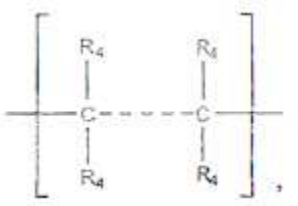
Claims

1. A method of forming a microelectronic structure, said method comprising: providing a substrate having a surface; optionally forming a primer layer on said substrate surface; forming a protective layer on said primer layer, if present, or on said substrate surface if no primer layer is present, to yield a protected stack, said protective layer being formed from a composition comprising a cycloolefin copolymer of recurring cycloolefin monomers and monomers of
(II):



Where: ---- is a single bond; and each R_4 is individually selected from the group consisting of -H, and alkyl groups; said cycloolefin copolymer being dissolved or dispersed in a solvent system,

and subjecting said protected stack to an acidic etching process,

wherein said protective layer will have less than 0.1 pinholes per cm^2 of substrate when observed under a microscope at 10x magnification; if etched said protective layer by 48% by weight aqueous HF solution having a temperature of 20-25 °C, for about 1-2 hours,

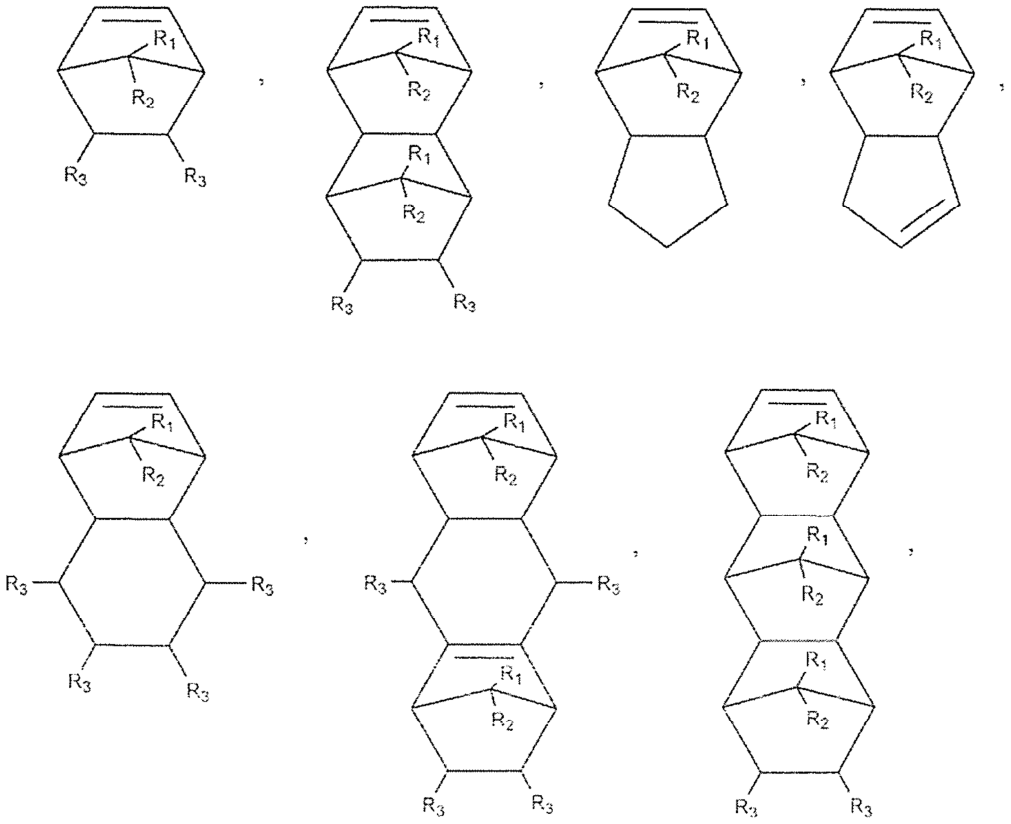
2. The method of claim 1, further comprising subjecting said protected stack to further processing steps prior to subject said stack to said acidic etching process.

3. The method of claim 1, further comprising exposing said protective layer to broadband UV radiation.

4. The method of claim 3, wherein said protective layer is photosensitive and said exposing yields exposed portions of said protective layer, said exposed portions comprising a crosslinked cycloolefin copolymer.

5. The method of claim 1 , wherein said acidic etching process comprises etching with an etchant selected from the group consisting of aqueous HF, HF vapor, HF/H_20 vapor, HF/alcohol vapor, HCl, phosphoric acid, $HCl/HN0_3$, buffered oxide etchant ("BOE ") , HF $/HN0_3/$ acetic acid, concentrated H_2S0_4, concentrated $HN0_3$, and mixtures of the foregoing.

6. The method of claim 1, wherein said cycloolefin copolymer is formed from the polymerization of a cyclic olefin selected from the group consisting of



and combinations of the foregoing,

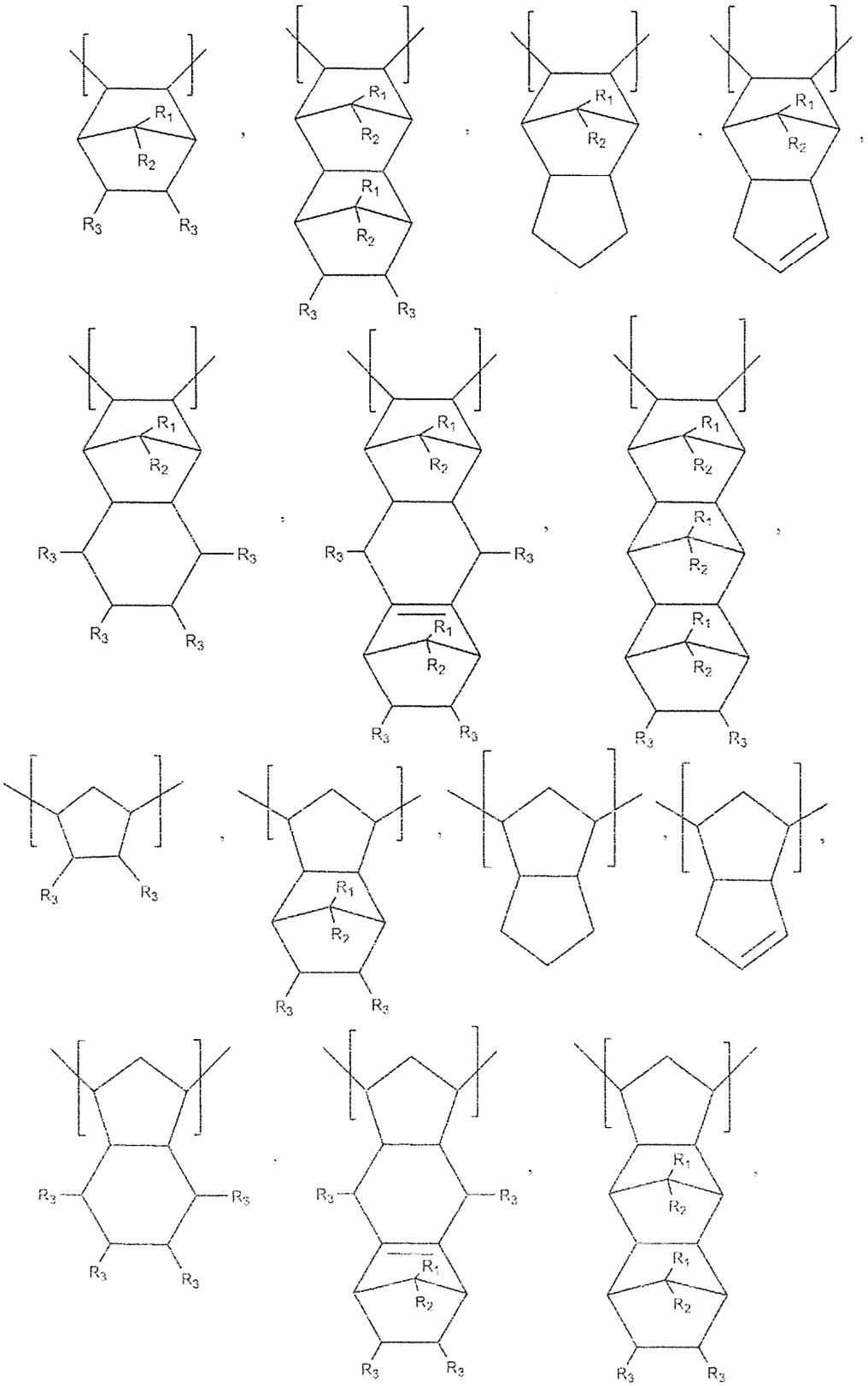
where:

each R_1 and R_2 is individually selected from the group consisting of -H, and alkyl groups; and

each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups, cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, nitriles, and combinations thereof.

7. The method of claim 1, wherein said cycloolefin recurring monomers are selected from the group consisting of:

(I)



and combinations of the foregoing,

where:

each R_1 and R_2 is individually selected from the group consisting of -H, and alkyl groups; and

each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups, cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, combinations thereof.

8. The method of claim 1, wherein a primer layer is formed on said substrate surface.

9. The method of claim 8, wherein said primer layer is formed from composition comprising a basic polymer in a solvent system.

10. The method of claim 9, wherein said basic polymer is selected from the group consisting of polyvinyl pyridine, polymelamines, polyethylenimine, triazine-containing copolymers, styrene maleimide resin, poly (4-vinyl pyridine-co-styrene), and poly (2-vinyl pyridine-co-styrene) .

11. The method of claim 1, wherein said substrate is selected from the group consisting of thermal oxide substrates, Si substrates, $Si0_2$ substrates, Si_3N_4 substrates, $Si0_2$ on silicon substrates, Si_3N_4 on silicon substrates, glass substrates, quartz substrates, ceramic substrates, semiconductor substrates, and metal substrates.

12. An article having a protective layer comprising:

a substrate having a surface;

optionally a primer layer on said substrate surface; and a protective layer on said primer layer, if present, or on said

substrate surface if no primer layer is present, said protective layer being formed from a composition comprising a cycloolefin copolymer of cycloolefin monomers and monomers of

(II):



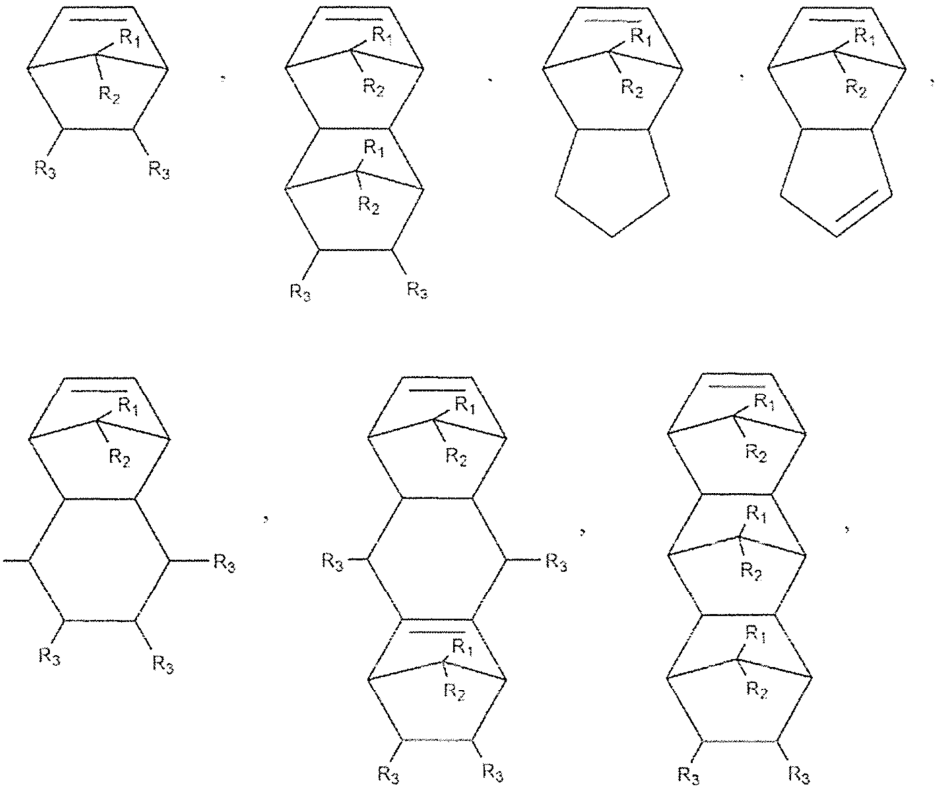
where: ---- is a single bond; and

each R_4 is individually selected from the group consisting of -H, and alkyl groups; said cycloolefin copolymer being dissolved or dispersed in a solvent system,

wherein said protective layer will have less than 0.1 pinholes per cm^2 of substrate when observed under a microscope at 10x magnification; if etched said protective layer by 48% by weight aqueous HF solution having a temperature of 20-25 °C, for about 1-2 hours,.

13. The article of claim 12, wherein said substrate is selected from the group consisting of thermal oxide substrates, Si substrates, SiO_2 substrates, Si_3N_4 substrates, SiO_2 on silicon substrates, Si_3N_4 on silicon substrates, glass substrates, quartz substrates, ceramic substrates, semiconductor substrates, and metal substrates.

14. The article of claim 12, wherein said cycloolefin copolymer is formed from the polymerization of a cyclic olefin selected from the group consisting of



and combinations of the foregoing.

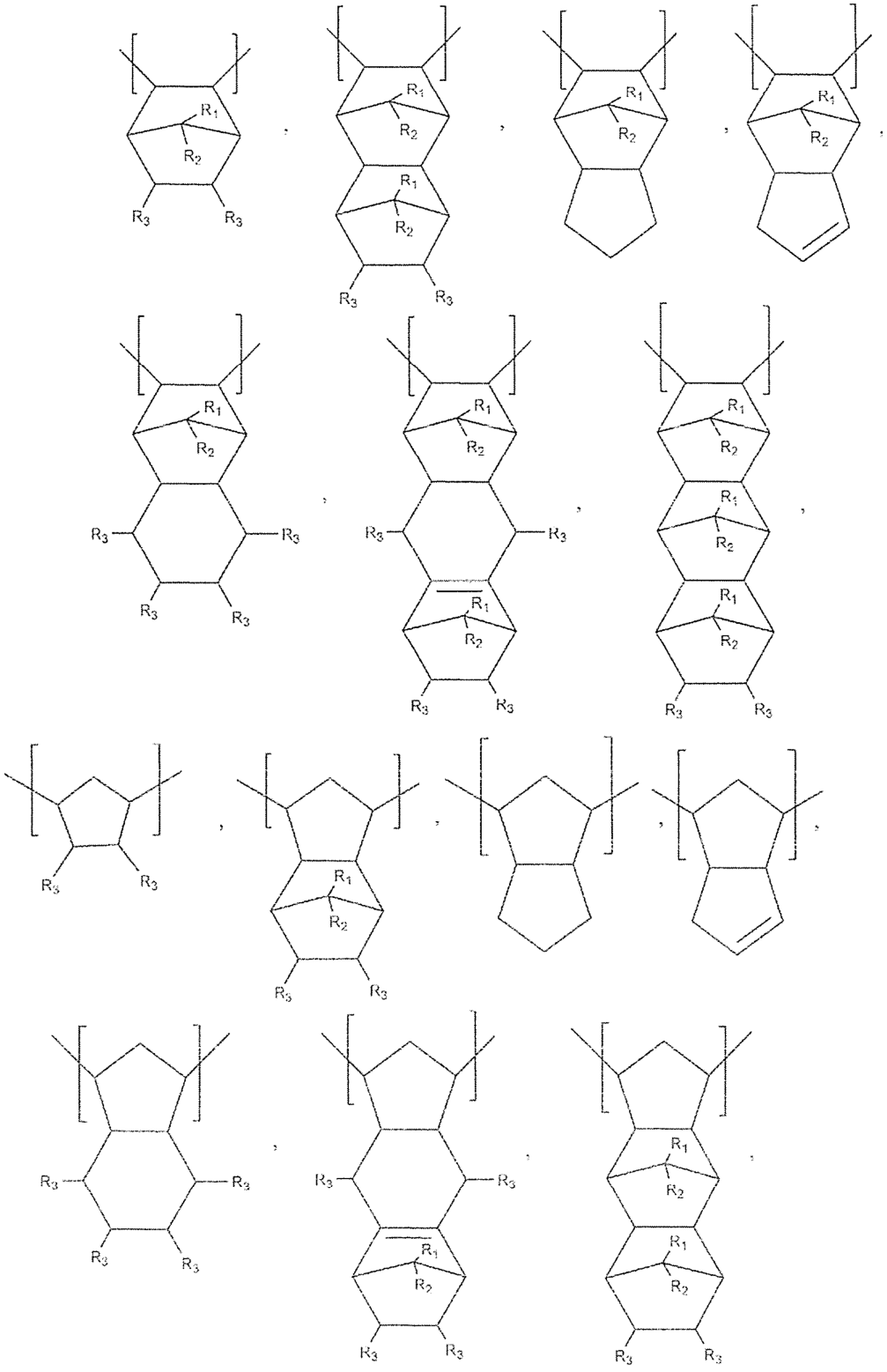
where:

each R_1 and R_2, is individually selected from the group consisting of -H , and alkyl groups; and

R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups , cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, nitriles, and combinations thereof.

15. The article of claim 12, wherein cycloolefin recurring monomers of are selected from the group consisting of:

(I)



and combinations of the foregoing,

where:

each R_1 and R_2 is individually selected from the group consisting of -H, and alkyl groups; and

each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups, cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, nitriles, and combinations thereof.

16. The article of claim 12, wherein said protective layer is photosensitive.

17. The article of claim 12, said protective layer has first and second sides, the first side being positioned said substrate side, and second side being positioned opposite side of the first side, and further comprising an acidic etchant on said second side.

18. The article of claim 17, said acidic etchant selected from the group consisting of aqueous HF, HF vapor, HF/H_20 vapor, HF/alcohol vapor, HCl, phosphoric acid, HCl/$HN0_3$, buffered oxide etchant ("BOE"), HF /$HN0_3$ /acetic acid, concentrated H_2S0_4, concentrated $HN0_3$, and mixtures of the foregoing.

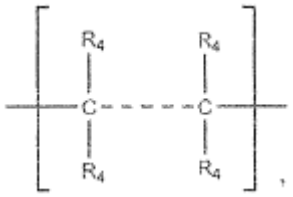
19. The article of claim 12, wherein said article includes a primer layer on said substrate surface.

20. The article of claim 19, wherein said primer layer is formed from a composition comprising a basic polymer in a solvent system.

21. The article of claim 20, wherein said basic polymer is selected from the group consisting of polyvinyl pridine, polymelamines, polyethylenimine, triazine-containing copolymers, styrene maleimide resin, poly (4-vinyl pyridine-co-styrene) , and poly (2-vinyl pyridine -co-styrene) .

22. A composition for forming a protective layer on a substrate, wherein said protective layer will have less than 0.1 pinholes per cm^2 of substrate when observed under a microscope at 10x magnification; if etched said protective layer by 48% by weight aqueous HF solution having a temperature of 20-25 °C, for about 1-2 hours, said composition comprising a cycloolefin copolymer of recurring cycloolefin monomers and monomers of

(II):



where: ---- is a single bond;

each R4 is individually selected from the group consisting of -H, and alkyl groups;

and a photosensitive crosslinking agent dissolved or dispersed in a solvent system.

23. The composition of claim 22, wherein said photosensitive crosslinking agent is selected from the group consisting of

2, 6 -bis - (4-azidobenzylidene) -4-methylcyclohexanone,

2, 6 -bis- (4'-azidobenzal) cyclohexanone,

2, 6 -bis- (4'-diazidobenzal) -4-methylcyclohexanone,

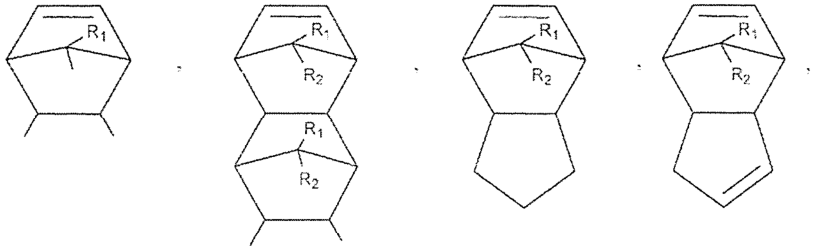
4, 4'- diazidostilbene, p -phenylenebisazide,

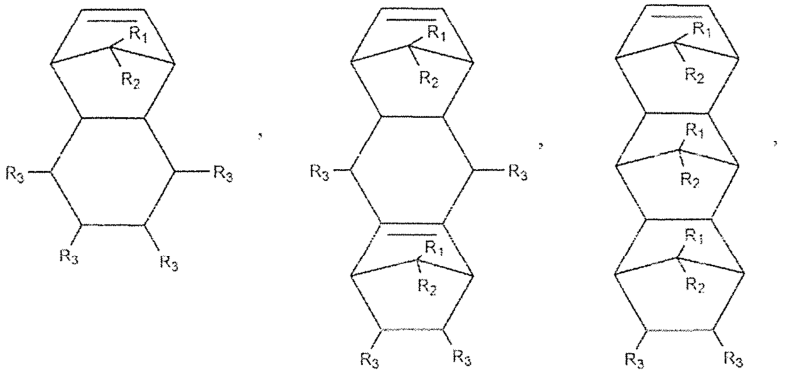
4, 4 '-diazidobenzophenone, 4, 4'-diazidodiphenylmethane,

4, 4 '-diazidocalcon, 4, 4'-diazidodiphenyl,

4, 4'-diazido-3, 3'-dimethyldiphenyl, and 2, 7-diazidofluorene.

24. The composition of claim 22, said cycloolefin copolymer being formed from the polymerization of a cyclic olefin selected from the group consisting of





and combinations of the foregoing,

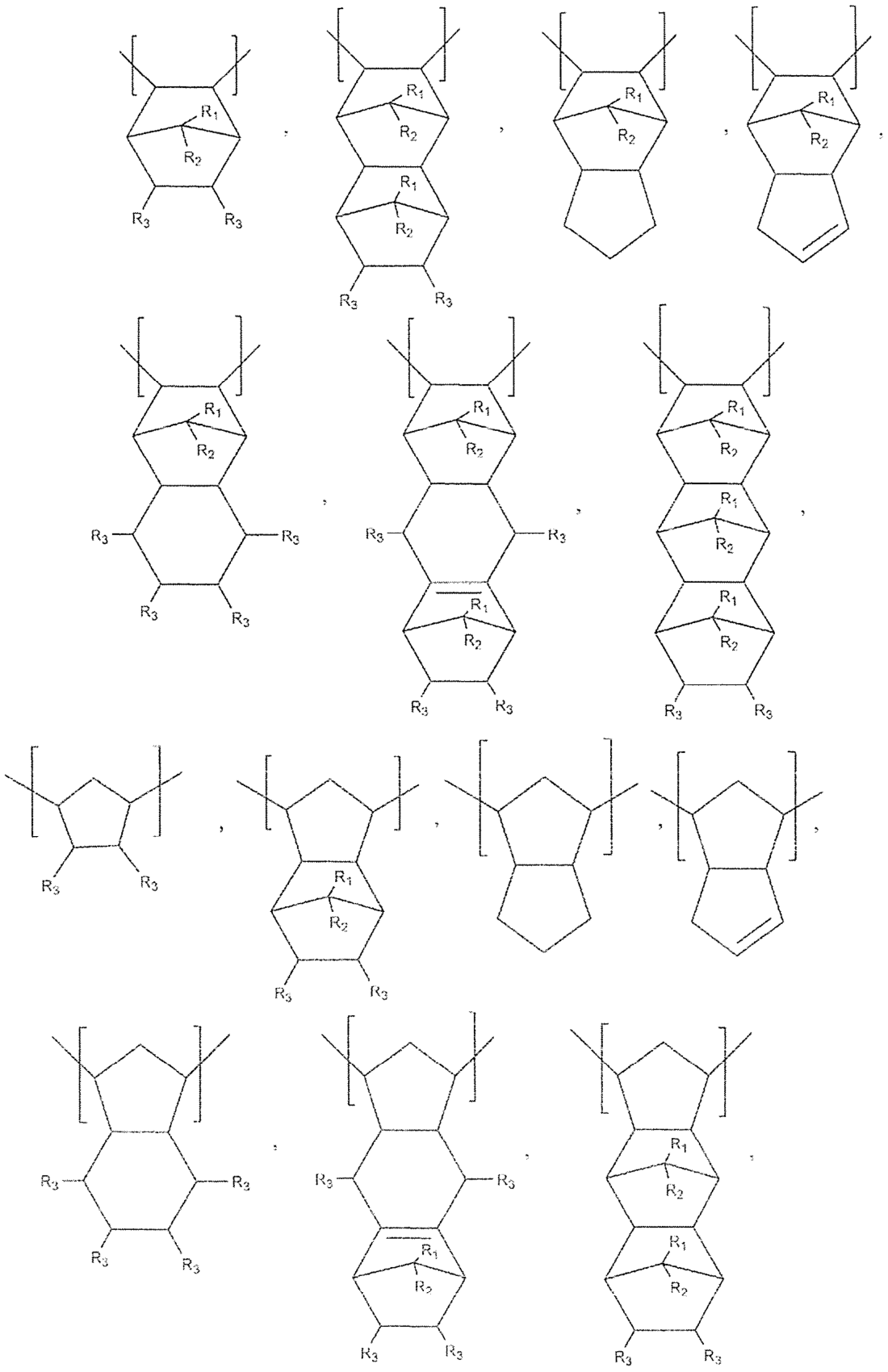
where:

each R_1 and R_2 is individually selected from the group consisting of -H , and alkyl groups; and

each R3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups, cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, nitriles, and combinations thereof.

25. The composition of claim 22, wherein said cycloolelin recurring monomers are selected from the group consisting of:

(I)



and combinations of the foregoing,

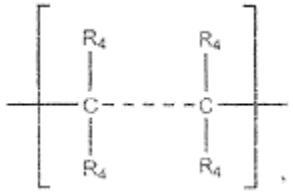
where:

each R_1, and R_2 is individually selected from the group consisting of - H , and alkyl groups; and

each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups, cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, nitriles, and combinations thereof.

26. The method of claim 1, wherein said protective layer exhibits less than 0.1 pinholes per cm^3 of said substrate when observed under a microscope at 10x magnification when subjected said protected stack to said acidic etching process.

27. A method of forming a microelectronic structure, said method comprising:
providing a substrate having a surface;
optionally forming a primer layer on said substrate surface;
forming a protective layer on said primer layer, if present, or on said substrate surface if no primer layer is present, to yield a protected stack, said protective layer being formed from a composition comprising a cycloolefin copolymer of recurring cycloolefin monomers and monomers of
(II):



where: ---- is a single bond;

each R_4 is individually selected from the group consisting of -H, and alkyl groups;
wherein said cycloolefin copolymer and a photosensitive crosslinking agent are dissolved or dispersed in a solvent system; and subjecting said protected stack to an acidic etching process,

wherein said protective layer will have less than 0. 1 pinholes cm_2 of substrate when observed under a microscope at 10x magnification; if etched said protective layer by 48% by weight aqueous HF solution having a temperature of 20-2S °C, for about 1-2 hours.

28. The method of claim 27, wherein said crosslinking agent is an azide-based photosensitive crosslinking agent.

29. The method of claim 1, wherein said cycloolefin copolymer has a glass transition temperature (Tg) of from 60°C to 200°C.

30. The method of claim 27, wherein said cycloolefin copolymer has a glass transition temperature (Tg) of from 60°C to 200°C.