alkyl groups of R^1, R^2, R^3, and R^4 have carbon number from 2 to 16 (preferably from 2 to 8, and more preferably from 2 to 4), and R^1, R^2, R^3, and R^4 are not all the same alkyl group.

[0014]

When the photoresist developer contains the quaternary ammonium ion represented by Formula (1), a better pattern shape is likely to be obtained than when an aqueous tetramethylammonium hydroxide solution is used as a photoresist developer. The reason why the good pattern shape is obtained is not clear, but the present inventors assume as follows.

[0015]

In photolithography using a photoresist developer, a photoresist layer provided on a substrate is irradiated with light through a photomask having a predetermined pattern to be exposed. At this time, the photoresist included in the exposed region of the exposed photoresist layer undergoes a chemical reaction by the light. On the other hand, the photoresist contained in the unexposed region of the photoresist layer does not undergo a chemical reaction. The reactivity, solubility in a solvent, and the like change between the photoresist that has undergone a chemical reaction and the photoresist that has not undergone a chemical reaction, whereby the developability changes. Then, the exposed photoresist layer is developed using a photoresist developer, thereby forming a resist pattern corresponding to the photomask.

In this way, the photoresist contained in the exposed region is chemically reacted by the light. However, this chemical reaction is less likely to proceed near the boundary of the photomask than near the center of the photomask. Thus, for example, when the photoresist is a positive photoresist, the photoresist near the boundary of the photomask does not have sufficient solubility in a developer, and a residue remains on the substrate, resulting in a defective pattern shape.

[0016]

On the other hand, in the quaternary ammonium ion represented by the above Formula (1), R^1, R^2, R^3, and R^4 are each independently an alkyl group having carbon number from 1 to 16, R^1, R^2, R^3, and R^4 are not all the same alkyl group, and the carbon number of one or more alkyl groups of R^1, R^2, R^3, and R^4 is from 2 to 16. Thus, the quaternary ammonium ion has an asymmetric shape with respect to the nitrogen atom as the center, and at least one alkyl group is an alkyl group having carbon number from 2 to 16. Accordingly, in the quaternary ammonium ion represented by Formula (1), an alkyl group having a long carbon chain becomes lipophilic. As a result, for example, in a case where the photoresist is a positive photoresist, the affinity for a portion where a chemical reaction due to exposure is unlikely to proceed is increased. This improves the contact between the developer and the photoresist, and even the photoresist near the boundary of the photomask where the chemical reaction has not sufficiently proceeded can be sufficiently dissolved, including the influence of the affinity to the developer in terms of polarity.

As a result, the residue at the time of development is less likely to remain, which makes it possible to obtain a good pattern shape.

filled in a container or transported, the influence of contamination can be reduced by the extent of dilution, as compared with a case where the dilution is not performed.

The concentration of the hydroxide of the quaternary ammonium ion represented by Formula (1) in the high-concentration photoresist developer before dilution is preferably from 10.0 to 50.0 mass%, and more preferably from 20.0 to 40.0 mass%. The concentration of the quaternary ammonium hydroxide can be confirmed by neutralization titration with an acid or the like.

[0030]

The concentration of the quaternary ammonium ion represented by Formula (1) in the photoresist developer is preferably from 0.8 to 52.9 mass%. In addition, the concentration is more preferably from 0.8 to 8.2 mass%, and still more preferably from 0.8 to 5.7 mass%.

The concentration of the quaternary ammonium ion represented by Formula (1) in the high-concentration photoresist developer is preferably from 8.0 to 40.7 mass%, and more preferably from 16.2 to 32.5 mass%.

The concentration of the hydroxide ion in the photoresist developer is preferably from 0.15 to 12.2 mass%. In addition, the concentration is more preferably from 0.15 to 1.9 mass%, and still more preferably from 0.15 to 1.3 mass%.

The concentration of the hydroxide ion in the high-concentration photoresist developer is preferably from 1.9 to 9.4 mass%, and more preferably from 3.7 to 7.5 mass%.

[0031]

The photoresist developer contains water. A form of water is not particularly limited. Known water can optionally be used, and it is particularly preferable that the water be ultrapure water in which metal impurities are decreased. The content of water in the photoresist developer is not particularly limited, but is preferably from 90.0 to 99.0 mass%, more preferably from 93.0 to 99.0 mass%, and still more preferably from 95.5 to 99.0 mass%.

[0032]

The photoresist developer can contain one or more compounds selected from the group consisting of an alcohol and an amine. A concentration of the one or more compounds selected from the group consisting of an alcohol and an amine in the photoresist developer is not particularly limited, but is preferably from 0.1 to 10000 mass ppm, and more preferably from 0.1 to 100 mass ppm.

The alcohol is not particularly limited, and a known alcohol can be used. Examples of the alcohol include primary alcohols such as methanol, ethanol, and 1-propanol, secondary alcohols such as 2-propanol and 2-butanol, and tertiary alcohols such as 2-methyl-2-propanol. The number of hydroxyl groups in the alcohol is not particularly limited, and a monohydric alcohol can be used, or a dihydric or higher alcohol can be used. Among them, an alcohol having carbon number of 16 or less (more preferably carbon number from 2 to 8, and still more preferably carbon number from 2 to 4) is preferred from the viewpoint of increasing the possibility of causing adsorption inhibition or the like during development when the alcohol has a long chain.

[0041]

The concentration of a tetramethylammonium ion in the photoresist developer is not particularly limited, and a photoresist developer containing tetramethylammonium hydroxide at a concentration of from 1.0 to 30.0 mass% is preferably manufactured. For example, the tetramethylammonium hydroxide is more preferably used at a concentration of from 0.1 to 5.0 mass%, and is still more preferably used at a concentration of from 0.5 to 3.0 mass%.

The tetramethylammonium hydroxide is preferably used at a molarity of from 0.01 to 0.55 mol/L, is more preferably used at a molarity of from 0.05 to 0.33 mol/L, and is still more preferably used at a molarity of from 0.1 to 0.27 mol/L.

[0042]

The concentration of the tetramethylammonium ion in the photoresist developer is preferably from 0.08 to 4.0 mass%. In addition, the concentration is more preferably from 0.4 to 2.4 mass%, and still more preferably from 0.8 to 2.0 mass%.

[0043]

The total concentration of the tetramethylammonium ion and the quaternary ammonium ion represented by Formula (1) in the photoresist developer is preferably from 0.5 to 6.0 mass%. In addition, the total concentration is more preferably from 1.0 to 5.0 mass%, and still more preferably from 1.2 to 4.0 mass%.

The total concentration of tetramethylammonium hydroxide and the hydroxide of the quaternary ammonium ion represented by Formula (1) in the photoresist developer is preferably from 0.4 to 5.0 mass%. In addition, the total concentration is more preferably from 0.8 to 4.0 mass%, and still more preferably from 1.0 to 3.2 mass%.

The total concentration of the tetramethylammonium ion and the quaternary ammonium ion represented by Formula (1) in the high-concentration photoresist developer is preferably from 10.0 to 50.0 mass%. In addition, the total concentration is more preferably from 15.0 to 40.0 mass%, and still more preferably from 20.0 to 30.0 mass%.

[0044]

As described above, the quaternary ammonium ion represented by Formula (1) is considered to also serve as a surfactant. As a result, the photoresist developer has a lower surface tension than that of an aqueous tetramethylammonium hydroxide solution. As a result, the wettability to the photoresist during development is likely to be improved. Also in a case where the photoresist developer contains a tetramethylammonium ion, the surface tension is lowered as compared with the aqueous tetramethylammonium hydroxide solution, which improves the development characteristics.

The surface tension is measured with a surface tensiometer DY-300 (available from Kyowa Interface Science Co., Ltd). The surface tension of the photoresist developer at 25°C is preferably 73.0 mN/m or less, more preferably 72.0 mN/m or less, and still more preferably 71.0 mN/m or less. The measurement is performed in accordance with “Test Method by Wilhelmy Surface Tensiometer” of JIS K 2241.

nm. Subsequently, the resist layer was irradiated with ArF excimer laser light (193 nm) using an ArF exposure apparatus through a mask pattern (1:1 line-and-space of line width of 100 nm). Thereafter, the resist layer was subjected to a heating treatment (post-exposure bake: PEB) at 130°C for 90 seconds. Subsequently, the resist film was subjected to puddle development for 20 seconds with an aqueous solution of quaternary ammonium hydroxide having a concentration shown in Table 1, washed with water for 60 seconds, and dried.

[0079]

[Evaluation of Shape]

The line-and-space state obtained by the formation of the pattern was observed with a scanning electron microscope (JSM-7800F Prime, available from JEOL Ltd.), the width of the exposed bottom portion was observed at 10 points, and the arithmetic average value of the observed widths was determined. Then, the dimensional difference of the arithmetic average value of the observed widths with respect to the size of the mask pattern was calculated by the following equation. The evaluation was made in accordance with the following criteria. The results are shown in Table 1 as "development shape".

(Dimensional difference (%)) = (size (nm) of mask pattern - arithmetic average value (nm) of width)/size (nm) of mask pattern × 100

(Evaluation Criteria)

A: Dimensional difference of less than 3%

B: Dimensional difference of 3% or more and less than 5%

C: Dimensional difference of 5% or more and less than 10%

D: Dimensional difference of 10% or more, or resist remains and bottom cannot be seen

[0080]

5) Surface Tension

The surface tension of the developer prepared in each of Examples and Comparative Examples at 25°C was measured using a surface tensiometer DY-300 (available from Kyowa Interface Science Co., Ltd.). The measurement was performed in accordance with “Test Method by Wilhelmy Surface Tensiometer” of JIS K 2241.

[0081]

(Example 8)

The development characteristics of the resist A were evaluated using the same photoresist developer as in Example 1 except that the Cl concentration of Example 1 was changed to 210 ppm. As a result, the developed shape was evaluated as B as in Example 1, but the proportion of the resist residue portion was increased as compared with Example 1.

[0082]

(Example 9)

The development characteristics of the resist A were evaluated using the same photoresist developer as in Example 2 except that the Cl concentration in Example 2 was changed to 85

ppm. As a result, the developed shape was evaluated as A as in Example 2, but the proportion of the resist residue portion was increased as compared with Example 2.

[Table 1]

	Quaternary ammonium hydroxide		TMAH	Surfactant		Hydroxide ion	Water	Halide ion		Dissolution rate	Development characteristics		Surface tension
	Type	mass %	mass %	Type	mass ppm	mass%	mass%	Type	mass ppm		Resist A	Resist B	mN/m
Example 1	ETMAH	2.7	-	-	-	0.44	97.3	Cl	0.03	B	B	B	72.8
Example 2	PTMAH	3.1	-	-	-	0.44	96.9	Cl	0.5	A	A	A	71.9
Example 3	BTMAH	3.5	-	-	-	0.44	96.5	Cl	0.3	A	A	A	70.6
Example 4	BTMAH	1.7	1.2	-	-	0.44	97.1	Cl	0.2	-	A	A	-
Example 5	BTMAH	0.4	2.1	-	-	0.44	97.5	Cl	0.1	-	B	B	-
Example 6	BTMAH	0.4	2.1	SURFYNOL 465	20	0.44	97.5	Cl	0.1	-	A	A	-
Example 7	PTMAH	0.4	2.1	SURFYNOL 465	20	0.44	97.5	Cl	0.2	-	A	A	-
Comparative Example 1	-	-	2.4	-	-	0.44	97.6	Cl	0.1	C	C	C	73.2
Comparative Example 2	TEAH	3.8	-	-	-	0.44	96.2	Cl	4	D	D	D	-
Comparative Example 3	-	-	2.4	SURFYNOL 465	20	0.44	97.6	Cl	0.1	-	C	C	-

In the table, "-" in the dissolution rate column and the surface tension column indicates that the measurement was not performed.

[0083]

As shown in Table 1, the results were that ETMAH, PTMAH, and BTMAH had a higher dissolution rate than that of TMAH, and had excellent development characteristics. During development, the protective group was likely to remain in the vicinity of the mask of the exposed portion, and in a case of only TMAH, the side surface of the exposed portion remained undissolved, and the width of the exposure bottom portion became narrower than the line width of the mask pattern. On the other hand, in ETMAH, PTMAH, and BTMAH, the amount of the undissolved residue on the side surface of the exposed portion was small, the width of the exposure bottom portion was close to the line width of the mask pattern, and it was possible to obtain a pattern having a more rectangular shape and having a side surface nearly perpendicular to the bottom portion. In addition, in a case of mixing BTMAH and TMAH as well, the amount of the undissolved residue on the side surface portion was smaller than that in the case of using only TMAH, and a more rectangular pattern was obtained. It was also found that the undissolved residue was further reduced in a case of adding a small amount of a surfactant.

Industrial Applicability

[0084]