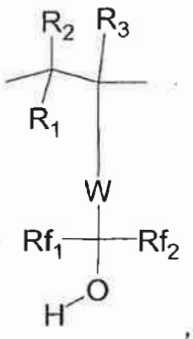
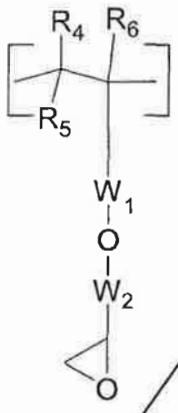
Claims

1. An underlayer composition comprising an organic titanate compound and a polymer, where the polymer comprises at least one fluoroalcohol group and at least one epoxy group.

2. The underlayer composition of claim 1, where the polymer comprises at least one unit with a fluoroalcohol group (1) and at least one unit with an epoxy group (2),



(1)

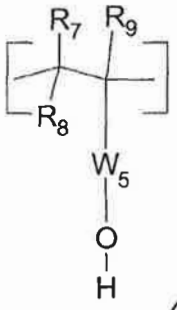


(2)

where, R_1 to R_6 are independently selected from hydrogen and C_1-C_4 alkyl, W is a linking group, Rf_1 and Rf_2 are independently selected from fluorinated (C_1-C_6) alkyl group and partially fluorinated (C_1-C_6) alkyl group; W_1 is selected from an arylene, a carbonyl (-(C=O)) and a carbonyloxyalkylene group (-C(=O)-O-W_4-) where W_4 is selected from a group consisting of C_1 to C_6 alkylene moiety, fluorinated (C_1-C_6) alkylene group and partially fluorinated (C_1-C_6) alkylene group; and, W_2 is a (C_1- C_6) alkylene moiety.

3. The underlayer composition of claim 1 or 2, where in the polymer the fluoroalcohol group ranges between 10 and 80 mole % and the epoxy group ranges between 20 and 90 mole%.

4. The underlayer composition according to one of claims 1 to 3, where the polymer further comprises unit of structure 3,

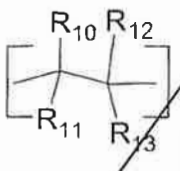


(3)

where R_7 to R_9 are independently selected from hydrogen and C_1-C_4 alkyl,

W_5 is selected from a direct valance bond, an arylene group, an ester (C(=O)-O-R_{14}) group, a C_1-C_{20} alkylene group and mixtures thereof, and R_{14} is selected from C_1-C_{20} alkylene, C_1-C_{20} alkylenearylene, arylene and substituted arylene, the repeat unit (3) ranging preferably between 1 and 40 mole %.

5. The underlayer composition according to one of claims 1 to 4, where the polymer further comprises a recurring unit (4),

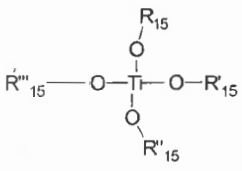


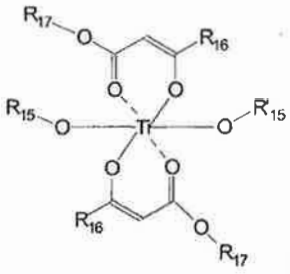
(4)

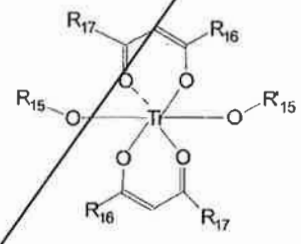
where, R_{10} to R_{12} are independently selected from hydrogen, nitrile and C_1-C_4 alkyl, R_{13} is an aryl group or an ester (-C(=O)-O-R_{15}) group, where R_{15} is selected from a group consisting of a C_1-C_{20} alkyl, C_1-C_{20} alkylenearyl, aryl, substituted

aryl, fluorinated alkyl group, partially fluorinated alkyl group or mixtures thereof, the repeat unit (4) ranging preferably between 1 and 30 mole %.

6. The underlayer composition of one of claims 1 to 5, where the organic titanate compound is selected from the group consisting of

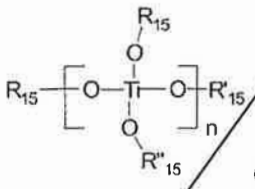

(5)


(6)


(7)

where R_{15}, R'_{15}, R''_{15}, and R'''_{15} are independently selected from C_1-C_{20} alkyl and C_1-C_{20} alkyl carbonyl, and R_{16} and R_{17} are independently selected from C_1-C_{20} alkyl and aryl group, the amount of monomeric titanate (5), (6) and (7) in the composition ranging preferably between 10 and 50 weight% of total solids.

7. The underlayer composition of one of claims 1 to 5, where the organic titanate is selected from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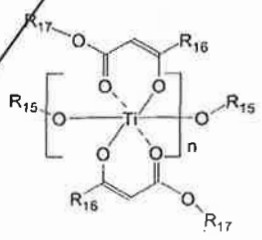
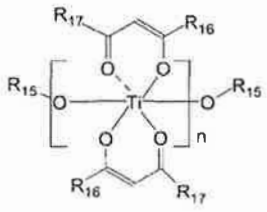

(9)


(10)

where n= 2-10 and R_{15}, R'_{15}, and R''_{15}, are independently selected from C_1-C_{20} alkyl and C_1-C_{20} alkyl carbonyl, and R_{16} and R_{17} are independently selected from C_1-C_{20} alkyl and aryl group, the level of polymeric titanate compound (8) (9) and (10) in the underlayer ranging preferably between 10 and 99.9 % of total solids.

8. The underlayer composition of one of claims 1 to 7 having a refractive index (n) between 1.5 and 1.9 and an absorption (k) between 0.1 and 0.6 at 193 nm.

9. A process for manufacturing a microelectronic device, comprising;

a) providing a substrate with a titanium underlayer film of one of claim 1 to 8;

b) curing the underlayer film by heating;

b) coating a photoresist layer above the underlayer coating layer;

c) imagewise exposing the photoresist layer;

d) developing the photoresist layer with an aqueous alkaline developing solution.

10. The process of claim 9, where the cured titanium underlayer film comprises titanium content ranging from 3 to 60%.

11. The process of claim 9 or 10, where imagewise exposure ranges from 250 nm to 12 nm.

12. The process according to one of claims 9 to 11, where the developing solution is an aqueous solution comprising a hydroxide base.

13. The process according to one of claims 9 to 12, where the substrate has one or more antireflective coatings coated over the substrate, preferably at least one high carbon antireflective coating film coated over the substrate.

14. The process according to one of claims 9 to 13, further comprising dry etching the titanium underlayer film after step d).

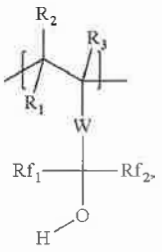
15. The process according to one of claims 9 to 13, further comprising dry etching the titanium under layer film and the high carbon antireflective coating film separately after step d).

The invention claimed is:

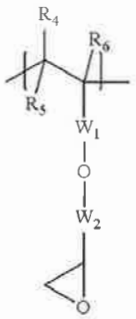
1. An underlayer composition comprising an organic titanate compound and a polymer, where the polymer comprises at least one fluoroalcohol group and at least one epoxy group.

2. The underlayer composition of claim 1, where the polymer comprises at least one unit with a fluoroalcohol group (1) and at least one unit with an epoxy group (2),

(1)



(2)

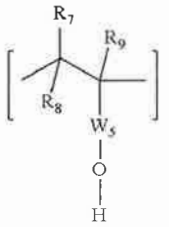


where, R_1 to R_6 are independently selected from hydrogen and C_1-C_4 alkyl, W is a linking group, Rf_1 and Rf_2 are independently selected from fluorinated (C_1-C_6) alkyl group and partially fluorinated (C_1-C_6) alkyl group; W_1 is selected from an arylene group, a carbonyl group having the structure (—(C=O)) and a carbonyloxyalkylene group having the structure (—C(=O)—O—W_4—) where W_4 is selected from a group consisting of C_1 to C_6 alkylene group, fluorinated (C_1-C_6) alkylene group and partially fluorinated (C_1-C_6) alkylene group; and, W_2 is a (C_1-C_6) alkylene group.

3. The underlayer composition of claim 2 where in the polymer the fluoroalcohol group (I) ranges between 10 and 80 mole % and the epoxy group (II) ranges between 20 and 90 mole %.

4. The underlayer composition according to claim 1 where the polymer further comprises unit of structure 3,

(3)

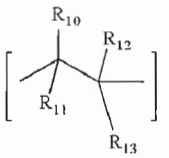


where R_7 to R_9 are independently selected from hydrogen and C_1-C_4 alkyl,
W_5 is selected from a direct valance bond, an arylene group, an ester group having the structure (C(=O)—O—R_{14}), a C_1-C_{20} alkylene group and mixtures thereof, and R_{14} is selected from a group consisting of C_1-C_{20} alkylene group, C_1-C_{20} alkylenearylene group, arylene group and substituted arylene group.

5. The underlayer composition of claim 4 where the repeat unit (3) ranges between 1 and 40 mole % of the total repeat units.

6. The underlayer composition according to claim 1, where the polymer further comprises a recurring unit (4),

(4)

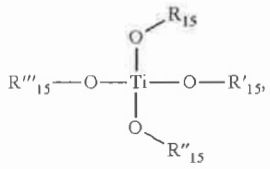


where, R_{10} to R_{12} are independently selected from hydrogen, nitrile and C_1-C_4 alkyl, R_{13} is an aryl group or an ester group having the structure (—C(=O)—O—R_{15}), where R_{15} is selected from a group consisting of a C_1-C_{20} alkyl group, C_1-C_{20} alkylenearyl group, aryl group, substituted aryl group, fluorinated alkyl group, partially fluorinated alkyl group and mixtures thereof.

7. The underlayer composition of claim 6, where the repeat unit (4) ranges between 1 and 30 mole % of total recurring units.

8. The underlayer composition of claim 1 where the organic titanate compound is selected from the group consisting of

(5)



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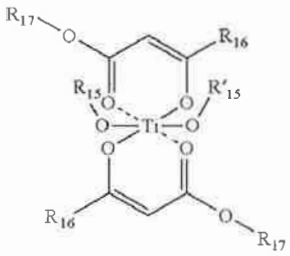

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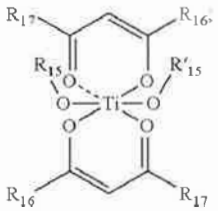
(7)

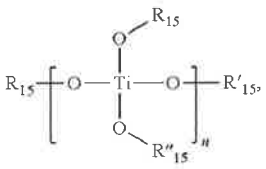


wherein R_{15}, R'_{15}, R''_{15}, and R'''_{15} are independently selected from C_1-C_{20} alkyl and C_1-C_{20} alkyl carbonyl, and further wherein R_{16} and R_{17} are independently selected from C_1-C_{20} alkyl and aryl group.

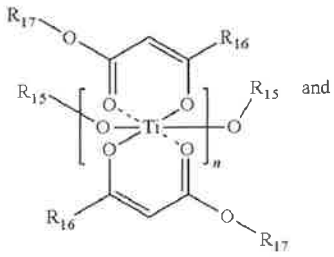
9. The underlayer composition of claim 8 where the amount of organic titanate (5), (6) and (7) in the composition ranges between 10 and 50 weight % of total solids.

10. The underlayer composition of claim 1 where the organic titanate is selected from the group consisting of

(8)



(9)



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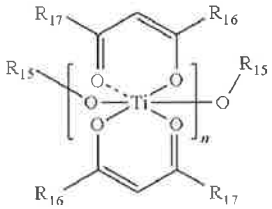
(10)



wherein n=2-10 and R_{15}, R'_{15}, and R''_{15}, are independently selected from the group consisting of C_1-C_{20} alkyl and C_1-C_{20} alkyl carbonyl, and further wherein R_{16} and R_{17} are independently selected from the group consisting of C_1-C_{20} alkyl and aryl group.

11. The underlayer composition of claim 10 where the level of polymeric titanate compound (8) (9) and (10) in the underlayer composition ranges between 10 and 99.9 weight % of total solids.

12. The coated underlayer film cured between 90° C. to 300° C. from the composition of claim 1 having a refractive index (n) between 1.5 and 1.9 and an absorption (k) between 0.1 and 0.6 at 193 nm.

13. A process for manufacturing a microelectronic device, comprising;

a) providing a substrate with an underlayer film of claim 1;
b) curing the underlayer film by heating;
b) coating a photoresist layer above the underlayer coating layer;
c) imagewise exposing the photoresist layer to deep ultraviolet or extreme ultraviolet radiation;
d) developing the photoresist layer with an aqueous alkaline developing solution.

14. The process of claim 13, where the cured titanium underlayer film comprises titanium content ranging from 3 to 60 weight %.

15. The process of claim 13, where imagewise exposure is done with radiation whose wavelength ranges from 250 nm to 12 nm.

16. The process according to claim 13, where the developing solution is an aqueous solution comprising a hydroxide base.

17. The process according to claim 13, where the substrate optionally has one or more antireflective coatings coated over the substrate.

18. The process according to claim 13, where the substrate has at least one high carbon antireflective coating film coated over the substrate.

19. The process according to claim 13, further comprising dry etching the titanium underlayer film after step d).

20. The process according to claim 18, further comprising dry etching the titanium under layer film and the high carbon antireflective coating film separately after step d).