What is Claimed is:

1. A photoresist composition comprising

a thiol derivative where the thiol moiety is attached to an SP2 carbon which is part of a ring which has structures (H1), (H2) (H3), or (H4), and where this thiol derivative is present in a range of 0.5 wt. % to 3 wt. % of total solids, wherein

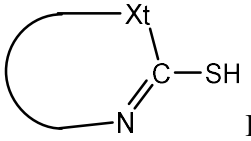
in said structure (H1), Xt is selected from the group consisting of $N(Rt_3)$, $C(Rt_1)(Rt_2)$, O, S, Se, and Te;

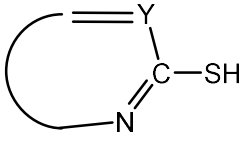
in said structure (H2), Y is selected from the group consisting of $C(Rt_3)$ and N;

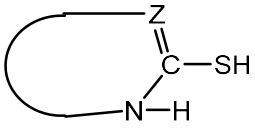
in said structure (H3), Z is selected from the group consisting of $C(Rt_3)$ and N; and

in said structure (H4), where Arene is selected from an unsubstituted phenyl, a substituted phenyl, an unsubstituted polycyclic arene moiety and a substituted polycyclic arene moiety, Rt_1, Rt_2, and Rt_3 are independently selected from the group consisting of H, a substituted alkyl group having 1 to 8 carbon atoms, an unsubstituted alkyl group having 1 to 8 carbon atoms, a substituted alkenyl group having 2 to 8 carbon atoms, unsubstituted alkenyl group having 2 to 8 carbon atoms, a substituted alkynyl group having 2 to 8 carbon atoms, unsubstituted alkynyl group having 2 to 8 carbon atoms, a substituted aromatic group having 6 to 20 carbon atoms, a substituted heteroaromatic group having 3 to 20 carbon atoms, unsubstituted aromatic group having 6 to 20 carbon atoms and unsubstituted heteroaromatic group having 3 to 20 carbon atoms,

Rt_4 is independently selected from the group consisting of H, OH, a substituted alkyl group having 1 to 8 carbon atoms, an unsubstituted alkyl group having 1 to 8 carbon atoms, a substituted alkenyl group having 2 to 8 carbon atoms, unsubstituted alkenyl group having 2 to 8 carbon atoms, a substituted alkynyl group having 2 to 8 carbon atoms, unsubstituted alkynyl group having 2 to 8 carbon atoms, a substituted aromatic group having 6 to 20 carbon atoms, a substituted heteroaromatic group having 3 to 20 carbon atoms, unsubstituted aromatic group having 6 to 20 carbon atoms and unsubstituted heteroaromatic group having 3 to 20 carbon atoms,



H1)


H2)


H3) Rt_4-Arene-SH (H4), and further wherein . said photoresist composition is selected from the group consisting of compositions I), II), III), IV), (V), (VI) and (VII)

I) a photoresist composition which is a positive chemically amplified photoresist comprising,
a component comprising a reaction product formed in the absence of an acid catalyst between (i) a Novolak polymer, (ii) a polymer comprising substituted or unsubstituted hydroxystyrene and acrylate, methacrylate or a mixture of acrylate and methacrylate, the acrylate and/or methacrylate being protected by an acid labile group that requires a high activation energy for deblocking, and (iii) a compound selected from a vinyl ether and an unsubstituted or substituted, unsaturated heteroalicyclic;
at least one PAG, and
an organic spin casting solvent;
II) a photoresist composition which is a positive chemically amplified photoresist developable in aqueous base, comprising,
a component comprising a reaction product formed in the absence of an acid catalyst between (i) a Novolak polymer, (ii) a polymer comprising substituted or unsubstituted hydroxystyrene and acrylate, methacrylate or a mixture of acrylate and methacrylate, the acrylate and/or methacrylate being protected by an acid labile group that requires a high activation energy for deblocking, and (iii) a compound selected from a vinyl ether and an unsubstituted or substituted, unsaturated heteroalicyclic;
at least one polymer comprising repeat units derived from 4-hydroxystyrene, repeat units derived from an acetal protected 4-hydrostyrene, and a repeat unit derived from a (meth)acrylic acid protected with a high energy protecting group,
at least one PAG,
an organic spin casting solvent;
III) a photoresist composition which is a negative non-chemically amplified photoresist which is developable in aqueous base comprising,
at least one alkali-soluble polymer, where the polymer comprises at least one unit of structure (INR),
(INR);
where, R' is selected independently from hydrogen, (C1-C4)alkyl, chlorine and bromine, and m is an integer from 1 to 4;
at least one monomer of structure (IINR),
(IINR)

where, W is a multivalent linking group, R1 to R6 are independently selected from hydrogen, hydroxy, (C1-C20) alkyl and chlorine, X1 and X2 are independently oxygen or N-R7, where R7 is hydrogen or (C1-C20) alkyl, and n is an integer equal to or greater than 1; and,

at least one radical photoinitiator and

an organic spin casting solvent;

IV) s photoresist composition which is a negative non-chemically amplified photoresist, developable in aqueous base, comprising

at least one Novolak type resin which is soluble in about 0.26 N TMAH,

at least one radical photoinitiator,

at least one (meth)acrylate crosslinker and

an organic spin casting solvent.;

V) a photoresist composition which is a negative non-chemically amplified (meth)acrylate type photoresist, developable in aqueous base, comprising

at least one (meth)acrylate polymer comprising a (meth)acrylic acid derived repeat unit, a repeat unit derived from at least one of styrene and benzyl (meth)acrylate, which is soluble in about 0.26 N TMAH,

at least one radical photoinitiator,

at least one (meth)acrylate crosslinker and

an organic spin casting solvent;

VI) a photoresist composition which is a negative chemically amplified photoresist developable in aqueous base;

VII) a photoresist composition which is a negative chemically amplified photoresist developable in aqueous base, comprising,

at least one phenolic film-forming polymeric binder resin having ring bonded hydroxyl groups, selected from a Novolak resin, a hydroxystyrene copolymer, or mixtures thereof which is soluble in 0.26 N TMAH

at least one PAG,

a crosslinking agent that forms a carbonium ion upon exposure to acid photogenerated by the PAG and which comprises an etherified aminoplast polymer or oligomer and

an organic spin casting solvent.

2. The composition of claim 1, wherein said thiol derivative is present at a loading from 0.6 wt. % to 3 wt. % of total solids.

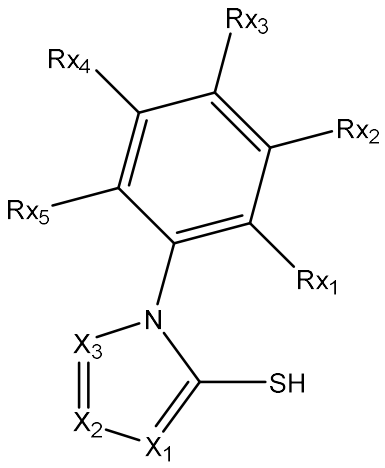
3. The composition of any one of claims 1 or 2, wherein said thiol derivative has structure (H2).

4. The composition of any one of claims 1 or 2, wherein said thiol derivative has structure (H3).

5. The composition of any one of claims 1 or 2, wherein said thiol derivative has structure (H1).

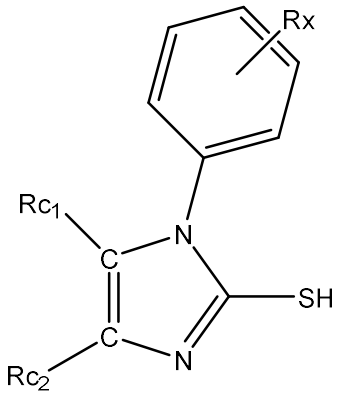
6. The composition of any one of claims 1, 2 and 5, wherein said thiol derivative has structure (H1) and where Xt is $N(Rt_3)$.

7. The composition of any one of claims 1, 2 and 5 to 6, wherein said thiol derivative has structure (H1-A), wherein X_1 is N, X_2 and X_3 are individually selected from the group consisting of N, and $C(Rt_3)$ and Rx_1, Rx_2, Rx_3, Rx_4, and Rx_5 are individually selected from the group consisting of H, OH, a halide, a C-1 to C-8 alkyl, an aryl, a C-1 to C-8 alkylenehydroxy (-alkylene-OH), a C-2 to C-8 alkyleneoxyalkyl (-alkylene-O-alkyl), and a C-5 to C-15 polyalkyleneoxyakyl (-(alkylene-$O)_{pa}$-alkyl), where pa is an integer ranging from 2 to 4), and Rt_3 is independently selected from the group consisting of H, a substituted alkyl group having 1 to 8 carbon atoms, an unsubstituted alkyl group having 1 to 8 carbon atoms, a substituted alkenyl group having 2 to 8 carbon atoms, unsubstituted alkenyl group having 2 to 8 carbon atoms, a substituted alkynyl group having 2 to 8 carbon atoms, unsubstituted alkynyl group having 2 to 8 carbon atoms, a substituted aromatic group having 6 to 20 carbon atoms, a substituted heteroaromatic group having 3 to 20 carbon atoms, unsubstituted aromatic group having 6 to 20 carbon atoms and unsubstituted heteroaromatic group having 3 to 20 carbon atoms,



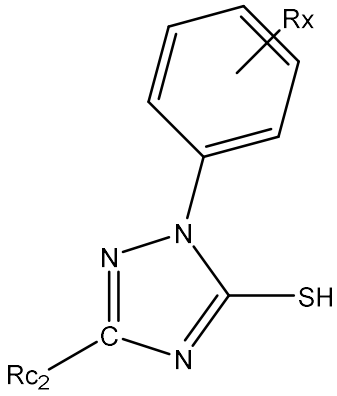
(H1-A).

8. The composition of any one of claims 1, 2 and 5 to 7, wherein said thiol derivative has structure (H1-B), wherein Rx, is selected from the group consisting of H, OH, a halide, a C-1 to C-8 alkyl, an aryl, a C-1 to C-8 alkylenehydroxy (-alkylene-OH), a C-2 to C-8 alkyleneoxyalkyl (-alkylene-O-alkyl), and a C-5 to C-15 polyalkyleneoxyakyl (-(alkylene-O)$_{pa}$-alkyl), where pa is an integer ranging from 2 to 4), Rc_2 is selected from H and a C-1 to C-8 alkyl, Rc_1 is selected from H and a C-1 to C-8 alkyl,



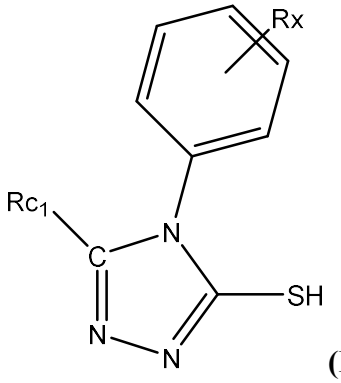
(H1-B).

9. The composition of any one of claims 1, 2 and 5 to 7, wherein said thiol derivative has structure (H1-C), wherein Rc_2 is selected from H and a C-1 to C-8 alkyl, and Rx, is selected from H, OH, a halide, a C-1 to C-8 alkyl, an aryl, a C-1 to C-8 alkylenehydroxy (-alkylene-OH), a C-2 to C-8 alkyleneoxyalkyl (-alkylene-O-alkyl), and a C-5 to C-15 polyalkyleneoxyakyl (-(alkylene-O)$_{pa}$-alkyl), where pa is an integer ranging from 2 to 4),



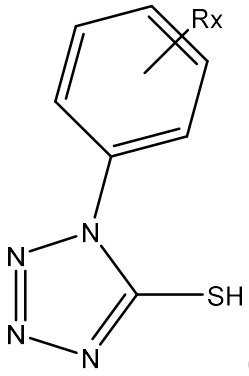
(H1-C).

10. The composition of any one of claims 1, 2 and 5 to 7, wherein said thiol derivative has structure (H1-D), wherein Rc_1 is selected from H and a C-1 to C-8 alkyl, and Rx, is selected from H, OH, a halide, a C-1 to C-8 alkyl, an aryl, a C-1 to C-8 alkylenehydroxy (-alkylene-OH), a C-2 to C-8 alkyleneoxyalkyl (-alkylene-O-alkyl), and a C-5 to C-15 polyalkyleneoxyakyl (-(alkylene-O)$_{pa}$-alkyl), where pa is an integer ranging from 2 to 4).



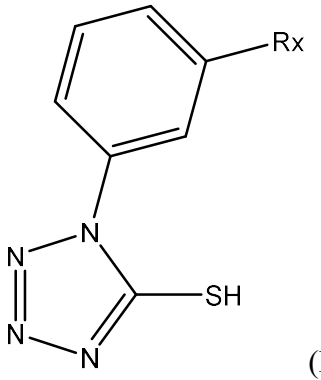
(H1-D).

11. The composition of any one of claims 1, 2 and 5 to 7, wherein said thiol derivative has structure (H1-E), wherein Rx is selected from H, OH, a halide, a C-1 to C-8 alkyl, an aryl, a C-1 to C-8 alkylenehydroxy (-alkylene-OH), a C-2 to C-8 alkyleneoxyalkyl (-alkylene-O-alkyl), and a C-5 to C-15 polyalkyleneoxyakyl (-(alkylene-O)$_{pa}$-alkyl), where pa is an integer ranging from 2 to 4),



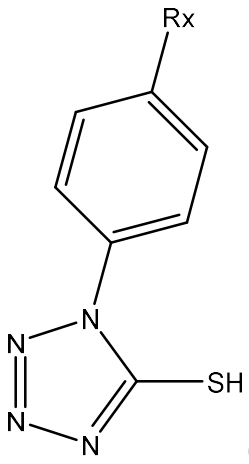
(H1-E).

12. The composition of any one of claims 1, 2, and 5 to 7 and 11, wherein said thiol derivative has structure (H1-EA), wherein Rx, is selected from H, OH, a halide, a C-1 to C-8 alkyl, an aryl, a C-1 to C-8 alkylenehydroxy (-alkylene-OH), a C-2 to C-8 alkyleneoxyalkyl (-alkylene-O-alkyl), and a C-5 to C-15 polyalkyleneoxyakyl (-(alkylene-O)$_{pa}$-alkyl), where pa is an integer ranging from 2 to 4),



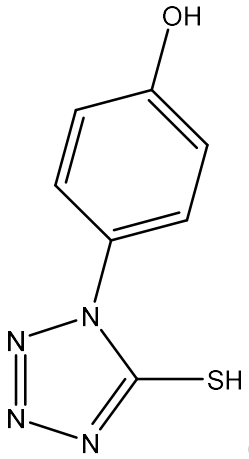
(H1-EA).

13. The composition of any one of claims 1, 2, and 5 to 7 and 11, wherein said thiol derivative has structure (H1-EB), wherein Rx, is selected from H, OH, a halide, a C-1 to C-8 alkyl, an aryl, a C-1 to C-8 alkylenehydroxy (-alkylene-OH), a C-2 to C-8 alkyleneoxyalkyl (-alkylene-O-alkyl), and a C-5 to C-15 polyalkyleneoxyakyl (-(alkylene-O)$_{pa}$-alkyl), where pa is an integer ranging from 2 to 4),



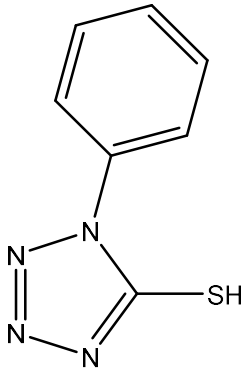
(H1-EB).

14. The composition of any one of claims 1, 2, 5 to 7 and 11, wherein said thiol derivative has structure (H1-EC),



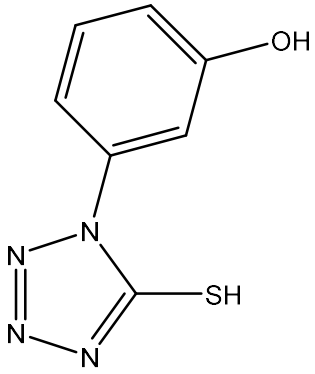
(H1-EC).

15. The composition of any one of claims 1, 2, 5 to 7 and 11, wherein said thiol derivative has structure (H1-ED),



(H1-ED).

16. The composition of any one of claims 1, 2, 5 to 7, 11, and 12, wherein said thiol derivative has structure (H1-EE),



(H1-EE).

17. The composition of any one of claims 1 or 2, wherein said thiol derivative has structure (H4), where Arene is selected from an unsubstituted phenyl, a substituted phenyl, an unsubstituted polycyclic arene moiety and a substituted polycyclic arene moiety.

18. The composition of any one of claims 1 or 2 and 17, wherein said thiol derivative has structure (H4) and said Arene is a substituted or unsubstituted phenyl.

19. The composition of claim 1 wherein said photoresist composition is photoresist compostion I), which is a positive chemically amplified photoresist comprising,

a component comprising a reaction product formed in the absence of an acid catalyst between (i) a Novolak polymer, (ii) a polymer comprising substituted or unsubstituted hydroxystyrene and acrylate, methacrylate or a mixture of acrylate and methacrylate, the acrylate and/or methacrylate being protected by an acid labile group that requires a high activation energy for deblocking, and (iii) a compound selected from a vinyl ether and an unsubstituted or substituted, unsaturated heteroalicyclic;

at least one PAG, and

an organic spin casting solvent.

20. The composition of claim 1 wherein said photoresist composition is photoresist composition II), which is a positive chemically amplified photoresist developable in aqueous base, comprising,

a component comprising a reaction product formed in the absence of an acid catalyst between (i) a Novolak polymer, (ii) a polymer comprising substituted or unsubstituted hydroxystyrene and acrylate, methacrylate or a mixture of acrylate and methacrylate, the acrylate and/or methacrylate being protected by an acid labile group that requires a high activation energy for deblocking, and (iii) a compound selected from a vinyl ether and an unsubstituted or substituted, unsaturated heteroalicyclic;

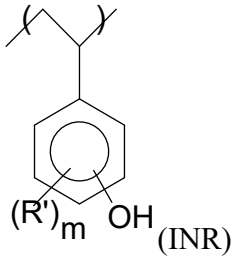
at least one polymer comprising repeat units derived from 4-hydroxystyrene, repeat units derived from an acetal protected 4-hydrostyrene, and a repeat unit derived from a (meth)acrylic acid protected with a high energy protecting group,

at least one PAG, and

an organic spin casting solvent.

21. The composition of claim 1 wherein said photoresist is a negative non-chemically amplified photoresist which is developable in aqueous base comprising,

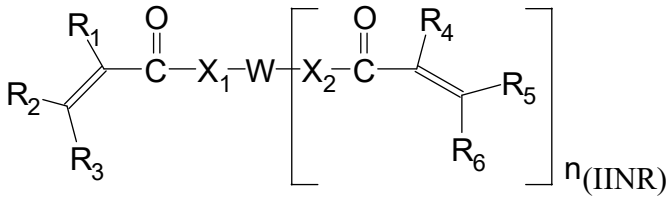
at least one alkali-soluble polymer, where the polymer comprises at least one unit of structure (INR),



(INR)

where, R' is selected independently from hydrogen, (C_1-C_4)alkyl, chlorine and bromine, and m is an integer from 1 to 4;

at least one monomer of structure (IINR),



(IINR)

where, W is a multivalent linking group, R_1 to R_6 are independently selected from hydrogen, hydroxy, (C_1-C_{20}) alkyl and chlorine, X_1 and X_2 are independently oxygen or N-R_7, where R_7 is hydrogen or (C_1-C_{20}) alkyl, and n is an integer equal to or greater than 1; and,

at least one radical photoinitiator and

an organic spin casting solvent.

22. The composition of any one of claim 1 to 18 wherein said photoresist composition is photoresist composition IV), which is a negative non-chemically amplified photoresist, developable in aqueous base, comprising

at least one Novolak type resin which is soluble in 0.26 N TMAH,

at least one radical photoinitiator,

at least one (meth)acrylate crosslinker and

an organic spin casting solvent.

23. The composition of any one of claim 1 to 18 wherein said photoresist composition is photoresist composition V), which is a negative non-chemically amplified (meth)acrylate type photoresist, developable in aqueous base, comprising

at least one (meth)acrylate polymer comprising a (meth)acrylic acid derived repeat unit, a repeat unit derived from at least one of styrene and benzyl (meth)acrylate, which is soluble in 0.26 N TMAH,

at least one radical photoinitiator,

at least one (meth)acrylate crosslinker and

an organic spin casting solvent.

24. The composition of any one of claims 1 to 18 wherein said photoresist composition is a negative chemically amplified photoresist developable in aqueous base.

25. The composition of any one of claims 1 to 18 wherein said photoresist composition is photoresist composition VII), which is a negative chemically amplified photoresist developable in aqueous base, comprising,

at least one phenolic film-forming polymeric binder resin having ring bonded hydroxyl groups, selected from a Novolak resin, a hydroxystyrene copolymer, or mixtures thereof which is soluble in 0.26 N TMAH

at least one PAG,

a crosslinking agent that forms a carbonium ion upon exposure to acid photogenerated by the PAG and which comprises an etherified aminoplast polymer or oligomer and

an organic spin casting solvent.

26. A process of patterning a metal substrate, comprising

i) cleaning a metal substrate overlying a semiconductor with a 1 to 5 wt. % aqueous solution of a tri or dicarboxylic acid, followed by distilled water rinse to obtain a cleaned metal substrate,

ii) spin drying the cleaned metal substrate,

iii) applying the composition of any one of claims 1 to 39 on the cleaned and dry metal substrate to obtain a photoresist coating,

iv) baking the photoresist coating to remove solvent at a temperature between 90 and 120°C,

v) patterning the photoresist with UV radiation followed by development with an aqueous base developer, to obtain a patterned of photoresist etch barrier overlying the metal substrate,

vi) using the patterned photoresist as a etch barrier, treat with a wet acidic chemical etchant to produce an anisotropically etched metal pattern, overlaid with the patterned photoresist etch barrier,

vii) remove the overlying patterned photoresist etch barrier with a stripper, producing an anisotropically etched metal substrate.

27. The process of claim 40, wherein the metal substrate is a metal substrate overlying a semiconductor substrate and step vii) produces an anisotropically etched metal substrate overlying a semiconductor substrate.

28. A process of patterning a metal substrate, to produce an anisotropically etched metal substrate which comprises the following steps:

ia) cleaning a metal substrate overlying a semiconductor with a 1 to 5 wt. % aqueous solution of a tri or dicarboxylic acid, followed by a distilled water rinse to obtain a cleaned metal substrate,

iia) spin drying the cleaned metal substrate,

iiia) applying a composition comprising a thiol derivative on the cleaned metal substrate to obtain a treated metal substrate wherein, said composition comprising a thiol derivative is one where the thiol moiety is attached to an SP2 carbon which is part of a ring which either has structures (H1), (H2) (H3), or (H4), has structure (H1-E), and an organic spin casting solvent wherein said thiol derivative is present at a loading from about 1 wt. % to about 10 wt. % of the composition, and said thiol derivative comprises from about 98 wt. % to 100 wt. % of total solids, and further wherein,

in said structure (H1), Xt is selected from the group consisting of $N(Rt_3)$, $C(Rt_1)(Rt_2)$, O, S, Se, and Te;

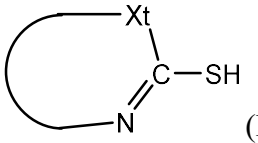
in said structure (H2), Y is selected from the group consisting of $C(Rt_3)$ and N;

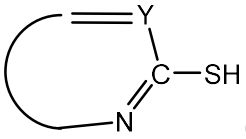
in said structure (H3), Z is selected from the group consisting of $C(Rt_3)$ and N; and

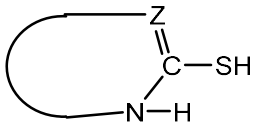
in said structure (H4), where Arene is selected from an unsubstituted phenyl, a substituted phenyl, an unsubstituted polycyclic arene moiety and a substituted polycyclic arene moiety, Rt_1, Rt_2, and Rt_3 are independently is selected from the group consisting of H, a substituted alkyl group having 1 to 8 carbon atoms, an unsubstituted alkyl group having 1 to 8 carbon atoms, a substituted alkenyl group having 2 to 8 carbon atoms, unsubstituted alkenyl group having 2 to 8 carbon atoms, a substituted alkynyl group having 2 to 8 carbon atoms, unsubstituted alkynyl group having 2 to 8 carbon atoms, a substituted aromatic group having 6 to 20 carbon atoms, a substituted heteroaromatic group having 3 to 20 carbon atoms, unsubstituted aromatic group having 6 to 20 carbon atoms and unsubstituted heteroaromatic group having 3 to 20 carbon atoms,

Rt_4 is independently selected from the group consisting of H, OH, a substituted alkyl group having

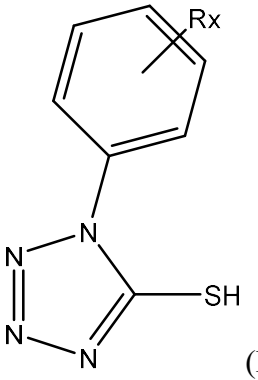
1 to 8 carbon atoms, an unsubstituted alkyl group having 1 to 8 carbon atoms, a substituted alkenyl group having 2 to 8 carbon atoms, unsubstituted alkenyl group having 2 to 8 carbon atoms, a substituted alkynyl group having 2 to 8 carbon atoms, unsubstituted alkynyl group having 2 to 8 carbon atoms, a substituted aromatic group having 6 to 20 carbon atoms, a substituted heteroaromatic group having 3 to 20 carbon atoms, unsubstituted aromatic group having 6 to 20 carbon atoms and unsubstituted heteroaromatic group having 3 to 20 carbon atoms, and where Rx is selected from H, OH, a halide, a C-1 to C-8 alkyl, an aryl, a C-1 to C-8 alkylenehydroxy (-alkylene-OH), a C-2 to C-8 alkyleneoxyalkyl (-alkylene-O-alkyl), and a C-5 to C-15 polyalkyleneoxyakyl (-(alkylene-O)$_{pa}$-alkyl), where pa is an integer ranging from 2 to 4),



(H1)


(H2)


(H3) Rt$_4$-Arene-SH (H4)



(H1-E).

iva) baking the treated metal substrate to remove solvent at a temperature between 90 and 120°C, then rinsing with an organic spin casting solvent.

va) applying a photoresist developable after UV irradiation whit aqueous base to the treated and dry metal substrate to form a photoresist coating,

via) baking the photoresist coating to remove solvent at a temperature between 90 and 120°C,

viia) patterning the photoresist with UV radiation followed by development with an aqueous base developer, to obtain a patterned of photoresist etch barrier overlying the metal substrate,

viiia) using the patterned photoresist as a etch barrier, treat with a wet acidic chemical etchant to produce an anisotropically etched metal pattern, overlaid with the patterned photoresist etch barrier,

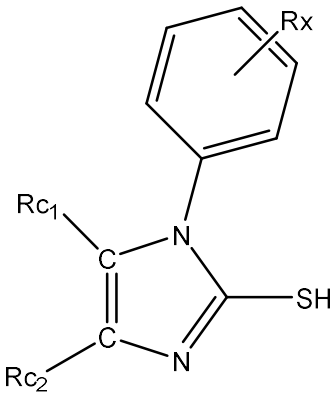
viva) remove the overlying patterned photoresist etch barrier with a stripper, producing an anisotropically etched metal substrate.

29. The process of claim 28, wherein the metal substrate is a metal substrate overlying a semiconductor substrate and further wherein step viva) produces an anisotropically etched metal substrate overlying a semiconductor substrate.

30. The photoresist composition of claim 1 comprising a thiol derivative,

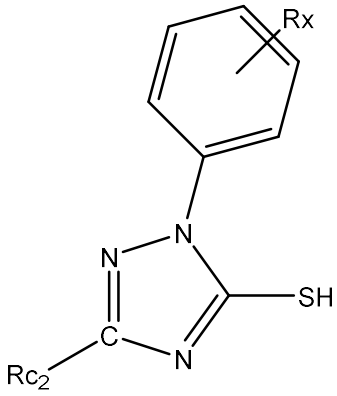
wherein said thiol derivative is selected from the groups consisting of,

a thiol derivative which has structure (H1-B), wherein Rx, is selected from the group consisting of H, OH, a halide, a C-1 to C-8 alkyl, an aryl, a C-1 to C-8 alkylenehydroxy (-alkylene-OH), a C-2 to C-8 alkyleneoxyalkyl (-alkylene-O-alkyl), and a C-5 to C-15 polyalkyleneoxyakyl (-(alkylene-O)$_{pa}$-alkyl), where pa is an integer ranging from 2 to 4), Rc_2 is selected from H and a C-1 to C-8 alkyl, Rc_1 is selected from H and a C-1 to C-8 alkyl,



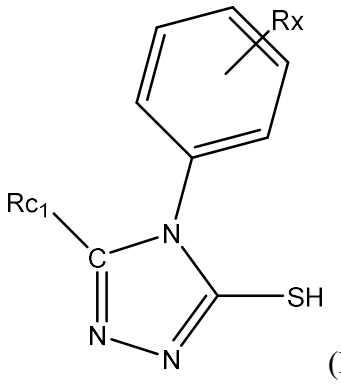
(H1-B),

a thiol derivative which has structure (H1-C), wherein Rc_2 is selected from H and a C-1 to C-8 alkyl, and Rx, is selected from H, OH, a halide, a C-1 to C-8 alkyl, an aryl, a C-1 to C-8 alkylenehydroxy (-alkylene-OH), a C-2 to C-8 alkyleneoxyalkyl (-alkylene-O-alkyl), and a C-5 to C-15 polyalkyleneoxyakyl (-(alkylene-O)$_{pa}$-alkyl), where pa is an integer ranging from 2 to 4),



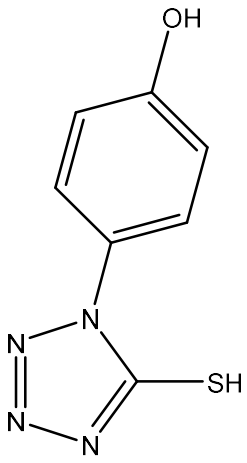
(H1-C),

a said thiol derivative which has structure (H1-D), wherein Rc_1 is selected from H and a C-1 to C-8 alkyl, and Rx, is selected from H, OH, a halide, a C-1 to C-8 alkyl, an aryl, a C-1 to C-8 alkylenehydroxy (-alkylene-OH), a C-2 to C-8 alkyleneoxyalkyl (-alkylene-O-alkyl), and a C-5 to C-15 polyalkyleneoxyakyl (-(alkylene-O)$_{pa}$-alkyl), where pa is an integer ranging from 2 to 4).



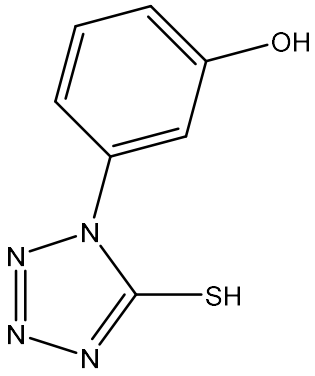
(H1-D),

a thiol derivative has structure (H1-EC),



(H1-EC),

a thiol derivative has structure (H1-EE),



(H1-EE).

a thiol derivative of structure (H4), wherein Rt_4 is selected from an unsubstituted phenyl, a substituted phenyl, an unsubstituted polycyclic arene moiety and a substituted polycyclic arene moiety.

Rt_4-Arene-SH (H4).