene at the region. BPT-DEVE has a low absorption in 248 nm such as poly(p-hydroxystyrene) but has a strong absorption in 193 nm. However, BCT-DEVE in which cyclohexyl group replaces benzene ring shows high transparency. From this results, BCT-DEVE is possible to apply to VUV lithography.
3.3. DUV lithography Evaluation

Photopolymer solutions composed of poly(TCDA-co-MAA) and 25 wt% vinyl ether cross-linker (BPT-DEVE or BCT-DEVE) and 3.0 wt% PAG relative to the polymer were spin-coated on Si-wafer to give a 1 µm thick film. The films were PB at 120 °C for 20 min and exposed with the low pressure mercury lamp. PEB was carried out at 100 °C for 5 min and developed in a 2.38 wt% tetramethyl ammonium hydroxide (TMAH) solution.

Fig. 5 shows the sensitivity curves of the resist. BPT-DEVE and BCT-DEVE containing photoresists demonstrated high sensitivity of 1.6 and 1.28 mJ/cm² by irradiation of 254 nm light, respectively.

3.4. Relationship between cross-linking and acid diffusion.

We investigated acid diffusion by change of cross-linking ratio using bilayer method [13].

Fig. 7 shows normalized film thickness of novolak resin with various weight ratio of BPT-DEVE after development. From difference before and after diffusion of acid, distance of diffusion can be compare. Films containing small amount of vinyl ether cross-linker have swelling.
but have not film decrease in aqueous solution. With increase of vinyl ether cross-linker, distance of acid diffusion decreased. This results indicate that making cross-link structure of polymer can control diffusion of acid in film.

4. Conclusion
We synthesized BPT-DEVE and BCT-DEVE as a novel vinyl ether cross-linkers using terpene derivatives. BPT-DEVE and BCT-DEVE works enough as a cross-linker in the positive-working resist. The positive-working resist has a high sensitivity in DUV lithography. Moreover, cross-link structure in film can controls acid diffusion. Therefore it is advantageous to high resolution. BCT-DEVE has a high transparency in VUV region. Therefore BCT-DEVE can also be applied to VUV lithography.

References