

## POSITIVE RESIST COMPOSITION AND PATTERN FORMING PROCESS

### CROSS-REFERENCE TO RELATED APPLICATION

[0001] This non-provisional application claims priority under 35 U.S.C. § 119(a) on Patent Application No. 2018-234513 filed in Japan on Dec. 14, 2018, the entire contents of which are hereby incorporated by reference.

### TECHNICAL FIELD

[0002] This invention relates to a positive resist composition and a patterning process using the composition.

### BACKGROUND ART

[0003] To meet the demand for higher integration density and operating speed of LSIs, the effort to reduce the pattern rule is in rapid progress. The wide-spreading flash memory market and the demand for increased storage capacities drive forward the miniaturization technology. As the advanced miniaturization technology, manufacturing of microelectronic devices at the 10-nm node by the immersion ArF lithography has been implemented in a mass scale. The candidates for the next generation 7-um node devices and next-but-one generation 5-nm node devices include extreme ultraviolet (EUV) lithography of wavelength 13.5 nm and double patterning version of the ArF lithography, on which active research efforts have been made.

[0004] The exposure system for mask manufacturing made a transition from the laser beam exposure system to the EB exposure system to increase the accuracy of line width. Since a further size reduction became possible by increasing the accelerating voltage of the electron gun in the EB exposure system, the accelerating voltage increased from 10 kV to 30 kV and reached 50 kV in the current mainstream system, with a voltage of 100 kV being under investigation.

[0005] As the accelerating voltage increases, a lowering of sensitivity of resist film becomes of concern. As the accelerating voltage increases, the influence of forward scattering in a resist film becomes so reduced that the contrast of electron image writing energy is improved to ameliorate resolution and dimensional control whereas electrons can pass straightforward through the resist film so that the resist film becomes less sensitive. Since the mask exposure tool is designed for exposure by direct continuous writing, a lowering of sensitivity of resist film leads to an undesirably reduced throughput. Due to a need for higher sensitivity, chemically amplified resist compositions are studied.

[0006] As the feature size reduces, image blurs due to acid diffusion become a problem. To insure resolution for fine patterns with a size of 45 nm et seq., not only an improvement in dissolution contrast is important as previously reported, but control of acid diffusion is also important as reported in Non-Patent Document 1. Since chemically amplified resist compositions are designed such that sensitivity and contrast are enhanced by acid diffusion, an attempt to minimize acid diffusion by reducing the temperature and/or time of post-exposure bake (PEB) fails, resulting in drastic reductions of sensitivity and contrast.

[0007] A triangular tradeoff relationship among sensitivity, resolution, and edge roughness has been pointed out.

Specifically, a resolution improvement requires to suppress acid diffusion whereas a short acid diffusion distance leads to a loss of sensitivity.

[0008] The addition of an acid generator capable of generating a bulky acid is an effective means for suppressing acid diffusion. It was then proposed to incorporate in a polymer recurring units derived from an onium salt having a polymerizable unsaturated bond. Since this polymer functions as an acid generator, it is referred to as polymer-bound acid generator. Patent Document 1 discloses a sulfonium salt having a polymerizable unsaturated bond, capable of generating a specific sulfonic acid and a similar iodonium salt. Patent Document 2 discloses a sulfonium salt having a sulfonic acid anion directly attached to the backbone.

[0009] Patent Documents 3 and 4 disclose resist materials comprising a polymer comprising amino-containing recurring units. Polymeric amines are highly effective for suppressing acid diffusion. Patent Document 5 discloses a resist material based on a polymer comprising recurring units of acid generator and recurring units of amine. It is a single component resist in which both an acid generator function and a quencher function are assigned to a common polymer. However, if the acid diffusion distance is too short, there arises the problem that both dissolution contrast and sensitivity drop.

### CITATION LIST

- [0010] Patent Document 1: JP-A 2006-045311 (U.S. Pat. No. 7,482,108)
- [0011] Patent Document 2: JP-A 2006-178317
- [0012] Patent Document 3: JP-A 2008-133312
- [0013] Patent Document 4: JP-A 2009-181062
- [0014] Patent Document 5: JP-A 2011-039266
- [0015] Non-Patent Document 1: SPIE Vol. 6520 65203L-1 (2007)

### SUMMARY OF INVENTION

[0016] An object of the present invention is to provide a positive resist composition which exhibits a higher sensitivity and resolution than conventional positive resist compositions, low edge roughness (LER, LWR) and small size variation, and forms a pattern of good profile after exposure and development, and a patterning process using the resist composition.

[0017] Making extensive investigations in search for a positive resist material capable of meeting the current requirements including high resolution, low edge roughness and small size variation, the inventors have found the following. To meet the requirements, the acid diffusion distance should be minimized. This invites a lowering of sensitivity and a drop of dissolution contrast, raising the problem that the resolution of a two-dimensional pattern such as hole pattern is reduced. Unexpectedly, when a polymer comprising recurring units of nitrogen-containing tertiary ester structure is used as a base polymer, the dissolution contrast is increased and at the same time, the acid diffusion distance is minimized. Better results are obtainable using the polymer as a base polymer in a chemically amplified positive resist composition.

[0018] Further, for improving the dissolution contrast, recurring units having a carboxyl or phenolic hydroxyl group in which the hydrogen is substituted by an acid labile group are incorporated into the base polymer. There is