Supercritical carbon dioxide may be utilized to remove fluorine-based etch residues such as those residues left when etching dielectrics in fluorine-based plasma gases. The supercritical carbon dioxide may have dissolved in it various reagents and fluorocarbon materials that, together, cause the residue to swell and to be exposed for reactions with the reagents, the supercritical carbon dioxide, and the fluorocarbons. As a result, relatively hard to penetrate fluorine-based residues may be entered and removed using aggressive chemistries.
SCCO₂ + FLUOROCARBON + REAGENT

RESIDUE

DIELECTRIC

FIG. 1

SWOLLEN RESIDUE

DIELECTRIC

FIG. 2

DIELECTRIC

FIG. 3
REMOVING FLUORINE-BASED PLASMA ETCH RESIDUES

BACKGROUND

[0001] This invention relates generally to processes for manufacturing semiconductor integrated circuits and, particularly, to the removal of residues from fluorine-based plasma etching.

[0002] Fluorine-based plasma etching is commonly used to etch photoresist to generate patterns on a semiconductor device. A residue is left behind on the etched wafer that essentially includes constituents of the plasma gas and the material etched. Normally, gases composed of carbon and fluorine are used for plasma etching resulting in a residue made of carbon and fluorine. Further, the residue may be polymerized due to the generation of free radicals and ions in the high-energy plasma environment.

[0003] Particularly with photoresists in advanced semiconductor processes, such as the 193 nm photoresist, wherein a fluorine-rich plasma etch is used, and with 157 nm, in which case the photoresist itself being fluorine-based. This residue may include carbon, hydrogen, and fluorine, and is highly chemically inert and is, therefore, relatively difficult to remove with conventional wet chemical etches. The use of delicate interlayer dielectrics, including porous materials, may prevent the use of ashing for residue removal. Conventional wet cleans may not work well with this relatively inert chemical residue. Few liquid solvents can penetrate fluorine-based polymers like teflon.

[0004] Thus, there is a need for a better way to remove fluorine-based etch residues.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] FIG. 1 is an enlarged schematic depiction of one embodiment of the present invention;

[0006] FIG. 2 is an enlarged cross-sectional view which schematically depicts the result of the process illustrated in FIG. 1 in accordance with one embodiment of the present invention; and

[0007] FIG. 3 shows the removal of the swollen residue in accordance with one embodiment of the present invention.

DETAILED DESCRIPTION

[0008] Supercritical carbon dioxide has gas-like diffusivity and viscosity and liquid-like densities, while being almost chemically inert, hence a host of chemically reactive agents are almost always used in conjunction during supercritical carbon dioxide-based cleans. Carbon dioxide becomes supercritical at temperatures above 30°C and pressures above 1000 pounds per square inch.

[0009] Fluorine-based and siloxane-based polymers interact favorably with supercritical carbon dioxide. Supercritical carbon dioxide can dissolve in a fluorine-based polymer and the polymer in turn can dissolve in supercritical carbon dioxide based on the molecular weight, cross-linking density, and side groups involved. Further, small chains of fluorocarbons, such as perfluoroalkanes, perfluoroaromatics, and perfluoro-cyclohydrocarbons, are soluble in supercritical carbon dioxide and can be used as co-solvents.

[0010] Dissolved fluorocarbons in supercritical carbon dioxide may be quickly transported into residues left after fluorine-based etches of photoresist due to the high diffusivity of supercritical carbon dioxide and, particularly, the diffusivity of supercritical carbon dioxide in polymers and small molecules in polymers swollen by supercritical carbon dioxide. Since the fluorocarbons are chemically similar to the etch residue, the etch residue swells. This further increases the access of the supercritical carbon dioxide into the interior of the etch residue and weakens the residue. The fluorocarbon also breaks into the hard crust of the residue, which the supercritical carbon dioxide by itself may be unable to enter and swell, to introduce the reactive agents into the residue.

[0011] A variety of chemically reactive agents are soluble in supercritical carbon dioxide, such as solvents for dimethyl acetamide (DMAC), sulfolane, organic peroxides, ethers, glycols, organic bases, and strong organic and mineral acids, to mention a few examples. The higher degree of swelling of the fluorine-based residue by fluorocarbons dissolved in supercritical carbon dioxide and increased diffusion of supercritical carbon dioxide and the dissolved reagents therein (fluorocarbons and the other chemical reagents) may enhance residue deterioration and removal. A high flow rate of supercritical carbon dioxide may lend the ability to use highly reactive chemicals as opposed to conventional wet chemistries, which have a long contact time with the dielectric material.

[0012] Thus, the supercritical carbon dioxide plus fluorocarbons and chemical reagents may be used to attack residues remaining after fluorine-based etches, such as fluorine-based plasma etches of photoresist. The residue may swell as a result of interaction with the supercritical carbon dioxide, with the fluorocarbon aiding in the swelling process. The supercritical carbon dioxide may act as a carrier and an additional swelling agent.

[0013] Thus, referring to FIG. 1, a residue may be left on a dielectric material following the etching of the photoresist. The residue may then be exposed to supercritical carbon dioxide containing fluorocarbon and active chemical reagents. This may result in swollen residue as shown in FIG. 2. The swollen residue may be removed by the supercritical carbon dioxide as shown in FIG. 3.

[0014] While the present invention has been described with respect to a limited number of embodiments, those skilled in the art will appreciate numerous modifications and variations therefrom. It is intended that the appended claims cover all such modifications and variations as fall within the true spirit and scope of this present invention.

What is claimed is:

1. A method comprising:

   forming a fluorine-based etch residue on a dielectric or having a fluorine-based photoresist to begin with as in 157 nm process; and
   exposing said dielectric to supercritical carbon dioxide.

2. The method of claim 1 including removing said etch residue using said supercritical carbon dioxide.

3. The method of claim 2 including providing a fluorocarbon material with said supercritical carbon dioxide.
4. The method of claim 1 including providing a reagent that is soluble in supercritical carbon dioxide to dissolve said residue.

5. The method of claim 1 including causing the fluorine-based etch residue to swell.

6. A cleaner for cleaning fluorine-based etch residue comprising:
   supercritical carbon dioxide;
   a fluorocarbon material; and
   at least one chemical reagent that is soluble in supercritical carbon dioxide.

7. The cleaner of claim 6 wherein said fluorocarbon is selected from the group consisting of perfluoralkanes, perfluoroaromatics, and perfluoro-cyclohydrocarbons.

8. The cleaner of claim 6 wherein the chemically reactive agent is selected from the group composed of dimethyl acetamide, sulfolane, organic peroxides, ethers, glycols, organic bases, and organic and mineral acids.

9. A method comprising:
   exposing a fluorine-based etch residue to supercritical carbon dioxide and a fluorocarbon;
   causing said fluorine-based etch residue to swell; and
   cleaning said fluorine-based etch residue.

10. The method of claim 9 including providing a reagent that is soluble in supercritical carbon dioxide to dissolve said residue.

11. The method of claim 9 including breaking through the hard crust of the residue using the fluorocarbon.

12. The method of claim 11 including introducing a reactive agent into said residue after breaking through said hard crust using the fluorocarbon.

13. The method of claim 9 including flowing said supercritical carbon dioxide over said residue.

14. The method of claim 9 including exposing said residue to a fluorocarbon selected from the group including perfluoralkanes, perfluoroaromatics, and perfluoro-cyclohydrocarbons.

15. The method of claim 9 including removing dissolved residues in a flow of supercritical carbon dioxide.

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