

IODINE-CONTAINING COMPOUNDS FOR ETCHING SEMICONDUCTOR STRUCTURES

Cross Reference to Related Applications

[0001] The present application claims the benefit of U.S. Application No. 15/396,220 filed December 30, 2016, being incorporated herein by reference in its entirety for all purposes.

Technical Field

[0002] Methods for etching silicon-containing films are disclosed. The method includes the steps of introducing the vapor of an iodine-containing etching compound into a reaction chamber containing the silicon-containing film on a substrate. The iodine-containing etching compound have 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 $a=2$, and $x+y+z=6$ or 8 when $a=3$. Preferably the iodine-containing etching compound is CF_2I_2 , C_2F_3I , C_2H_2FI , $C_2H_3F_2I$, C_2H_4FI , $C_2F_4I_2$, C_3F_5I , C_3HF_4I , $C_3H_2F_3I$, C_3HF_6I , $C_3H_2F_5I$, $C_3H_3F_4I$, $C_3H_4F_3I$, C_3HF_4I , $C_3H_2F_3I$, $C_3H_2F_5I$, $C_3H_3F_4I$, and $C_3H_4F_3I$; or combinations thereof. An inert gas is introduced into the reaction chamber. A plasma is activated to produce an activated iodine-containing etching compound capable of etching the silicon-containing film from the substrate.

Background

[0003] In memory applications in the semiconductor industries, plasma etching removes silicon-containing films, such as silicon oxide or silicon nitride layers, from semiconductor substrates. DRAM and 2D NAND are exemplary memory applications. For 3D NAND, etching of stacks of multiple SiO/SiN or SiO/poly-Silicon (p-Si) layers is critical. See, *e.g.*, US 2011/0180941 to Samsung Electronics Co., Ltd. An etchant having high selectivity between the mask and layers being etched is essential. Furthermore, the etched structure should have a straight vertical profile without bowing and low line edge roughness (LER).

[0004] Traditional etch gases include octafluorocyclobutane (cC_4F_8), hexafluoro-1,3-butadiene (C_4F_6), CF_4 , CH_2F_2 , CH_3F , and/or CHF_3 . It is well known that selectivity

sccm	standard cubic centimeters per minute
slm	standard liter per minute
ONON	silicon oxide and silicon nitride alternating layers
TCAT	terabit cell array transistor
P-BICS	pipe-shaped bit cost scalable
QMS	Quadrupole mass spectrometer
ARC or BARC	Anti-reflecting coating or Bottom anti-reflecting coating
a-C	amorphous carbon
CAS	chemical abstract service
PCTFE	Polychlorotrifluoroethene
PVDF	polyvinylidene fluoride
PTFE	Polytetrafluoroethylene
SEM	scanning electron microscope
NAND	Not AND or Negative-NAND or Negated AND
TEOS	Tetraethylorthosilicate
LDTEOS	low deposition rate TEOS
BPSG	Borophosphosilicateglass
p-Si	poly-silicon
XPS	X-ray photoelectron spectroscopy
SiN	Silicon nitride
SiO	Silicon oxide

[0013] As used herein, the term "etch" or "etching" means to use a plasma to remove material via ion bombardment, remote plasma, or chemical vapor reaction between the etching gas and substrate. The etch process may be anisotropic or isotropic. For example, plasma dry etching process produces anisotropic etching; chemical etching or wet etching process produces isotropic etching. The etching process may be used to produce apertures, such as vias, trenches, channel holes, gate trenches, staircase contacts, capacitor holes, contact holes, *etc.*, in the substrate.

[0014] The term "pattern etch" or "patterned etch" refers to etching a non-planar structure, such as a patterned mask layer on a stack of silicon-containing films.

[0015] The term "mask" refers to a layer that resists etching. The mask layer may be located above the layer to be etched.

[0016] The term "etch stop layer" refers to a layer below the layer to be etched that protects layers underneath.

by these abbreviations (*e.g.*, Si refers to silicon, N refers to nitrogen, O refers to oxygen, C refers to carbon, H refers to hydrogen, F refers to fluorine, *etc.*).

[0025] The unique CAS registry numbers (*i.e.*, "CAS") assigned by the Chemical Abstract Service are provided to help better identify the molecules disclosed.

[0026] Please note that the silicon-containing films, such as silicon nitride and silicon oxide, are listed throughout the specification and claims without reference to their proper stoichiometry. The silicon-containing films may include pure silicon (Si) layers, such as crystalline Si, poly-silicon (p-Si or polycrystalline Si), or amorphous silicon; silicon nitride (Si_kN_l) layers; or silicon oxide (Si_nO_m) layers; or mixtures thereof, wherein k, l, m, and n, inclusively range from 0.1 to 6. Preferably, silicon nitride is Si_kN_l , where k and l each range from 0.5 to 1.5. More preferably silicon nitride is Si_3N_4 . Preferably silicon oxide is Si_nO_m , where n ranges from 0.5 to 1.5 and m ranges from 1.5 to 3.5. More preferably, silicon oxide is SiO_2 . Herein, SiN and SiO in the following description are used to represent Si_kN_l and Si_nO_m containing layers, respectively. The silicon-containing film could also be a silicon oxide based dielectric material such as organic based or silicon oxide based low-k dielectric materials such as the Black Diamond II or III material by Applied Materials, Inc. with a formula of SiOCH . Silicon-containing film may also include $\text{Si}_a\text{O}_b\text{N}_c$ where a, b, c range from 0.1 to 6. The silicon-containing films may also include dopants, such as B, C, P, As and/or Ge.

Description of Drawings

For a further understanding of the nature and objects of the present invention, reference should be made to the following detailed description, taken in conjunction with the accompanying drawings, in which like elements are given the same or analogous reference numbers and wherein:

FIG. 1a is a cross-sectional side view of exemplary layers in a 3D NAND stack;

FIG. 1b is a cross-sectional side view of the exemplary layers in the 3D NAND stack showing polymer deposited on a sidewall during etching of the 3D NAND stack;

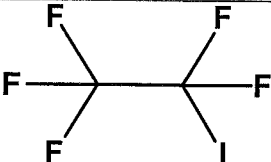
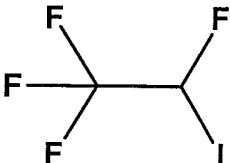
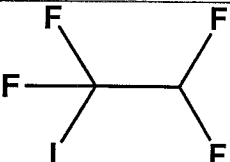
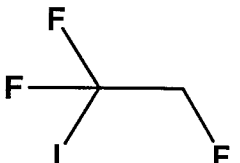
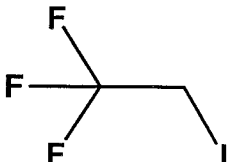
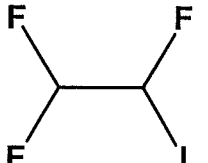
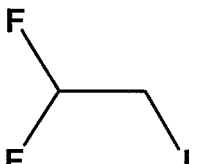
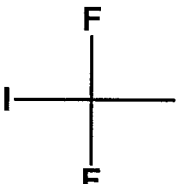
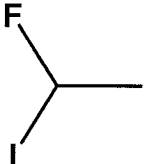
FIG. 1c is a cross-sectional side view of the exemplary layers in the 3D NAND stack showing particles generated during alternating SiO/SiN layer etching of a 3D NAND stack;

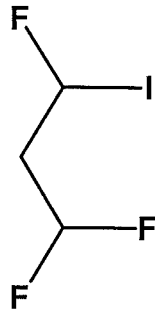
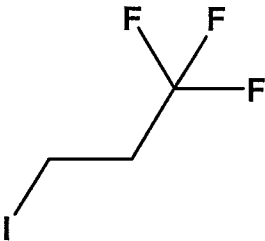
more easily ionized by the plasma than fluorine. Iodine may also behave similarly to the inert gases in the plasma and accelerate towards the wafer. Fluorine's ionization threshold serves to maintain it as a neutral species. As a result, fluorine typically participates in the etching process via chemical reactions. Iodine exhibits less chemical reactivity than fluorine and is ionized and bombards the surface during the plasma etch process. The bond energy for C-I is also less than the bond energy for C-F, thereby causing the C-I bond to more easily break in the plasma compared to C-F bonds.

[0030] As shown in the examples that follow, the iodide ion dissociates from the disclosed etching compounds at low eVs (i.e., <20 eV). The resulting iodide ion may be too large to enter features having narrow widths or diameters. However, iodide ion implantation into the mask feature is likely. This implantation may help to strengthen the mask feature and help it maintain its shape during the etching process.

[0031] The disclosed iodine-containing etching compounds have 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 $a=2$, and $x+y+z=6$ or 8 when $a=3$. Exemplary iodine-containing etching compounds are listed in Table 2. These molecules are commercially available or may be synthesized by methods known in the art. Their structure formula, CAS numbers and boiling points are included in Table 2.

Table 2. Commercially available etching compounds

1,1,1,2,2-pentafluoro-2-iodoethane	C_2F_5I		354-64-3	13
1,1,1,2-tetrafluoro-2-iodo-ethane	C_2HF_4I		3831-49-0	~39
1,1,2,2-tetrafluoro-1-iodo-ethane	C_2HF_4I		354-41-6	~41
1,1,2-trifluoro-1-iodo-ethane	$C_2H_2F_3I$		20705-05-9	~58
1,1,1-trifluoro-2-iodo-ethane	$C_2H_2F_3I$		353-83-3	54.5
1,1,2-trifluoro-2-iodo-ethane	$C_2H_2F_3I$		116239-01-1	~71
1,1-difluoro-2-iodo-ethane	$C_2H_3F_2I$		598-39-0	86.8-87.1
1,1-difluoro-1-iodo-ethane	$C_2H_3F_2I$		420-47-3	45
1-fluoro-1-iodo-ethane	C_2H_4FI		87508-83-6	~68

1,1,3-trifluoro-3-iodo-propane	$C_3H_4F_3I$		58706-45-9	~112
1,1,1-trifluoro-3-iodo-propane	$C_3H_4F_3I$		460-37-7	90

“~” indicates boiling points that have been predicted by the SciFinder database

[0032] When $a=1$, the disclosed iodine-containing etching compounds have the formula $CH_xF_yI_z$, wherein $x=0-2$, $y=1-2$, $z=1-2$, $x+y+z=4$. Exemplary compounds include CF_3I , CF_2I_2 , CHF_2I , CH_2FI , and $CHFI_2$, preferably CF_2I_2 . Applicants believe that the etch rate of SiN may be enhanced while maintaining high selectivity to the mask layer when the disclosed iodine-containing etching compounds include at least one H. Iodine-containing etching compounds having one H when $a=1$ have the formula $CH_xF_yI_z$, wherein $x=1-2$, $y=1-2$, and $z=1-2$. Exemplary compounds include CHF_2I , CH_2FI , and $CHFI_2$.

[0033] Applicants believe that the molecules having 2-3 carbon atoms may provide better sidewall protection during the etching process than the C1 molecules.

[0034] For sidewall protection, the C3 molecules are preferred because Applicants believe they will produce thicker passivation layers. C3 iodine-containing etching compounds have the formula $C_3H_xF_yI_z$, wherein $x=0-6$, $y=1-7$, $z=1-2$, and $x+y+z=6$ or 8. Exemplary C3 iodine-containing etching compounds include C_3F_5I , C_3HF_4I , $C_3H_2F_3I$, C_3F_7I , C_3HF_6I , $C_3H_2F_5I$, $C_3H_3F_4I$, and $C_3H_4F_3I$, preferably C_3F_5I , C_3HF_4I , $C_3H_2F_3I$, C_3HF_6I , $C_3H_2F_5I$, $C_3H_3F_4I$, or $C_3H_4F_3I$, even more preferably, C_3HF_4I , $C_3H_2F_3I$, $C_3H_2F_5I$, $C_3H_3F_4I$, or $C_3H_4F_3I$.

[0035] However, the C2 molecules may be easier to deliver to the reactor or, for some applications, thinner passivation layers may be desired. C2 iodine-containing etching compounds have the formula $C_2H_xF_yI_z$, wherein $x=0-4$, $y=1-5$, $z=1-2$, and

GF120XSD), MKS Instruments, *etc.*, may be used. The pressure of the reaction chamber is set at approximately 30 mTorr. No gas source heating may be necessary if the vapor pressure is sufficient. The distance between the two CCP electrodes is kept at 1.35 cm and the top electrode RF power is fixed at 750 W. The bottom electrode RF power is varied to analyze the performance of the molecule. The reaction chamber contains a substrate having silicon-containing films thereon, similar to those shown in **FIG. 1a**. The antireflective coating layer **108** is patterned/etched by a fluorocarbon (*e.g.*, CF_4 and CH_2F_2) and oxygen-containing gas (*e.g.*, O_2). The amorphous carbon mask layer is patterned/etched by an oxygen-containing gas. The SiO and SiN layers **104** are patterned by the plasma of the disclosed iodine-containing etching compounds (*e.g.*, 1,1,3,3-tetrafluoro-3-iodo-1-propene) and Argon. Argon is independently introduced into the chamber at a 250 sccm flow rate. 1,1,3,3-tetrafluoro-3-iodo-1-propene is independently introduced into the chamber at 15 sccm. O_2 is independently introduced into the chamber and varied from 0 sccm to 20 sccm to determine optimum etching conditions. An aperture having an aspect ratio equal to or greater than 30:1 is produced, which may be used as a channel hole in vertical NAND. Similar example may be used for other stack layers as shown in **Figs 2 and 3a**.

[0076] In another non-limiting exemplary plasma etch process, 1,2-difluoro-1-iodo-ethene is introduced into a 200 mm Dual CCP plasma etch tool using a controlled gas flow device. The controlled gas flow device may be a mass flow controller. In case of high boiling point molecules, a special low pressure drop mass flow controller from BrooksAutomation (No. GF120XSD), MKS Instruments, *etc.*, may be used. The pressure of the reaction chamber is set at approximately 30 mTorr. No gas source heating may be necessary if the vapor pressure is sufficient. The distance between the two CCP electrodes is kept at 1.35 cm and the top electrode RF power is fixed at 750 W. The bottom electrode RF power is varied to analyze the performance of 1,2-difluoro-1-iodo-ethene. The reaction chamber contains a substrate **100** having a thick SiO layer **104a** thereon, similar to the layer shown in **FIG. 2**. Prior to this process, the antireflective coating layer **108** is removed by a fluorocarbon (*e.g.*, CF_4) and oxygen-containing gas (*e.g.*, O_2) and the a-C mask layer **106** is removed by an oxygen-containing gas. Argon is independently introduced into the chamber at a 250 sccm flow rate. 1,2-difluoro-1-iodo-ethene is independently

[0107] FIG. 17 is a graph demonstrating etch rates of SiO, SiN, p-Si and a-C with C_3F_5I and O_2 . In **FIG. 17**, the positive y-axis represents etch rates while the negative y-axis represents deposition rates; the x-axis is O_2 flow rate in sccm; the C_3F_5I flow rate is fixed at 15 sccm while the O_2 flow rate is varied from 0 to 15 sccm.

[0108] FIG. 18 is a graph demonstrating etch rates of SiO, SiN, p-Si and a-C with C_3F_7I and O_2 . In **FIG. 18**, the y-axis represents etch rates; the x-axis is O_2 flow rate in sccm; the C_3F_7I flow rate is fixed at 15 sccm while the O_2 flow rate is varied from 0 to 20 sccm.

[0109] Addition of iodine gives increased fragmentation due to the C-I weaker bond. The lower ionization threshold of the I ion bombarding the surface yields increased selectivity for etching oxide versus amorphous carbon (a-C) or polysilicon (poly-Si). **FIGS 14, 16, and 17** are from polymerizing gases having H or unsaturation and show deposition and infinite selectivity for etching oxide to a-c, polySi, and SiN. Whereas the saturated molecules of **FIGS 13, 15, and 18** do not exhibit deposition and therefore do not have infinite selectivity, but still exhibit higher selectivity than non-iodine containing etch gases.

Example 3

[0110] In order to enhance the etch rates of SiO, comparable to the performance of cC_4F_8 , CF_4 is added to the etch gas mixture of 250 sccm Ar and 15 sccm C_2F_3I .

[0111] FIG. 19 is a graph demonstrating etch rates of SiO, SiN, p-Si and a-C with C_2F_3I and CF_4 . In **FIG. 19**, the y-axis represents etch rates and the x-axis is CF_4 flow in sccm. The C_2F_3I flow rate is fixed at 15 sccm and the CF_4 flow rate is varied from 10 to 15 sccm.

[0112] FIG. 19 demonstrates that by adding CF_4 to the process gas mixture, the etch rates of SiO have increased up to almost 500 nm/min while maintaining good selectivity to p-Si and a-C. Additives like C_xF_{2x+2} ($x=1$ to 5), C_xF_{2x} ($x=3$ to 5), C_xF_{2x-2} ($x=4$ to 5) may be added to the mixture to enhance Oxide etch rate.

[0113] As compared to **FIG 14**, substituting CF_4 for oxygen improves selectivity to a-C while also increasing the SiO_2 etch rate which is important for throughput.

[0114] In summary, the evaluation of the dry etching of SiO, SiN, p-Si and a-C films with iodine-containing etching compounds shows that the iodine-containing HFCs

What is claimed is:

1. A method of forming a patterned structure, the method comprising:
introducing a vapor of an iodine-containing etching compound into a reaction chamber containing a silicon-containing film on a substrate, wherein the iodine-containing etching compound is selected from the group consisting of CF_2I_2 , $\text{C}_2\text{F}_3\text{I}$, $\text{C}_2\text{H}_2\text{FI}$, $\text{C}_2\text{H}_3\text{F}_2\text{I}$, $\text{C}_2\text{H}_4\text{FI}$, $\text{C}_2\text{F}_4\text{I}_2$, $\text{C}_3\text{F}_5\text{I}$, $\text{C}_3\text{HF}_4\text{I}$, $\text{C}_3\text{H}_2\text{F}_3\text{I}$, $\text{C}_3\text{HF}_6\text{I}$, $\text{C}_3\text{H}_2\text{F}_5\text{I}$, $\text{C}_3\text{H}_3\text{F}_4\text{I}$, $\text{C}_3\text{H}_4\text{F}_3\text{I}$, $\text{C}_3\text{HF}_4\text{I}$, $\text{C}_3\text{H}_2\text{F}_3\text{I}$, $\text{C}_3\text{H}_2\text{F}_5\text{I}$, $\text{C}_3\text{H}_3\text{F}_4\text{I}$, and $\text{C}_3\text{H}_4\text{F}_3\text{I}$;
introducing an inert gas into the reaction chamber; and
activating a plasma to produce an activated iodine-containing etching compound capable of etching the silicon-containing film from the substrate to form the patterned structure.
2. The method of claim 1, further comprising removing volatile by-products from the reaction chamber, wherein the activated iodine-containing etching compound reacts with the silicon-containing film to form the volatile by-products.
3. The method of claim 2, further comprising introducing an oxidizer into the reaction chamber.
4. The method of claim 3, wherein the oxidizer is selected from the group consisting of O_2 , O_3 , CO , CO_2 , NO , N_2O , NO_2 , and combinations thereof.
5. The method of claim 2, further comprising introducing an etch gas into the reaction chamber.
6. The method of claim 5, wherein the etch gas is selected from the group consisting of cC_4F_8 , cC_5F_8 , C_4F_6 , CF_4 , CH_3F , CF_3H , CH_2F_2 , COS , $\text{F-C}\equiv\text{N}$, CS_2 , SO_2 , *trans*-1,1,1,4,4,4-hexafluoro-2-butene (*trans*- $\text{C}_4\text{H}_2\text{F}_6$), *cis*-1,1,1,4,4,4-hexafluoro-2-butene (*cis*- $\text{C}_4\text{H}_2\text{F}_6$), hexafluoroisobutene ($\text{C}_4\text{H}_2\text{F}_6$), *trans*-1,1,2,2,3,4-hexafluorocyclobutane (*trans*- $\text{C}_4\text{H}_2\text{F}_6$), 1,1,2,2,3-pentafluorocyclobutane ($\text{C}_4\text{H}_3\text{F}_5$), 1,1,2,2-tetrafluorocyclobutane ($\text{C}_4\text{H}_4\text{F}_4$), and *cis*-1,1,2,2,3,4-hexafluorocyclobutane (*cis*- $\text{C}_4\text{H}_2\text{F}_6$).

7. The method of claim 1, wherein the inert gas is selected from the group consisting of He, Ar, Xe, Kr, Ne, N₂ or combinations thereof.
8. The method of any of claims 1 to 7, wherein the silicon-containing film comprises a layer of silicon oxide, silicon nitride, polysilicon, crystalline silicon, low-*k* SiCOH, SiOCN, SiON, Si_aO_bH_cC_dN_e, where $a > 0$; b, c, d and $e \geq 0$, or combinations thereof.
9. The method of any of claims 1 to 7, wherein the silicon-containing film is selectively etched from an amorphous carbon layer or a photoresist layer.
10. The method of any of claims 1 to 7, wherein the silicon oxide layer is selectively etched from a silicon nitride, polysilicon or amorphous carbon layer.
11. The method of any of claims 1 to 7, wherein the method produces an aperture in the silicon-containing film having an aspect ratio between approximately 10:1 and approximately 200:1.
12. A method of minimizing damage to a patterned mask layer while forming a via or trench 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 a patterned mask layer disposed on the silicon-containing layer, wherein the iodine-containing etching compound is selected from the group consisting of C₂H₂FI, C₂H₃F₂I, or C₂H₄FI;
introducing an inert gas into the reaction chamber; and
etching the silicon-containing film from the substrate to form the via or trench by activating a plasma to form an activated iodine-containing etching compound.
13. The method of claim 12, wherein the activated iodine-containing etching compound produces iodine ions that strengthen the patterned mask layer.

14. A method of reinforcing a patterned mask layer while forming a via or trench 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 a patterned mask layer disposed on the silicon-containing layer, wherein the iodine-containing etching compound is selected from the group consisting of C_2H_2FI , $C_2H_3F_2I$, or C_2H_4FI ;

introducing an inert gas into the reaction chamber; and

implanting an I ion from the iodine-containing etching compound into the patterned mask while etching the silicon-containing film from the substrate to form the via or trench by activating a plasma to form an activated iodine-containing etching compound.