SPIN-ON CARBON COMPOSITIONS FOR LITHOGRAPHIC PROCESSING

BACKGROUND OF THE INVENTION

Related Applications

This application claims the priority benefit of a provisional application entitled SPIN-ON CARBON COMPOSITIONS FOR LITHOGRAPHIC PROCESSING, Serial No. 61/545,313, filed October 10, 2011, incorporated by reference herein.

Field of the Invention

The present invention relates to methods of forming a carbon-rich (spin-on carbon) layer from a polyamic acid for use in a multilayer stack and the microelectronic structures thereof.

Description of the Prior Art

As the semiconductor industry continues to shrink the size of features, a single layer photoresist lacks sufficient thickness to complete pattern transfer to a substrate. As a result, trilayer stacking (photoresist-hardmask-carbon layers) is typically used to transfer the pattern made by the photoresist to the substrate. The carbon layer can be formed by chemical vapor deposition (CVD) or spin-coating. However, CVD processes are expensive, have low-throughput, and subject the wafer to harsh conditions. Currently, epoxy cresol novolacs are the most common material for fabrication of spin-on carbon ("SOC") layers, but this material has low thermal stability and low carbon content, leading to high sublimation and poor wiggling resistance during pattern transfer to silicon substrates. Additionally such a layer is difficult to remove after curing. Other SOC layers have been formed that are removable by dry etching. However, drying etching requires harsh processing conditions and special equipment, making the process less than desirable.

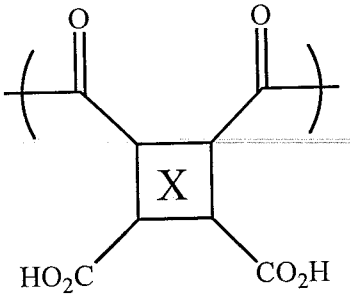
There is a need for improved SOC layers that exhibit high thermal stability and optical constants, while also being wet removable (developer soluble). Furthermore, these layers should prevent or minimize line "wiggling," which is present in many prior art processes.

SUMMARY

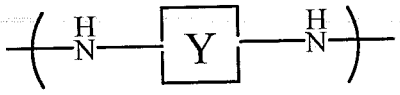
The present disclosure provides a method of forming a microelectronic structure. The method comprises providing a substrate having a surface. Optionally, one or more intermediate

layers are formed on the surface, there being an uppermost intermediate layer on the surface, if one or more intermediate layers are present. A composition is applied to the uppermost intermediate layer, if present, or to the substrate surface, if no intermediate layers are present. The composition comprises a polyamic acid dissolved or dispersed in a solvent system. The composition is heated to form a spin-on carbon or carbon-rich layer, with the carbon-rich layer being developer soluble, and exhibiting a weight loss of less than about 10% at a temperature of about 400°C for about 10 minutes.

In one aspect, there is provided a method of forming a microelectronic structure, said method comprising: providing a substrate having a surface; optionally forming one or more intermediate layers on said substrate surface, there being an uppermost intermediate layer on said substrate surface, if one or more intermediate layers are present; applying a composition to said uppermost intermediate layer, if present, or to said substrate surface, if no intermediate layers are present, said composition comprising a polyamic acid dissolved or dispersed in a solvent system, wherein said polyamic acid includes recurring monomers having the formulas



and



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where each of X and Y is individually selected from the group consisting of aliphatic and aryl groups; heating said composition to form a carbon-rich layer, said carbon-rich layer being capable of being removed with an aqueous alkaline developer, and exhibiting a weight loss of less than about 10% at a temperature of about 400°C for about 10 minutes.

The present disclosure also provides a novel microelectronic structure. The structure comprises a microelectronic substrate having a surface and optionally one or more intermediate layers on the surface. There is an uppermost intermediate layer on the surface, if one or more intermediate layers are present. A carbon-rich layer is on the uppermost intermediate layer, if present, or on the substrate surface, if no intermediate layers are present.

The carbon-rich layer: comprises a crosslinked polyamic acid; is developer soluble; and exhibits a weight loss of less than about 10% at a temperature of about 400°C for about 10 minutes.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

Figure ("Fig.") 1 is a scanning electron microscope ("SEM") photograph of the positive-tone development photolithography (40L/80P, 16.8 mJ) demonstrated in Example 26;

Fig. 2 is an SEM photograph of the negative-tone development photolithography (53S/105P, 19.6 mJ) carried out in Example 27;

Fig. 3 is an SEM photograph of the etched, spin-on carbon layer formed in Example 28;

Fig. 4 shows the thermogravimetric analysis ("TGA") curve of SOC formulation E-2 from Example 29;

Fig. 5 is an SEM photograph of SOC formulation E-2 filling isolated deep contact hole, as described in Example 30;

Fig. 6 is an SEM photograph of SOC formulation E-2 filling dense deep contact hole, as described in Example 30;

Fig. 7 is an SEM photograph showing an OptiStack® SOC110D pattern after C_4F_8/Ar etching, as described in Example 32; and

Fig. 8 is an SEM photograph showing the pattern of Formulation E-2 after C_4F_8/Ar etching, as described in Example 33.

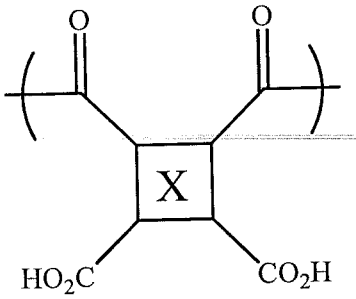
We Claim:

1. A method of forming a microelectronic structure, said method comprising:

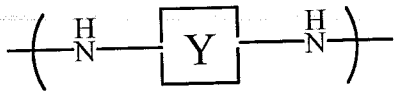
providing a substrate having a surface;

optionally forming one or more intermediate layers on said substrate surface, there being an uppermost intermediate layer on said substrate surface, if one or more intermediate layers are present;

applying a composition to said uppermost intermediate layer, if present, or to said substrate surface, if no intermediate layers are present, said composition comprising a polyamic acid dissolved or dispersed in a solvent system, wherein said polyamic acid includes recurring monomers having the formulas



and



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where each of X and Y is individually selected from the group consisting of aliphatic and aryl groups;

heating said composition to form a carbon-rich layer, said carbon-rich layer being capable of being removed with an aqueous alkaline developer, and exhibiting a weight loss of less than about 10% at a temperature of about 400°C for about 10 minutes.

2. The method of claim 1, there being at least one intermediate layer on said substrate surface.

3. The method of claim 1, further comprising forming an imaging layer on said carbon-rich layer.

4. The method of claim 1, further comprising forming at least one additional intermediate layer on said carbon-rich layer.

5. The method of claim 4, further comprising forming an imaging layer on said at least one additional intermediate layer.

6. The method of claim 1, wherein said composition comprises greater than about 50% by weight carbon, based upon the weight of the solids in the composition taken as 100% by weight.

7. The method of claim 1, wherein said composition comprises less than about 10% by weight hydrogen, based upon the total weight of the total solids in the composition taken as 100% by weight.

8. The method of claim 1, wherein said carbon-rich layer comprises greater than about 50% by weight carbon, based upon the weight of the layer taken as 100% by weight.

9. The method of claim 1, wherein said carbon-rich layer comprises less than about 10% by weight hydrogen, based upon the total weight of the layer taken as 100% by weight.

10. The method of claim 1, wherein said polyamic acid is a copolymer of a dianhydride and a diamine, wherein:

said dianhydride is selected from the group consisting of 5-(2,5-dioxotetrahydrol)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride, cyclobutane tetracarboxylic dianhydride, 1,2,3,4-cyclopentanetetracarboxylic acid dianhydride, tetrahydrofuran-2,3,4,5-tetracarboxylic dianhydride, 4-(2,5-

dioxotetrahydrofuran-3-yl)-1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic anhydride, bicyclo (2,2,2) oct-7-ene-2,3,5,6-tetracarboxylic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride, pyromellitic dianhydride, 3,3',4,4'-biphenyl tertracarboxylic dianhydride, 2,2'-bis-(3,4-dicarboxy phenyl) hexafluoropropane dianhydride, 4,4'-oxydiphthalic anhydride, 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride, 4,4'-bisphenol A dianhydride, hydroquinone diphtatic anhydride, 3,4,9,10-perylene-tetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, and ethylene glycol bis(trimellitic anhydride); and

said diamine is selected from the group consisting of 1,3-bis(aminomethyl)-cyclohexane, 1,4-bis(aminimethyl)-cyclohexane, 4,4'-methylenebis(cyclohexylamine), 4,4'-methylene bis(2-methylcyclohexyl)amine, 3-aminobenzylamine, 1,3-bis(3-aminophenoxy)-benzene, 1,3-bis(4-aminophenoxy)-benzene, 1,4-bis(4-aminophenoxy)benzene, 4,4'-bis(4-aminophenoxy)-biphenyl, 2,2-bis[4-4-aminophenoxy)-phenyl] hexafluoroproprane, bis[4-(4-aminophenoxy)-phenyl] propane, bis[4-(4-aminophenoxy)-phenyl] sulfone, bis[4-(4-aminophenoxy)-phenyl] sulfone, 1,1'-bis(4-aminophenyl)-clohexane, 9,9'-bis(4-aminophenyl0-fluorene, 2,2'-bis(4-aminophenyl)-hexafluoropropane, bis(2-aminophenyl) sulfide, bis(4-aminophenyl) sulfide, bis(3-aminophenyl) sulfone, bis(4-aminophenyl) sulfone, 4,4'-diamino-3,3'-dimethyl-diphenylmethane, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl methane, 3,4'-diaminodiphenyl methane, 2,7-diaminofluorene, 1,5-diaminonaphthalene, 4,4'-diaminooctafluorobiphenyl, 2,5-dimethyl-1,4-phenylenediamine, 4,4'-ethylenedianiline, 1,3-phenylenediamine, 1,4-phenylenediamine, 2,3,5,6-tetramethyl-1,4-phenylenediamine, m-xylylenediamine, and p-xylylenediamine.

11. The method of claim 1, wherein said polyamic acid has a weight average molecular weight of less than about 15,000 Daltons.

12. The method of claim 1, said composition further comprising a crosslinking agent.

13. The method of claim 1, wherein said heating results in crosslinking of said polyamic acid.

14. The method of claim 1, wherein said substrate is a microelectronic substrate selected from the group consisting of silicon, SiGe, SiO_2, Si_3N_4, SiON, aluminum, tungsten, tungsten silicide, gallium arsenide, germanium, tantalum, tantalum nitride, coral, black diamond, phosphorous or boron doped glass, Ti_3N_4, hafnium, HfO_2, ruthenium, indium phosphide, and mixtures of the foregoing.

15. The method of claim 1, wherein said carbon-rich layer has an n value of at least about 1.40.

16. The method of claim 1, said method further comprising:

optionally forming one or more intermediate layers on said carbon-rich layer, there being an uppermost intermediate layer on said carbon-rich layer, if one or more intermediate layers are present on said carbon-rich layer; and

forming an imaging layer on said uppermost intermediate layer on said carbon-rich layer, if present, or on said carbon-rich layer, if no intermediate layers are present on said carbon-rich layer.

17. The method of claim 16, said method further comprising:

patterning said imaging layer to form a pattern therein; and

transferring said pattern to said intermediate layers on said carbon-rich layer, if present, and to said carbon-rich layer, wherein said pattern comprises a plurality of lines, and said lines exhibit little to no wiggling.

18. The method of claim 17, wherein said patterning comprises:

exposing said imaging layer to light to yield light-exposed portions of the imaging layer; and

contacting said imaging layer with a developer after light exposure so as to remove said light-exposed portions.

19. The method of claim 18, wherein said contacting results in portions of said carbon-rich layer being removed, thus forming said lines.

20. The method of claim 1, said carbon-rich layer exhibiting a weight loss of less than about 5% at a temperature of about 400°C for about 10 minutes.

21. The method of claim 20, said carbon-rich layer exhibiting a weight loss of about 0% at a temperature of about 400°C for about 10 minutes.

22. The method of claim 1, said carbon-rich layer being capable of being removed with an aqueous alkaline developer selected from the group consisting of tetramethyl ammonium hydroxide, potassium hydroxide, sodium hydroxide, and mixtures thereof.

23. The method of claim 1, wherein said carbon-rich layer is soluble in an aqueous alkaline developer.