

as the quencher. Examples of the sulfonium or iodonium salt to be added as the quencher include sulfonium or iodonium salts of carboxylic acid, sulfonic acid, imide acid and saccharin. The carboxylic acid used herein may or may not be fluorinated at α -position.

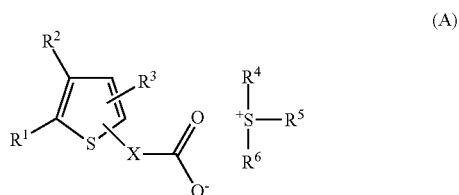
[0047] For the LWR improving purpose, it is effective to prevent a polymer and/or acid generator from agglomeration. Effective means for preventing agglomeration of a polymer is by reducing the difference between hydrophobic and hydrophilic properties or by lowering the glass transition temperature (T_g) thereof. Specifically, it is effective to reduce the polarity difference between a hydrophobic acid labile group and a hydrophilic adhesive group or to lower the T_g by using a compact adhesive group like monocyclic lactone. One effective means for preventing agglomeration of an acid generator is by introducing a substituent into the triphenylsulfonium cation. In particular, with respect to a methacrylate polymer containing an alicyclic protective group and a lactone adhesive group for ArF lithography, a triphenylsulfonium composed solely of aromatic groups has a heterogeneous structure and low compatibility. As the substituent to be introduced into triphenylsulfonium, an alicyclic group or lactone similar to those used in the base polymer is regarded adequate. When lactone is introduced in a sulfonium salt which is hydrophilic, the resulting sulfonium salt becomes too hydrophilic and thus less compatible with a polymer, with a likelihood that the sulfonium salt will agglomerate. When a hydrophobic alkyl group is introduced, the sulfonium salt may be uniformly dispersed within the resist film. WO 2011/048919 discloses the technique for improving LWR by introducing an alkyl group into a sulfonium salt capable of generating an α -fluorinated sulfone imide acid.

[0048] The dispersion of a quencher is a crucial factor for LWR improvement. Even when the dispersion of an acid generator in a resist film is improved, LWR is still low if a quencher is unevenly distributed. For a quencher of sulfonium salt type, the introduction of an alkyl or similar substituent into the triphenylsulfonium cation moiety is effective for LWR improvement.

[0049] The sulfonium salt of thiophenecarboxylic acid exerts a LWR reducing effect, which may stand good either in positive and negative tone pattern formation by alkaline development or in negative tone pattern formation by organic solvent development.

[0050] Sulfonium Salt

[0051] The sulfonium salt in the resist composition is a thiophenecarboxylic acid sulfonium salt having the formula (A).



[0052] Herein R^1 , R^2 and R^3 are each independently hydrogen, hydroxyl, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, C_2 - C_6 acyl, C_2 - C_6 alkoxycarbonyl, C_6 - C_{10} aryl, C_2 - C_{10} heteroaryl, halogen, nitro, amino, or cyano group. In these groups, at least

one (one or more or even all) hydrogen may be substituted by C_1 - C_6 alkyl, hydroxyl, halogen, nitro or amino moiety, or at least one carbon may be substituted by an ether bond or thioether bond. R^1 and R^2 may bond together to form an alicyclic or aromatic ring with the carbon atom to which they are attached, at least one (one or more or even all) hydrogen on the ring may be substituted by C_1 - C_6 alkyl, hydroxyl, halogen, nitro or amino moiety.

[0053] Suitable halogens include fluorine, chlorine, bromine and iodine. Examples of the alkyl group which may be straight, branched or cyclic include methyl, ethyl, n-propyl, isopropyl, cyclopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, cyclobutyl, n-pentyl, cyclopentyl, n-hexyl and cyclohexyl. Examples of the alkyl moiety in the alkoxy, acyl and alkoxycarbonyl groups are as exemplified just above for the alkyl group. Examples of the aryl group include phenyl, naphthyl, anthryl, and phenanthryl. Examples of the heteroaryl group include thienyl, imidazolyl, oxazolynyl, furyl, pyrrolyl, 2-pyridyl and quinolyl. Preferably, R^1 , R^2 and R^3 are selected from hydrogen, hydroxyl, halogen, C_1 - C_6 alkyl, phenyl and thienyl.

[0054] X is a single bond or a C_1 - C_{10} divalent aliphatic hydrocarbon group in which at least one (one or more or even all) hydrogen may be substituted by halogen, or at least one carbon may be substituted by an ether bond, ester bond or carbonyl moiety. The divalent aliphatic hydrocarbon groups are preferably straight or branched and examples thereof include C_1 - C_6 alkylene groups and C_2 - C_6 alkenylene groups. Preferably X is selected from a single bond, C_1 - C_4 alkylene groups, and C_2 - C_4 alkenylene groups.

[0055] R^4 , R^5 and R^6 are each independently halogen or a C_1 - C_{20} monovalent hydrocarbon group which may contain a heteroatom. Any two of R^4 , R^5 and R^6 may bond together to form a ring with the sulfur atom to which they are attached. The monovalent hydrocarbon group may be straight, branched or cyclic and examples thereof include C_1 - C_{12} alkyl groups, C_2 - C_{12} alkenyl groups, C_2 - C_{12} alkynyl groups, C_6 - C_{20} aryl groups, and C_7 - C_{12} aralkyl groups. Also included are substituted forms of the foregoing in which at least one (one or more or even all) hydrogen is substituted by hydroxyl, carboxyl, halogen, cyano, amide, nitro, mercapto, sultone, sulfone moiety or sulfonium salt-containing moiety, or in which at least one carbon is substituted by an ether bond, ester bond, carbonyl moiety, carbonate moiety or sulfonic acid ester bond.

[0056] Examples of the anion in the sulfonium salt having formula (A) are given below, but not limited thereto.

