[0006] Bowing may result from sidewall etching of the mask layer, which may often be an amorphous carbon (a-C) material. The a-C materials may be etched by oxygen radicals in the plasma which may cause increased opening of the mask and result in bow-like, or angled/curved, etch structures.

[0007] Iodine-containing compounds have been used as etching gases and/or reduction of global warming potential (GWP). For example, Gupta et al. (US 10,607,850) disclose the iodine-containing etching compound has the formula $C_aH_xF_yI_z$, wherein a=1-3, x=0-6, y=1-7, z=1-2, x+y+z=4 when a=1, x+y+z=4 or 6 when a=2, x+y+z=6 or 8 when a=3. Chung (US Pat. No. 9,460,935) discloses etching first and second etching layers under plasma generated using, among others, 1,1,2,2-tetrafluoro-1-iodo-ethane. See also Karecki et al., "Plasma etching of dielectric films with novel iodofluorocarbon chemistries: iodotrifluoroethylene and 1-iodoheptafluoropropane", J. Vac. Sci. Technol. A 16, 755 (1998); JP2006/108484; and TWI343601. Iodine-containing etching compounds have been shown significant reductions in global warming emissions compared to perfluorocarbon compounds (see S. Karecki, L. Pruette, and R. Reif, J. Electrochem. Soc. 145, 4305 (1998))

[0008] It is important to minimize bowing and to achieve high aspect ratio (*i.e.*, up to 200:1) needed for current applications (*e.g.*, contact etch or 3D NAND). Additionally, etching today has not been limited to selectivity to the photoresist mask. It is equally important to get high selectivity among other materials such as a-C, SiN, p-Si, SiC or other forms of $Si_aC_bO_cH_dN_e$ materials (where a>0; b, c, d and e ≥0).

[0009] Thus, a need remains for etch gas compositions suitable for use in plasma etching applications which maintain selectivity and high aspect ratios for a wide range of process conditions.

Summary

[0010] Disclosed are methods of forming a patterned structure, the method comprising:

introducing a vapor of an iodine-containing etching compound into a reaction chamber containing a substrate having a silicon-containing film disposed thereon and a patterned mask layer disposed on the silicon-containing film, wherein the iodine-containing etching compound has the formula $C_nH_xF_yI_z$, wherein $4 \leq n \leq 10$, $0 \leq x \leq 21$, $0 \leq y \leq 21$, and $1 \leq z \leq 4$;

activating a plasma to produce an activated iodine-containing etching compound; and

allowing an etching reaction to proceed between the activated iodine-containing etching compound and the silicon-containing film to selectively etch the silicon-containing film from the patterned mask layer, thereby forming the patterned structure. The disclosed methods may include one or more of the following aspects:

- introducing the iodine-containing etching compound separately from the additional etch gas;
- adding approximately 0.01% v/v to approximately 99.99% v/v of the additional etch gas to the iodine-containing etching compound;
- activating the plasma by applying RF power;
- activating the plasma by a RF power ranging from approximately 25 W to approximately 100,000 W;
- etching pressure ranging from approximately 1 mTorr to approximately 10 Torr;
- etching pressure being 30 mTorr;
- introducing the iodine-containing etching compound at a flow rate ranging from approximately 0.1 sccm to approximately 1 slm;
- maintaining the substrate at a temperature ranging from approximately -196°C to approximately 500°C;
- maintaining the substrate at a temperature ranging from approximately -120°C to approximately 300°C;
- maintaining the substrate at a temperature ranging from approximately -100°C to approximately 50°C;
- maintaining the substrate at a temperature ranging from approximately -10°C to approximately 40°C; and
- measuring the iodine-containing etching compound under plasma by Quadrupole mass spectrometer, optical emission spectrometer, FTIR, or other radical/ion measurement tool.

[0011] Also disclosed are methods of reinforcing, strengthening and/or minimizing damage of a patterned mask layer while forming a patterned structure in a substrate, the method comprising:

introducing a vapor of an iodine-containing etching compound into a reaction chamber containing a substrate having a silicon-containing film disposed thereon and the patterned mask layer disposed on the silicon-containing film, wherein the iodine-containing etching compound has the formula $C_nH_xF_yI_z$, wherein $4 \leq n \leq 10$, $0 \leq x \leq 21$, $0 \leq y \leq 21$, and $1 \leq z \leq 4$; and

etching the silicon-containing film from the patterned mask layer to form the patterned structure using an activated iodine-containing etching compound formed by activating a plasma,

wherein the activated iodine-containing etching compound produces iodine ions, which are implanted into the patterned hardmask layer, thereby strengthening the patterned mask layer. The disclosed methods may include one or more of the following aspects:

- the iodine-containing etching compound being a fluorine-containing hydrocarbon compound;
- the iodine-containing etching compound being a fluorocarbon compound;
- the iodine-containing etching compound being an organofluorine compound;
- the iodine-containing etching compound being a hydrocarbon compound;
- the activated iodine-containing etching compound produces iodine ions that strengthens the patterned mask layer;
- the iodine-containing etching compound is C_4F_9I, $C_5F_{11}I$, $C_6F_{13}I$, $C_7F_{15}I$, $C_8F_{17}I$, $C_9F_{19}I$ $C_{10}F_{21}I$ or their isomers; and
- the iodine-containing etching compound is C_4F_9I or its isomers.

[0012] Also disclosed are method of increasing etch resistance of a patterned mask layer, for example, by doping with iodine the pattern mask layer and/or by modifying with iodine the surface of the pattern mask layer, in a process of forming a patterned structure in a substrate, the method comprising:

introducing a vapor of an iodine-containing etching compound into a reaction chamber containing a substrate having a silicon-containing film disposed thereon and the patterned mask layer disposed on the silicon-containing film, wherein the iodine-containing etching compound has the formula $C_nH_xF_yI_z$, wherein $4 \leq n \leq 10$, $0 \leq x \leq 21$, $0 \leq y \leq 21$, and $1 \leq z \leq 4$;

activating a plasma to produce an activated iodine-containing etching compound capable of doping iodine into the patterned mask layer; and

implanting iodine ions from the activated iodine-containing etching compound into the patterned mask layer while etching the silicon-containing film from the patterned mask layer to form the patterned structure, thereby modifying the patterned mask layer with iodine to increase the etch resistance of the patterned mask layer. The disclosed methods may include one or more of the following aspects:

- the iodine-containing etching compound being a fluorine-containing hydrocarbon compound;
- the iodine-containing etching compound being a fluorocarbon compound;
- the iodine-containing etching compound being a hydrocarbon compound;
- the iodine-containing etching compound being an organofluorine compound;
- the iodine-containing etching compound is C_4F_9I, $C_5F_{11}I$, $C_6F_{13}I$, $C_7F_{15}I$, $C_8F_{17}I$, $C_9F_{19}I$ and$C_{10}F_{21}I$ or their isomers;
- the iodine-containing etching compound is C_4F_9I or its isomers;

- implanting the iodine ion from the activated iodine-containing etching compound into the surface and/or the bulk of the patterned mask layer while etching the silicon-

What is claimed is:

1. A method for forming a patterned structure, the method comprising the steps of:

introducing a vapor of an iodine-containing etching compound into a reaction chamber containing a substrate having a silicon-containing film disposed thereon and a patterned mask layer disposed on the silicon-containing film, wherein the iodine-containing etching compound has the formula $C_nH_xF_yI_z$, wherein $4 \leq n \leq 10$, $0 \leq x \leq 21$, $0 \leq y \leq 21$, and $1 \leq z \leq 4$;

activating a plasma to produce an activated iodine-containing etching compound; and

allowing an etching reaction to proceed between the activated iodine-containing etching compound and the silicon-containing film to selectively etch the silicon-containing film from the patterned mask layer, thereby forming the patterned structure.

2. The method of claim 1, further comprising the step of introducing an oxidizer into the reaction chamber, wherein the oxidizer is selected from O_2, O_3, CO, CO_2, NO, N_2O, NO_2, H_2O, H_2O_2, COS, SO_2 and combinations thereof.

3. The method of claim 1, further comprising the step of introducing an inert gas into the reaction chamber, wherein the inert gas is selected from the group consisting of He, Ar, Xe, Kr, Ne and N_2.

4. The method of claim 1, wherein the iodine-containing etching compound is C_4F_9I or its isomers.

5. The method of claim 1, wherein the silicon-containing film comprises a layer of silicon oxide (SiO), silicon nitride (SiN), crystalline Si, poly-silicon (p-Si), polycrystalline silicon, amorphous silicon, low-*k* SiCOH, SiOCN, SiC, SiON and $Si_aO_bH_cC_dN_e$, where $a>0$; b, c, d and $e \geq 0$, alternating SiO and SiN (ONON) layers, alternating SiO and p-Si (OPOP) layers.

6. The method of any claims from 1 to 5, wherein an etch rate of etching the silicon oxide layer using the iodine-containing etching compound is higher than an etch rate of etching the silicon oxide layer using as an alternative etching gases cC_4F_8, C_4F_6, CF_4, CH_3F, CF_3H, CH_2F_2, and combinations thereof.

7. The method of any claims from 1 to 5, wherein the iodine-containing etching compound plasma etches the alternating SiO and SiN (ONON) layers having a selectivity between approximately 1:2 to approximately 2:1 with respect to the SiO layer versus SiN layer.

8. The method of any claims from 1 to 5, wherein the iodine-containing etching compound plasma etches the alternating SiO and p-Si (OPOP) layers having a selectivity between approximately 1:2 to approximately 2:1 with respect to the SiO layer versus p-Si layer.

9. The method of any claims from 1 to 5, wherein the patterned mask layer is an amorphous carbon layer, a doped amorphous carbon layer, a photoresist layer, an anti-reflective layer, an organic planarization layer, and combinations thereof.

10. The method of any claims from 1 to 5, wherein the activated iodine-containing etching compound selectively etches the silicon-containing film from a landing layer located at the bottom of the silicon-containing film to be etched, wherein the landing layer is a metal layer, a metal oxide layer or a metal nitride layer.

11. The method of any claims from 1 to 5, wherein the patterned structure formed in the silicon-containing film has an aspect ratio between approximately 1:1 and approximately 200:1.

12. A method of reinforcing and/or strengthening and/or minimizing damage of a patterned mask layer while forming a patterned structure in a substrate, the method comprising:

introducing a vapor of an iodine-containing etching compound into a reaction chamber containing a substrate having a silicon-containing film disposed thereon and the patterned mask layer disposed on the silicon-containing film, wherein the iodine-containing etching compound has the formula $C_nH_xF_yI_z$, wherein $4 \leq n \leq 10$, $0 \leq x \leq 21$, $0 \leq y \leq 21$, and $1 \leq z \leq 4$; and

etching the silicon-containing film from the patterned mask layer to form the patterned structure using an activated iodine-containing etching compound formed by activating a plasma,

wherein the activated iodine-containing etching compound produces iodine ions,

which are implanted into the patterned hardmask layer, thereby strengthening the patterned mask layer.

13. The method of claim 12, wherein the iodine-containing etching compound is C_4F_9I or its isomers.

14. A method of increasing etch resistance of a patterned mask layer in a process of forming a patterned structure in a substrate, the method comprising:

introducing a vapor of an iodine-containing etching compound into a reaction chamber containing a substrate having a silicon-containing film disposed thereon and the patterned mask layer disposed on the silicon-containing film, wherein the iodine-containing etching compound has the formula $C_nH_xF_yI_z$, wherein $4 \leq n \leq 10$, $0 \leq x \leq 21$, $0 \leq y \leq 21$, and $1 \leq z \leq 4$;

activating a plasma to produce an activated iodine-containing etching compound capable of doping iodine into the patterned mask layer; and

implanting iodine ions from the activated iodine-containing etching compound into the patterned mask layer while etching the silicon-containing film from the patterned mask layer to form the patterned structure,

thereby modifying the patterned mask layer with iodine to increase the etch resistance of the patterned mask layer.

15. The method of claim 14, wherein the iodine-containing etching compound is C_4F_9I or its isomers.