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DESCRIPTION

IMPROVED TOP ANTI-REFLECTIVE COATING FILMS

Field of the Invention

5 The present invention relates to improved compositions for enhancing the performance of aqueous developable photoresists by substantially eliminating pattern distortion caused by reflections over non-planar features on the substrate being patterned. The invention is directed to improved water soluble, anti-reflective top coating compositions which are easy to apply, provide better process control of image formation, and are aqueous soluble and, therefore, are easily removed using existing lithographic processing, which minimize environmental hazards and do not significantly add to lithographic process costs.

Background of the Invention

15 The use of anti-reflection coatings for optical devices, such as lenses in photographic and other equipment is well known in the prior art. These coatings take advantage of the relationship described in the Fresnel formulae. It is well established that the refractive index of an overlying material should be about the square root of the refractive index of the underlying material and that the thickness of the coating or layer should be an odd integer multiple of one-quarter of the wavelength of the incident radiation, the so-called "quarter-wavelength thickness".

20 In U.S. Patent No. 4,759,990 to Y-T. Yen, the anti-reflective coating concept is extended for use over optical membrane elements (pellicles) which are used in the manufacture of semiconductor wafers. The pellicle is typically made from a nitrocellulose film which is stretched over a pellicle holder. The use of an aromatic vinyl polymer such as polyvinyl naphthalene, polymethylstyrene or polystyrene as a first coating layer, followed by a fluorocarbon layer, such as 3M's FC-721 or FC-77, is disclosed. Pellicles may be used a number of times before they suffer either mechanical break down or cover contamination. Such pellicles are either cleaned, reworked or replaced.



8-2 29 10 3



5 Tanaka et al., J. Electrochem. Soc., 137, 3900 (1990) (Tanaka I) discloses a process for directly applying an antireflective coating on top of a photoresist. This technique attempts to overcome problems which have been encountered due to reflectivity when increasing the degree of pattern densification, in trying to achieve ULSI having sub-0.5 μm geometries.

10 Light interference leads to linewidth variations and degraded detection of through-the-lens (TTL) alignment marks. Tanaka I discloses the formation of an anti-reflective film on a photoresist surface, which is sufficient to suppress the multiple interference effects due to repeated reflection of incident light in the resist film. The anti-reflective film is clear, has its thickness and refractive index optimized and is used in a process which entails the steps of coating and baking a photoresist in the conventional way, spin-coating a film of the anti-reflective coating on the photoresist, imaging the composite structure, removing the anti-reflective film, and developing the photoresist. This process adds the steps of spin-coating and removal
15 of the anti-reflective film.

Using the Fresnel formulae, Tanaka I determined that the refractive index of the anti-reflective material should be about the square root of the refractive index of the imaging photoresist used. Tanaka I used a photoresist having a refractive index of 1.64 and, thus, the ideal anti-reflective coating refractive index was 1.28. The
20 Tanaka I material falls into two categories: (1) those which suppress reflection effects and which require organic solvent strip; and (2) those which are aqueous strippable, but which provide little process benefit. (Refractive index ≥ 1.48 .)

Tanaka et al., J. App. Phys., 67, 2617 (1990) (Tanaka II) discloses the use of perfluoroalkyl polyether and di-propoxy-bis(acetyl-acetate)titanium as anti-
25 reflective materials for single and bilayer films, to control the interface reflectivities, as well as methods to measure such reflectivities. Tanaka II entails the use of baking steps to fix the one and two layer coatings disclosed. He is silent on the use of post exposure and develop methods to remove the anti-reflective layer(s).

30 Tanaka et al., Chem. Abs. 107:87208y (1987) (Tanaka III) is directed to the subject matter of JP 62 62,520. It discloses a process for coating a photoresist with an anti-reflective coating which may comprise perfluoroalkyl- polyether,

perfluoroalkylamine, or a perfluoroalkyl- polyether-perfluoroalkylamine mixed film. The reflection-preventive film is removed after pattern wise exposure using a Freon®, a chloro-fluorocarbon ("CFC") solvent.

5 The Tanaka materials having the desired refractive indices are expensive to use. There is the required additional process step to remove the anti-reflective material. In addition, the removal step requires an organic solvent which is expensive to make or purchase and requires time and expense to safely handle and dispose of. Finally, the nature of Tanaka's solvents, as CFC's, requires extreme care to protect against environmental damage. The waste management aspects of the
10 Tanaka reflection-preventative materials weigh heavily against their use.

U.S. Patent 4,701,390 to Grunwald et al., discloses a process for thermally stabilizing a photoresist image layer formed on a substrate wherein the image layer, prior to being subjected to a post-development bake, is coated with a protective material which bonds to the photoresist, but is readily rinsed from the exposed
15 substrate after post bake and does not interfere with the desired operation of any of the subsequent steps of pattern generation, including final removal of the photoresist image. The protective (thermally stabilizing) material may be a compound or a mixture of two or more compounds selected from chromotropic acid, perfluorocarbon carboxylic acids, perfluorocarbon sulfonic acids, perfluorocarbon phosphoric acids
20 (and alkali metal, ammonium and amine salts of such acids), ethoxylated perfluorocarbon alcohols and quaternary ammonium salts of N-perfluoro-N',N"-dialkylamines.

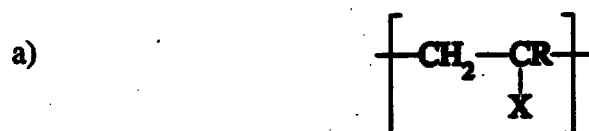
Summary of the Invention

25 In order to overcome the deficiencies of the materials and top anti-reflective processes of the prior art, the present invention provides anti-reflective coating compositions having a refractive index of from greater than about 1.20 to about 1.40, preferably from about 1.29 to about 1.40, which is capable of being applied in a single quarter wavelength thickness and are removable with water or with the developer for the underlying photoresist.



The present invention relates to a new water soluble anti-reflective top coat material for photoresists. The novel material comprises a new group of fluorinated polymers and, preferably, an additive to enhance the water solubility of such polymers. Preferably the additive is a surfactant, most preferably it is a fluorinated surfactant. The top coat is spin coated onto the photoresist and imaging is done in the normal manner. The unique materials of the top coat are water soluble, so when the top coat solution is spin coated onto the photoresist, no intermixing between the two layers occurs. Additionally, a water based top coat is environmentally safer than organic based solutions. In cases where the fluorinated polymers are themselves soluble in water or are soluble in water upon heating, no additive is required.

The family of polymers which comprises the anti-reflective coating of the present invention have a refractive index of from greater than about 1.20 to about 1.40, may be applied in a single quarter wavelength thickness, are removable with water or with the developer for the photoresist and are copolymers containing the following units:



where X is CO_2L , SO_3L , OH , $\text{CO}(\text{OC}_2\text{H}_4)_x\text{OH}$, $\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{L}$, PO_3L_2 or CONH_2 where $\text{L} = \text{H}$, a Group I or Group II cation or NH_4^+ and $x = 0-10$



where Y is Fluorine or a Fluorine containing aliphatic organic substituent, preferably selected from $\text{COO}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{SO}_2\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{SO}_2(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$,





wherein the aliphatic chain can be branched or unbranched;

where R = H, halogen, CF_3 , $\text{C}_1\text{-C}_8$ alkyl or CN;

n = 0-14; and

5

x = 0-10.

The present invention also relates to a process for making an anti-reflective coating composition for a photoresist, the coating having a refractive index of from greater than about 1.20 to about 1.40, and being capable of being applied in a single quarter wavelength thickness and is removable with water or with a developer for the underlying photoresist; the process composition providing a copolymer containing the following units:

10



where X is CO_2L , SO_3L , OH, $\text{CO}(\text{OC}_2\text{H}_4)_x\text{OH}$, $\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{L}$, PO_3L_2 or CONH_2 where L = H, a Group I or Group II cation or NH_4^+ and x = 0-10

15



where Y is Fluorine or a Fluorine containing aliphatic organic substituent, preferably selected from $\text{COO}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$,

$\text{SO}_2\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$,

$\text{SO}_2(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$,

20





wherein the aliphatic chain can be branched or unbranched;

where R = H, halogen, CF₃, C₁-C₈ alkyl or CN;

n = 0-14; and

5

x = 0-10.

Preferably, the polymer is a copolymer of CH₂=CH-CO-O-(CH₂)₂(CF₂)_x-CF₃ and acrylic acid, where x = 7 to 11.

10

The additives are those compounds which aid in solubilizing the polymer if the polymer is itself insoluble, or not sufficiently soluble, in water. These compounds are typically surfactants, emulsifiers or dispersants. Preferably, surfactants that are water soluble are used. Additives that may be utilized include ammonium pentadecafluorooctanoate, the amine salt of perfluorooctanoic acid, ammonium perfluorooctanosulfonate and ammonium lauryl sulfate.

Example 1

15

To a 0.5 l flask with a reflux condensor and a stirrer was added the following chemicals:

185 ml cyclohexane

16 g Fluowet EA 812 acrylate (acrylic acid perfluoralkyl-ester with 8-12 C-atoms in the ester alcohol group),

20

4 g acrylic acid, and

0.4 g dilauroylperoxide.

The reaction mixture was then heated to reflux (80°C). After 20-30 minutes, the polymerization was determined by a white powder, that was precipitating. After an additional 3 hours stirring under reflux, the polymerization was completed. The



polymer (fine white powder) was isolated by filtration and was dried in a vacuum at 80°C.

Example 2

5 A resin was synthesized according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O}-(\text{CH}_2)_2-(\text{CF}_2)_x\text{CF}_3$ in the ratio 32/68, where x was between 7 and 11. A formulation was made as follows:

Resin - 0.31 g

Additive - 0.68g

Water - 18.0 g

10 The additive used was the tetramethylammonium salt of pentadecafluorooctanoic acid.

Example 3

A resin was synthesized according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O}-(\text{CH}_2)_2-(\text{CF}_2)_x\text{CF}_3$ in the ratio 32/68, where x was between 7 and 11. A formulation was made as follows:

Resin - 0.33 g

Additive - 4.0 g (25% active)

Water - 16.0 g

The additive used was the amine salt of perfluorooctanosulfonic acid.

20

Example 4

A resin was synthesized according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O}-(\text{CH}_2)_2-(\text{CF}_2)_x\text{CF}_3$ in the ratio 39/61, where x was between 7 and 11. A formulation was made as follows:

Resin - 0.32 g

25 Additive - 4.0 g (25% active)

Water - 16.0 g

The additive used was the amine salt of perfluorooctanosulfonic acid.



Example 5

A resin was synthesized according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O-(CH}_2)_2\text{-(CF}_2)_x\text{CF}_3$ in the ratio 39/61, where x was between 7 and 11. A formulation was made as follows:

- 5 Resin - 1.0 g
 Additive - 0.65 g
 Water - 15.0 g

The additive used was ammonium perfluorooctanoate.

Example 6

- 10 A resin was synthesized according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O-(CH}_2)_2\text{-(CF}_2)_x\text{CF}_3$ in the ratio 39/61, where x was between 7 and 11. A formulation was made as follows:

- Resin - 0.33 g
 Additive - 2.3 g (25% active)
15 Water - 17.4 g

The additive used was the amine salt of perfluorooctanesulfonic acid.

Example 7

- A resin was made according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O-(CH}_2)_2\text{-(CF}_2)_x\text{CF}_3$ in the ratio 39/61, where x was
20 between 7 and 11. A formulation was made as follows:

- Resin - 0.3 g
 Additive - 0.68 g
 Water - 18.0 g

The additive used was the tetramethyl ammonium salt of perfluorooctanoic acid.

25

Example 8

A resin was made according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O-(CH}_2)_2\text{-(CF}_2)_x\text{CF}_3$ in the ratio 20/80, where x was between 7 and 11. A formulation was made as follows:



Resin - 0.2 g
Additive - 0.68 g
Water - 18.0 g

The additive used was the tetramethyl ammonium salt of perfluorooctanoic acid.

5

Example 9

A resin was synthesized according to the procedure of Example 1 by polymerizing of acrylic acid and $\text{CH}_2=\text{CHCO-O}-(\text{CH}_2)_2-(\text{CF}_2)_x\text{CF}_3$ in the ratio 20/80, where x was between 7 and 11. A formulation was made as follows:

10 Resin - 0.32 g
Additive - 2.3 g (25% active)
Water - 17.4 g

The additive used was an amine salt of perfluorooctanosulfonic acid.

15

20

<u>Example Number or Sample</u>	<u>Refractive Index</u>
2	1.37
3	1.39
4	1.395
5	1.40
6	1.40
7	1.38
8	1.35
9	1.38
Polyacrylic Acid	1.51



Comparative Example 10

Several silicon substrates were spin coated with film thicknesses ranging from 0.9-1.3 μ m using AZ7500® resist (available from Hoechst Celanese Corporation) and then soft baked on a hot plate at 100°C for 60 seconds . The silicon substrates were exposed with varying doses of i-line energy on a 0.54 Nikon i-line stepper, post exposure baked at 120°C in an oven for 60 seconds and developed in 2.38 wt. percent tetramethyl ammonium hydroxide (TMAH) developer. The exposure energy at which the photoresist was fully developed away was plotted against the resist film thickness. The swing curve from the sinusoidal plot was calculated to be

$$\left(\frac{E_{\max} - E_{\min}}{2 (E_{\max} + E_{\min})} \right)$$

for a fixed node, where $E_{\max}$ and $E_{\min}$ are the respective exposure energies at the maximum and minimum of a node. The value of the swing curve was 35.3.

Example 11

Several silicon substrates were spin coated with AZ® 7500 photoresist with film thicknesses ranging from 0.9-1.3 μ m and soft baked on a hot plate at 100°C for 60 seconds. The solution from Example 8 was coated over the AZ 7500 resist, to give a film thickness of the top coat of 680 angstroms. The resist was exposed with varying doses of i-line radiation on a 0.54 Nikon i-line stepper. The resist was given a post exposure bake at 120°C for 60 seconds in an oven and developed in 2.38% TMAH developer. The exposure energy at which the photoresist was fully developed away was plotted against the resist film thickness. The swing curve was calculated as described in Example 10, and a value of 9.4 was found.





What is Claimed:

1. An anti-reflective coating composition for a photoresist, the coating having a refractive index of from greater than about 1.20 to about 1.40, which is capable of being applied in a single quarter wavelength thickness and is removable with a developer for the underlying photoresist; the coating composition comprising a copolymer containing the following units:



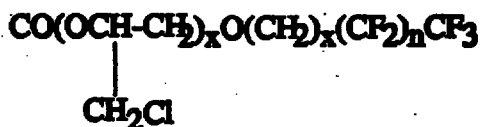
where X is CO_2L , SO_3L , OH , $\text{CO}(\text{OC}_2\text{H}_4)_x\text{OH}$, $\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{L}$, PO_3L_2 or CONH_2 where L = H, a Group I or Group II cation or NH_4^+ and x = 0-10



where Y is Fluorine or a Fluorine containing aliphatic organic substituent;
where R = H, halogen, CF_3 , $\text{C}_1\text{-C}_8$ alkyl or CN.

2. The anti-reflective coating of claim 1 comprising a copolymer of $\text{CH}_2=\text{CH}-\text{CO}-\text{O}-(\text{CH}_2)_2(\text{CF}_2)_x\text{CF}_3$ and acrylic acid, where x = 7 to 11.

3. The antireflective coating of claim 1, wherein Y is $\text{COO}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{SO}_2\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{SO}_2(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{CO}(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$ or



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wherein the aliphatic chain can be branched or unbranched;

$n = 0-14$; and

$x = 0-10$.

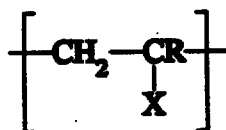
4. The anti-reflective coating of claim 1 further comprising a surfactant.

5. The anti-reflective coating of claim 4, wherein the surfactant comprises ammonium perfluorooctanoate, the amine salt of perfluorooctanoic acid, the tetramethylammonium salt of perfluorooctanoic acid, ammonium perfluorooctanosulfonate, ammonium hydroxide/tetramethylammonium hydroxide or ammonium lauryl sulfate.

6. A process for making an anti-reflective coating composition for a photoresist, the coating having a refractive index of from greater than about 1.20 to about 1.40, and being capable of being applied in a single quarter wavelength thickness and is removable with a developer for the underlying photoresist; the process composition providing a copolymer containing the following units:

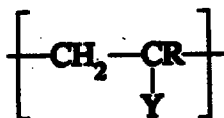
15

a)



where X is CO_2L , SO_3L , OH , $\text{CO}(\text{OC}_2\text{H}_4)_x\text{OH}$, $\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{L}$, PO_3L_2 or CONH_2 where $\text{L} = \text{H}$, a Group I or Group II cation or NH_4^+ and $x = 0-10$

b)



20

where Y is Fluorine or a Fluorine containing aliphatic organic substituent;
where R = H, halogen, CF_3 , $\text{C}_1\text{-C}_8$ alkyl or CN.

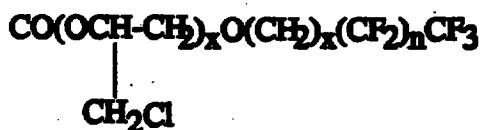




7. The process of claim 6, wherein the copolymer provided is a copolymer of $\text{CH}_2=\text{CH}-\text{CO}-\text{O}-(\text{CH}_2)_2(\text{CF}_2)_x\text{CF}_3$ and acrylic acid, where $x = 7$ to 11.

8. The process of claim 6, wherein Y is $\text{COO}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{SO}_2\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{SO}_2(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{CO}(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$

5 or



wherein the aliphatic chain can be branched or unbranched;

$n = 0-14$; and

$x = 0-10$.

9. The process of claim 6 further comprising adding a surfactant.

10. The process of claim 9 wherein the surfactant comprises ammonium perfluorooctanoate, the amine salt of perfluorooctanoic acid, the tetramethylammonium salt of perfluorooctanoic acid, ammonium perfluorooctanosulfonate or ammonium lauryl sulfate.

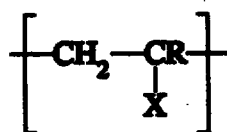


Abstract

IMPROVED TOP ANTI-REFLECTIVE COATING FILMS

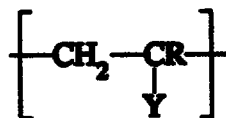
An anti-reflective coating composition for a photoresist and process for producing such a coating having a refractive index of from greater than about 1.20 to about 1.40, which is capable of being applied in a single quarter wavelength thickness and is removable with a developer for the underlying photoresist; the coating composition comprising a copolymer containing the following units:

a)

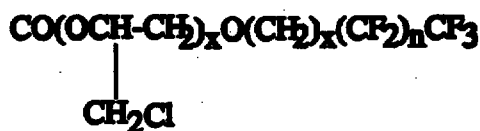


where X is CO_2L , SO_3L , OH, $\text{CO}(\text{OC}_2\text{H}_4)_x\text{OH}$, $\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{L}$, PO_3L_2 or CONH_2 where L = H, a Group I or Group II cation or NH_4^+ and x = 0-10

b)



where Y is Fluorine or a Fluorine containing aliphatic organic substituent, preferably selected from $\text{COO}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{SO}_2\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{SO}_2(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{CO}(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$ or



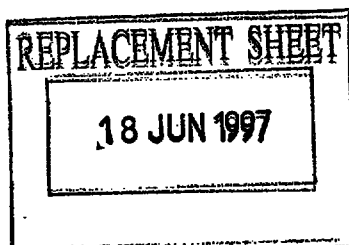
wherein the aliphatic chain can be branched or unbranched;

where R = H, halogen, CF_3 , $\text{C}_1\text{-C}_8$ alkyl or CN;

n = 0-14; and

x = 0-10.





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perfluoroalkylamine, or a perfluoroalkyl- polyether-perfluoroalkylamine mixed film. The reflection-preventive film is removed after pattern wise exposure using a Freon®, a chloro-fluorocarbon ("CFC") solvent.

5 The Tanaka materials having the desired refractive indices are expensive to use. There is the required additional process step to remove the anti-reflective material. In addition, the removal step requires an organic solvent which is expensive to make or purchase and requires time and expense to safely handle and dispose of. Finally, the nature of Tanaka's solvents, as CFC's, requires extreme care to protect against environmental damage. The waste management aspects of the

10 Tanaka reflection-preventative materials weigh heavily against their use.

U.S. Patent 4,701,390 to Grunwald et al., discloses a process for thermally stabilizing a photoresist image layer formed on a substrate wherein the image layer, prior to being subjected to a post-development bake, is coated with a protective material which bonds to the photoresist, but is readily rinsed from the exposed

15 substrate after post bake and does not interfere with the desired operation of any of the subsequent steps of pattern generation, including final removal of the photoresist image. The protective (thermally stabilizing) material may be a compound or a mixture of two or more compounds selected from chromotropic acid, perfluorocarbon carboxylic acids, perfluorocarbon sulfonic acids, perfluorocarbon phosphoric acids

20 (and alkali metal, ammonium and amine salts of such acids), ethoxylated perfluorocarbon alcohols and quaternary ammonium salts of N-perfluoro-N',N"-dialkylamines.

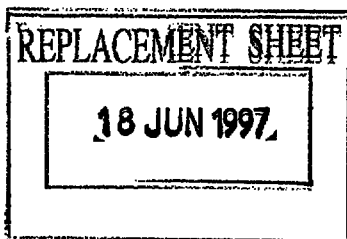
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REPLACEMENT SHEETS	SG
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105A/CD



- 3a -

In the US-A 5,139,879 an anti-reflection coating composition is disclosed, which comprises a blend of a crosslinkable, fluorinated terpolymer and an amorphous fluoropolymer. Upon heating the coating is cured. The coating compositions are soluble only in specific fluorinated organic solvents, but not in water. They are employed to produce an anti-reflection coating on eyeglasses, windows, displays and the like.

The anti-reflection coating composition according to EP-A 522 990 comprises a fluorocarbon polymer having a refractive index in the order of 1.3 to 1.4. The fluorocarbon polymer does not offer solubility or strippability in aqueous media. In order to render the anti-reflective coating water-soluble, suitable binders, such as polyvinyl-alcohol or poly(acrylic acid), are added to the composition. Without giving further details, there is also stated that "additional benefit may be derived by incorporating fluorine in the binder polymer as well".

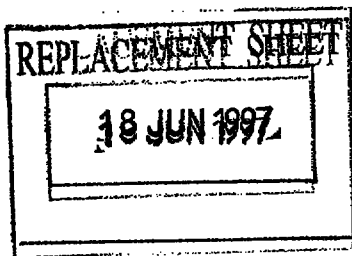
Summary of the Invention

In order to overcome the deficiencies of the materials and top anti-reflective processes of the prior art, the present invention provides anti-reflective coating compositions having a refractive index of from greater than about 1.20 to about 1.40, preferably from 1.29 to about 1.40, which is capable of being applied in a single quarter wavelength thickness and are removable with water or with the developer for the underlying photoresist.

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What is claimed:

1. A water-soluble anti-reflective coating composition for a photoresist, the coating having a refractive index of from greater than 1.20 to 1.40, the coating composition comprising a copolymer containing the following units:



where X is CO_2L , SO_3L , OH , $\text{CO}(\text{OC}_2\text{H}_4)_x\text{OH}$, $\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{L}$, PO_3L_2 or CONH_2 , where L = H, a Group I or Group II cation or NH_4^+ and $x = 0 - 10$

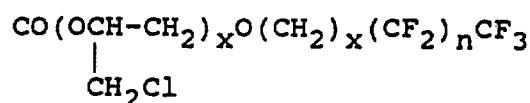


where Y is Fluorine or a Fluorine containing aliphatic organic substituent;

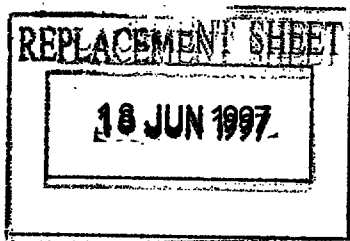
where R = H, halogen, CF_3 , $\text{C}_1\text{-C}_8$ alkyl or CN.

2. The anti-reflective coating composition of claim 1 comprising a copolymer of $\text{CH}_2=\text{CH}-\text{CO}-\text{O}-(\text{CH}_2)_2(\text{CF}_2)_x-\text{CF}_3$ and acrylic acid, where $x = 7$ to 11.

3. The anti-reflective coating composition of claim 1, wherein Y is $\text{COO}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{SO}_2\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{SO}_2(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{CO}(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$ or



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wherein the aliphatic chain can be branched or unbranched;

$n = 0 - 14$; and

$x = 0 - 10$.

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4. The anti-reflective coating composition of claim 1 further comprising a surfactant.

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5. The anti-reflective coating composition of claim 4, wherein the surfactant comprises ammonium perfluorooctanoate, the amine salt of perfluorooctanoic acid, the tetramethylammonium salt of perfluorooctanoic acid, ammonium perfluorooctanosulfonate, ammonium hydroxide/tetramethylammonium hydroxide or ammonium lauryl sulfate.

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6. A process for making a water-soluble anti-reflective coating composition for a photoresist, the coating having a refractive index of from greater than 1.20 to 1.40, the process composition providing a copolymer containing the following units:

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where X is CO_2L , SO_3L , OH , $\text{CO}(\text{OC}_2\text{H}_4)_x\text{OH}$, $\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{L}$, PO_3L_2 or CONH_2 , where $\text{L} = \text{H}$, a Group I or Group II cation or NH_4^+ and $x = 0 - 10$

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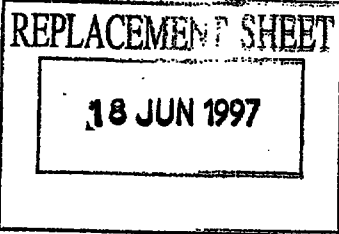


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where Y is Fluorine or a Fluorine containing aliphatic organic substituent; where $\text{R} = \text{H}$, halogen, CF_3 , $\text{C}_1\text{-C}_8$ alkyl or CN .



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11. Substrate with a photoresist layer and an anti-reflective top coating, said top coating being applied in a quarter-wavelength thickness, wherein the top coating consists of a composition as claimed in any of claims 1 to 5 and is removable with water or with the developer for the underlying photoresist layer.



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TOP ANTI-REFLECTIVE COATING FILMS

Field of the Invention

The present invention relates to improved compositions for enhancing the performance of aqueous developable photoresists by substantially eliminating pattern distortion caused by reflections over non-planar features on the substrate being patterned. The invention is directed to improved water soluble, anti-reflective top coating compositions which are easy to apply, provide better process control of image formation, and are aqueous soluble and, therefore, are easily removed using existing lithographic processing, which minimize environmental hazards and do not significantly add to lithographic process costs.

Background of the Invention

The use of anti-reflection coatings for optical devices, such as lenses in photographic and other equipment is well known in the prior art. These coatings take advantage of the relationship described in the Fresnel formulae. It is well established that the refractive index of an overlying material should be about the square root of the refractive index of the underlying material and that the thickness of the coating or layer should be an odd integer multiple of one-quarter of the wavelength of the incident radiation, the so-called "quarter-wavelength thickness".

In U.S. Patent No. 4,759,990 to Y-T. Yen, the anti-reflective coating concept is extended for use over optical membrane elements (pellicles) which are used in the manufacture of semiconductor wafers. The pellicle is typically made from a nitrocellulose film which is stretched over a pellicle holder. The use of an aromatic vinyl polymer such as polyvinyl naphthalene, polymethylstyrene or polystyrene as a first coating layer, followed by a fluorocarbon layer, such as 3M's FC-721 or FC-77, is disclosed. Pellicles may be used a number of times before they suffer either mechanical break down or cover contamination. Such pellicles are either cleaned, reworked or replaced.

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Tanaka et al., J. Electrochem. Soc., 137, 3900 (1990) (Tanaka I) discloses a process for directly applying an antireflective coating on top of a photoresist. This technique attempts to overcome problems which have been encountered due to reflectivity when increasing the degree of pattern densification, in trying to achieve ULSI having sub-0.5 μm geometries.

Light interference leads to linewidth variations and degraded detection of through-the-lens (TTL) alignment marks. Tanaka I discloses the formation of an anti-reflective film on a photoresist surface, which is sufficient to suppress the multiple interference effects due to repeated reflection of incident light in the resist film. The anti-reflective film is clear, has its thickness and refractive index optimized and is used in a process which entails the steps of coating and baking a photoresist in the conventional way, spin-coating a film of the anti-reflective coating on the photoresist, imaging the composite structure, removing the anti-reflective film, and developing the photoresist. This process adds the steps of spin-coating and removal of the anti-reflective film.

Using the Fresnel formulae, Tanaka I determined that the refractive index of the anti-reflective material should be about the square root of the refractive index of the imaging photoresist used. Tanaka I used a photoresist having a refractive index of 1.64 and, thus, the ideal anti-reflective coating refractive index was 1.28. The Tanaka I material falls into two categories: (1) those which suppress reflection effects and which require organic solvent strip; and (2) those which are aqueous strippable, but which provide little process benefit. (Refractive index ≥ 1.48 .)

Tanaka et al., J. App. Phys., 67, 2617 (1990) (Tanaka II) discloses the use of perfluoroalkyl polyether and di-propoxy-bis(acetyl-acetate)titanium as anti-reflective materials for single and bilayer films, to control the interface reflectivities, as well as methods to measure such reflectivities. Tanaka II entails the use of baking steps to fix the one and two layer coatings disclosed. He is silent on the use of post exposure and develop methods to remove the anti-reflective layer(s).

Tanaka et al., Chem. Abs. 107:87208y (1987) (Tanaka III) is directed to the subject matter of JP 62 62,520. It discloses a process for coating a photoresist with an anti-reflective coating which may comprise perfluoroalkyl- polyether.

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perfluoroalkylamine, or a perfluoroalkyl- polyether-perfluoroalkylamine mixed film. The reflection-preventive film is removed after pattern wise exposure using a Freon®, a chloro-fluorocarbon ("CFC") solvent.

The Tanaka materials having the desired refractive indices are expensive to use. There is the required additional process step to remove the anti-reflective material. In addition, the removal step requires an organic solvent which is expensive to make or purchase and requires time and expense to safely handle and dispose of. Finally, the nature of Tanaka's solvents, as CFC's, requires extreme care to protect against environmental damage. The waste management aspects of the Tanaka reflection-preventative materials weigh heavily against their use.

U.S. Patent 4,701,390 to Grunwald et al., discloses a process for thermally stabilizing a photoresist image layer formed on a substrate wherein the image layer, prior to being subjected to a post-development bake, is coated with a protective material which bonds to the photoresist, but is readily rinsed from the exposed substrate after post bake and does not interfere with the desired operation of any of the subsequent steps of pattern generation, including final removal of the photoresist image. The protective (thermally stabilizing) material may be a compound or a mixture of two or more compounds selected from chromotropic acid, perfluorocarbon carboxylic acids, perfluorocarbon sulfonic acids, perfluorocarbon phosphoric acids (and alkali metal, ammonium and amine salts of such acids), ethoxylated perfluorocarbon alcohols and quaternary ammonium salts of N-perfluoro-N',N"-dialkylamines.

EP-A2-0 583 918 discloses a reflection preventing film and process for forming resist pattern using the same, comprising a copolymer with recurring acrylic acid and acrylic acid fluoroalkyl ester units, the latter being different from the present invention.

Summary of the Invention

In order to overcome the deficiencies of the materials and top anti-reflective processes of the prior art, the present invention provides anti-reflective coating compositions having a refractive index of from greater than about 1.20 to about 1.40, preferably from about 1.29 to about 1.40, which is capable of being applied in a single quarter wavelength thickness and are removable with water or with the developer for the underlying photoresist.

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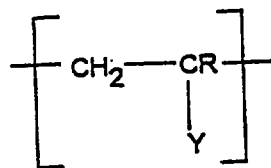
The present invention relates to a new water soluble anti-reflective top coat material for photoresists. The novel material comprises a new group of fluorinated polymers and, preferably, an additive to enhance the water solubility of such polymers. Preferably the additive is a surfactant, most preferably it is a fluorinated surfactant. The top coat is spin coated onto the photoresist and imaging is done in the normal manner. The unique materials of the top coat are water soluble, so when the top coat solution is spin coated onto the photoresist, no intermixing between the two layers occurs. Additionally, a water based top coat is environmentally safer than organic based solutions. In cases where the fluorinated polymers are themselves soluble in water or are soluble in water upon heating, no additive is required.

The family of polymers which comprises the anti-reflective coating of the present invention have a refractive index of from greater than about 1.20 to about 1.40, may be applied in a single quarter wavelength thickness, are removable with water or with the developer for the photoresist and are copolymers containing the following units:



where X is CO_2L , SO_3L , OH , $\text{CO}(\text{OC}_2\text{H}_5)_2$, OH , $\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{L}$, PO_3L_2 or CONH_2 where $\text{L} = \text{H}$, a Group I or Group II cation or NH_4^+ and $x = 0-10$

- b) an acrylic acid perfluoroalkyl-ester with 8 - 12 C-atoms in the ester alcohol group or



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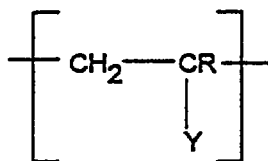
where Y is fluorine or a fluorine containing aliphatic organic substituent selected from the group consisting of $-\text{COO}-(\text{CH}_2)_2(\text{CF}_2)_{x1}-\text{CF}_3$, where $x1$ is 7 to 11; $-\text{SO}_2\text{O}(\text{CH}_2)_x(\text{CF}_2)_n-\text{CF}_3$, $-\text{SO}_2(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, where n is 0 - 14 and x is 0 - 10; and
 R is H, halogen, CF_3 , (C_1-C_8) alkyl or CN.

The present invention also relates to a process for making an anti-reflective coating composition for a photoresist, the coating having a refractive index of from greater than about 1.20 to about 1.40, and being capable of being applied in a single quarter wavelength thickness and is removable with water or with a developer for the underlying photoresist; the process composition providing a copolymer containing the following units:



where X is CO_2L , SO_3L , OH , $\text{CO}(\text{OC}_2\text{H}_4)_x\text{OH}$, $\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{L}$, PO_3L_2 or CONH_2 where $\text{L} = \text{H}$, a Group I or Group II cation or NH_4^+ and $x = 0-10$

b) an acrylic acid perfluoroalkyl-ester with 8 - 12 C-atoms in the ester alcohol group or



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where Y is fluorine or a fluorine containing aliphatic organic substituent selected from the group consisting of $-\text{COO}-(\text{CH}_2)_2(\text{CF}_2)_{x1}-\text{CF}_3$, where $x1$ is 7 to 11; $-\text{SO}_2\text{O}(\text{CH}_2)_x(\text{CF}_2)_n-\text{CF}_3$, $-\text{SO}_2(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, where n is 0 - 14 and x is 0 - 10; and

R is H, halogen, CF_3 , (C_1-C_8) alkyl or CN.

Preferably, the polymer is a copolymer of $\text{CH}_2=\text{CH}-\text{CO}-\text{O}-(\text{CH}_2)_2(\text{CF}_2)_x-\text{CF}_3$ and acrylic acid, where $x = 7$ to 11.

The additives are those compounds which aid in solubilizing the polymer if the polymer is itself insoluble, or not sufficiently soluble, in water. These compounds are typically surfactants, emulsifiers or dispersants. Preferably, surfactants that are water soluble are used. Additives that may be utilized include ammonium pentadecafluorooctanoate, the amine salt of perfluorooctanoic acid, ammonium perfluorooctanosulfonate and ammonium lauryl sulfate.

Example 1

To a 0.5 l flask with a reflux condensor and a stirrer was added the following chemicals:

185 ml	cyclohexane
16 g	Fluowet EA 812 acrylate (acrylic acid perfluoralkyl-ester with 8-12 C-atoms in the ester alcohol group),
4 g	acrylic acid, and
0.4 g	dilauroylperoxide.

The reaction mixture was then heated to reflux (80°C). After 20-30 minutes, the polymerization was determined by a white powder, that was precipitating. After an additional 3 hours stirring under reflux, the polymerization was completed. The

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polymer (fine white powder) was isolated by filtration and was dried in a vacuum at 80°C.

Example 2

A resin was synthesized according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O}-(\text{CH}_2)_x-(\text{CF}_2)_x\text{CF}_3$ in the ratio 32/68, where x was between 7 and 11. A formulation was made as follows:

Resin -	0.31 g
Additive -	0.68g
Water -	18.0 g

The additive used was the tetramethylammonium salt of pentadecafluorooctanoic acid.

Example 3

A resin was synthesized according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O}-(\text{CH}_2)_x-(\text{CF}_2)_x\text{CF}_3$ in the ratio 32/68, where x was between 7 and 11. A formulation was made as follows:

Resin -	0.33 g
Additive -	4.0 g (25% active)
Water -	16.0 g

The additive used was the amine salt of perfluorooctanosulfonic acid.

Example 4

A resin was synthesized according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O}-(\text{CH}_2)_x-(\text{CF}_2)_x\text{CF}_3$ in the ratio 39/61, where x was between 7 and 11. A formulation was made as follows:

Resin -	0.32 g
Additive -	4.0 g (25% active)
Water -	16.0 g

The additive used was the amine salt of perfluorooctanosulfonic acid.

Example 5

A resin was synthesized according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O}-(\text{CH}_2)_x-(\text{CF}_2)_x\text{CF}_3$ in the ratio 39/61, where x was between 7 and 11. A formulation was made as follows:

Resin -	1.0 g
Additive -	0.65 g
Water -	15.0 g

The additive used was ammonium perfluorooctanoate.

Example 6

A resin was synthesized according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O}-(\text{CH}_2)_x-(\text{CF}_2)_x\text{CF}_3$ in the ratio 39/61, where x was between 7 and 11. A formulation was made as follows:

Resin -	0.33 g
Additive -	2.3 g (25% active)
Water -	17.4 g

The additive used was the amine salt of perfluorooctanosulfonic acid.

Example 7

A resin was made according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O}-(\text{CH}_2)_x-(\text{CF}_2)_x\text{CF}_3$ in the ratio 39/61, where x was between 7 and 11. A formulation was made as follows:

Resin -	0.3 g
Additive -	0.68 g
Water -	18.0 g

The additive used was the tetramethyl ammonium salt of perfluorooctanoic acid.

Example 8

A resin was made according to the procedure of Example 1 by polymerizing acrylic acid and $\text{CH}_2=\text{CHCO-O}-(\text{CH}_2)_x-(\text{CF}_2)_x\text{CF}_3$ in the ratio 20/80, where x was between 7 and 11. A formulation was made as follows:

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Resin - 0.2 g
Additive - 0.68 g
Water - 18.0 g

The additive used was the tetramethyl ammonium salt of perfluorooctanoic acid.

Example 9

A resin was synthesized according to the procedure of Example 1 by polymerizing of acrylic acid and $\text{CH}_2=\text{CHCO-O}-(\text{CH}_2)_x-(\text{CF}_2)_2\text{CF}_3$ in the ratio 20/80, where x was between 7 and 11. A formulation was made as follows:

Resin - 0.32 g
Additive - 2.3 g (25% active)
Water - 17.4 g

The additive used was an amine salt of perfluorooctanosulfonic acid.

<u>Example Number or Sample</u>	<u>Refractive Index</u>
2	1.37
3	1.39
4	1.395
5	1.40
6	1.40
7	1.38
8	1.35
9	1.38
Polyacrylic Acid	1.51

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Comparative Example 10

Several silicon substrates were spin coated with film thicknesses ranging from 0.9-1.3 μ m using AZ7500® resist (available from Hoechst Celanese Corporation) and then soft baked on a hot plate at 100°C for 60 seconds. The silicon substrates were exposed with varying doses of i-line energy on a 0.54 Nikon i-line stepper, post exposure baked at 120°C in an oven for 60 seconds and developed in 2.38 wt. percent tetramethyl ammonium hydroxide (TMAH) developer. The exposure energy at which the photoresist was fully developed away was plotted against the resist film thickness. The swing curve from the sinusoidal plot was calculated to be

$$\left(\frac{E_{\max} - E_{\min}}{2(E_{\max} + E_{\min})} \right)$$

for a fixed node, where $E_{\max}$ and $E_{\min}$ are the respective exposure energies at the maximum and minimum of a node. The value of the swing curve was 35.3.

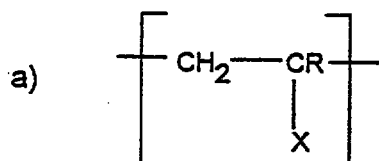
Example 11

Several silicon substrates were spin coated with AZ® 7500 photoresist with film thicknesses ranging from 0.9-1.3 μ m and soft baked on a hot plate at 100°C for 60 seconds. The solution from Example 8 was coated over the AZ 7500 resist, to give a film thickness of the top coat of 68 nm (680 angstroms). The resist was exposed with varying doses of i-line radiation on a 0.54 Nikon i-line stepper. The resist was given a post exposure bake at 120°C for 60 seconds in an oven and developed in 2.38% TMAH developer. The exposure energy at which the photoresist was fully developed away was plotted against the resist film thickness. The swing curve was calculated as described in Example 10, and a value of 9.4 was found.



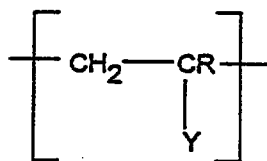
claims:

1. A water-soluble anti-reflective coating composition for a photoresist, the coating having a refractive index of from greater than 1.20 to 1.40, the coating composition comprising a copolymer containing the following units



where X is CO_2L , SO_3L , OH , $\text{CO}(\text{OC}_2\text{H}_4)_x\text{OH}$, $\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{L}$, PO_3L_2 or CONH_2 , where L is H, a Group I or Group II cation or NH_4^+ and x is 0 to 10;

- b) an acrylic acid perfluoroalkyl-ester with 8 - 12 C-atoms in the ester alcohol group or



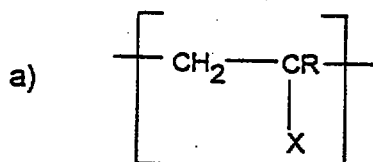
where Y is fluorine or a fluorine containing aliphatic organic substituent selected from the group consisting of $-\text{COO}-(\text{CH}_2)_2(\text{CF}_2)_{x1}-\text{CF}_3$, where $x1$ is 7 to 11; $-\text{SO}_2\text{O}(\text{CH}_2)_x(\text{CF}_2)_n-\text{CF}_3$, $-\text{SO}_2(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, where n is 0 - 14 and x is 0 - 10; and
R is H, halogen, CF_3 , $(\text{C}_1-\text{C}_8)\text{alkyl}$ or CN.



2. The anti-reflective coating of claim 1 comprising a copolymer of $\text{CH}_2=\text{CH}-\text{CO}-\text{O}-(\text{CH}_2)_7(\text{CF}_2)_x-\text{CF}_3$ and acrylic acid, where $x = 7$ to 11.
3. The anti-reflective coating of claim 1 further comprising a surfactant.
4. The anti-reflective coating of claim 3, wherein the surfactant comprises ammonium perfluorooctanoate, the amine salt of perfluorooctanoic acid, the tetramethylammonium salt of perfluorooctanoic acid, ammonium perfluorooctanosulfonate, ammonium hydroxide/tetramethylammonium hydroxide or ammonium lauryl sulfate.

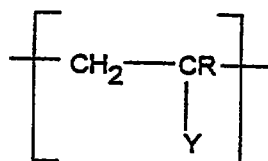


5. A process for making a water-soluble anti-reflective coating composition for a photoresist, the coating having a refractive index of from greater than 1.20 to 1.40, the process comprising preparing an aqueous solution of the copolymer containing the following units



where X is CO_2L , SO_3L , OH , $\text{CO}(\text{OC}_2\text{H}_4)_x\text{OH}$, $\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{L}$, PO_3L_2 or CONH_2 , where L is H, a Group I or Group II cation or NH_4^+ and x is 0 to 10;

- b) an acrylic acid perfluoroalkyl-ester with 8 - 12 C-atoms in the ester alcohol group or



where Y is fluorine or a fluorine containing aliphatic organic substituent selected from the group consisting of $-\text{COO}-(\text{CH}_2)_2(\text{CF}_2)_{x1}-\text{CF}_3$, where $x1$ is 7 to 11; $-\text{SO}_2\text{O}(\text{CH}_2)_x(\text{CF}_2)_n-\text{CF}_3$, $-\text{SO}_2(\text{OC}_2\text{H}_4)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, where n is 0 - 14 and x is 0 - 10; and

R is H, halogen, CF_3 , $(\text{C}_1-\text{C}_8)\text{alkyl}$ or CN.



6. The process of claim 5, wherein the copolymer provided is a copolymer of $\text{CH}_2=\text{CH}-\text{CO}-\text{O}-(\text{CH}_2)_2(\text{CF}_2)_x-\text{CF}_3$ and acrylic acid, where $x = 7$ to 11.

7. The process of claim 5 further comprising adding a surfactant.

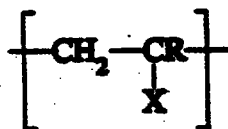
8. The process of claim 7 wherein the surfactant comprises ammonium perfluorooctanoate, the amine salt of perfluorooctanoic acid, the tetramethylammonium salt of perfluorooctanoic acid, ammonium perfluorooctanosulfonate or ammonium lauryl sulfate.

Abstract

TOP ANTI-REFLECTIVE COATING FILMS

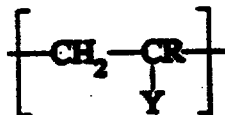
An anti-reflective coating composition for a photoresist and process for producing such a coating having a refractive index of from greater than about 1.20 to about 1.40, which is capable of being applied in a single quarter wavelength thickness and is removable with a developer for the underlying photoresist; the coating composition comprising a copolymer containing the following units:

a)

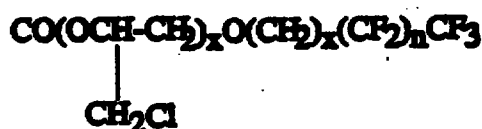


where X is CO_2L , SO_3L , OH, $\text{CO}(\text{OC}_2\text{H}_5)_x\text{OH}$, $\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{L}$, PO_3L_2 or CONH_2 where L = H, a Group I or Group II cation or NH_4^+ and x = 0-10

b)



where Y is Fluorine or a Fluorine containing aliphatic organic substituent, preferably selected from $\text{COO}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{SO}_2\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{SO}_2(\text{OC}_2\text{H}_5)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$, $\text{CO}(\text{OC}_2\text{H}_5)_x\text{O}(\text{CH}_2)_x(\text{CF}_2)_n\text{CF}_3$ or



wherein the aliphatic chain can be branched or unbranched;

where R = H, halogen, CF_3 , $\text{C}_1\text{-C}_8$ alkyl or CN;

n = 0-14; and

x = 0-10.

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