

includes: (a) contacting the substrate housed in a process chamber with an active hydrogen-containing species to modify the surface of the oxide on the substrate, wherein the active hydrogen-containing species is a compound containing one or more OH groups, or a hydrogen-containing species generated in a hydrogen plasma; 5 (b) removing non surface-bound active hydrogen species from the process chamber after the surface of the oxide is modified; (c) flowing an anhydrous HF into the process chamber after (b), wherein the anhydrous HF reacts with the modified surface of the oxide and wherein the reaction generates water; and (d) removing the water generated in (c) from the surface of the substrate. In some embodiments, modification 10 of the surface of the oxide in (a) is an adsorption of the active hydrogen-containing species on the surface of the oxide. In some embodiments, a single cycle of operations (a) – (d) removes about 0.5 – 10 atomic layers of oxide (referring to an average thickness removed). In some embodiments, the cycle is repeated and the operations (a) – (d) are performed at least twice during the etching.

15 In some embodiments, the HF reaction and removal of water from the surface of the substrate are performed concurrently under a temperature and pressure that does not permit water to stay adsorbed to the substrate surface, as water is generated in the reaction. In some embodiments, operations (a) – (d) are performed at a single temperature of at least about 80 °C, e.g., at least about 100 °C.

20 In some embodiments, the active hydrogen-containing species is an alcohol that is capable of adsorbing or staying adsorbed to the surface of the oxide under conditions when water is desorbed from the surface of oxide. Examples of such alcohols include alcohols that have a vapor pressure that is lower than the vapor pressure of water, or alcohols with a vapor pressure that is not significantly 25 higher than the vapor pressure of water, such as isopropanol, *n*-propanol, *n*-butanol, *tert*-butanol, ethylene glycol, propylene glycol, etc. In some embodiments, operations (a) – (d) are performed at a temperature and pressure, that do not permit these alcohols to be desorbed from the surface of the substrate.

30 In other embodiments the active hydrogen-containing species is formed from a hydrogen-containing plasma, and the hydroxyl (OH) bonds are formed on the surface of the oxide by contacting the substrate with a hydrogen containing plasma under conditions when water is desorbed from the surface of the oxide. The

In some embodiments water removal is achieved by raising the temperature of the substrate to a temperature that is sufficient to remove water. In some embodiments, the HF dosing is performed at a temperature that is sufficient to remove water. In some embodiments, the entire etching process, including treatment
5 with an active hydrogen-containing species and HF dosing are performed at a temperature that is sufficient to remove water from the surface of the substrate as it is generated. In some embodiments water removal is achieved by lowering the pressure in the process chamber to a pressure that is sufficient to remove water. In some
10 embodiments, the HF dosing is performed at a pressure that is sufficient to remove water. In some embodiments, water removal includes both raising the temperature and lowering the pressure to remove the water.

In some embodiments water may be removed from the surface using electromagnetic irradiation (e.g., UV irradiation or microwave irradiation), plasma treatment (i.e. electron, ion, and radical exposure) as well as electron beam treatment.
15 The irradiation, plasma and electron beam treatment energy is selected such as not to cause any damage to the surface of the substrate, and not to interfere with the isotropic nature of the etch. Therefore, relatively low-energy electrons, such as electrons with energy of between about 5 – 10 eV, are used in some embodiments for the electron (plasma or electron beam) treatment.

20 The timing of water removal can vary. Removal of water can be performed concurrently with HF treatment, may overlap with HF treatment for a portion of time, or may be performed after HF treatment. It is important to note that if the removal of water is performed in the beginning of HF treatment, then the selected water removal method should not completely deactivate the surface of silicon oxide to
25 HF etching. Thus, in some embodiments removal of water is performed under such conditions that do not result in desorption of alcohol or carboxylic acid from the surface of silicon oxide. The silicon tetrafluoride generated during the etching reaction is a volatile compound that typically is removed from the surface of the substrate with the water or before water is removed, as shown in Figure 2D.
30 Germanium tetrafluoride formed during etching of germanium oxide is similarly removed.

CLAIMS

1. A method of controllably etching an oxide layer on a substrate, the method comprising:

5 (a) contacting the substrate housed in a process chamber with an active hydrogen-containing species to modify the surface of the oxide on the substrate, wherein the active hydrogen-containing species is a compound containing one or more OH groups, or a hydrogen-containing species generated in a hydrogen plasma, and wherein the oxide is selected from the group consisting of silicon oxide,
10 germanium oxide, and combinations thereof;

(b) removing non surface-bound active hydrogen species from the process chamber after the surface of the oxide is modified;

(c) flowing an anhydrous HF into the process chamber after (b), wherein the anhydrous HF reacts with the modified surface of the oxide and
15 wherein the reaction generates water;

(d) removing the water generated in (c) from the surface of the substrate.

2. The method of claim 1, wherein (c) and (d) are concurrent, and
20 are performed at a temperature and pressure that do not permit water to stay adsorbed to the substrate surface as water is generated in the reaction.

3. The method of claim 1, wherein the active hydrogen-containing species is an alcohol that is capable of adsorbing or staying adsorbed to the surface of
25 the oxide under conditions when water is desorbed from the surface of the oxide.

4. The method of claim 1, wherein the active hydrogen-containing species is formed from a hydrogen-containing plasma, and wherein hydroxyl (OH) bonds are formed on the surface of the oxide by application of the hydrogen containing plasma under conditions when water is desorbed from the surface of the
5 oxide.

5. The method of claim 4, wherein the hydrogen containing plasma is formed from a gas that comprises a hydrogen-containing gas selected from the group consisting of H₂, ammonia, hydrazine, water, hydrogen fluoride, hydrogen
10 chloride, silane, disilane, methane, ethane, butane and combinations thereof.

6. The method of claim 5, wherein the hydrogen containing plasma is formed from a gas comprising the hydrogen-containing gas and a second gas selected from the group consisting of water vapor, oxygen, nitrous oxide, nitric
15 oxide, carbon dioxide, carbon monoxide and combinations thereof.

7. The method of claim 1, wherein the active hydrogen-containing species is selected from the group consisting of a propanol, a butanol, butoxyethanol, butanediol, ethylene glycol, methylene glycol, propylene glycol, amyl alcohol, a
20 carboxylic acid, and combinations thereof.

8. The method of claim 1, wherein the active hydrogen-containing species is a butanol.

25 9. The method of claim 8, wherein (c) and (d) are performed concurrently, and wherein water is being removed as it is generated in the reaction.

10. The method of claim 1, wherein the active hydrogen-containing species is selected from the group consisting of methanol, ethanol, propanol, butanol, butoxyethanol, ethylene glycol, methylene glycol, propylene glycol, amyl alcohol and combinations thereof, wherein the operations (a) – (d) are performed at the same temperature, and wherein water is being removed from the surface of the oxide as it is generated in the reaction.

11. The method of claim 1, wherein the active hydrogen-containing species is characterized by a saturated vapor pressure that is lower or is substantially the same as the saturated vapor pressure of water for selected conditions, wherein the operations (a) – (d) are performed at the same temperature, and wherein water is being removed from the surface of the oxide as it is generated in the reaction.

12. The method of claim 1, wherein the active hydrogen-containing species is selected from the group consisting of methanol, ethanol, water and a water-alcohol azeotrope that adsorbs to the surface of the oxide in (a), and wherein the anhydrous HF is provided in (c) in a controlled, limited amount.

13. The method of claim 1, wherein the active hydrogen-containing species is methanol or ethanol that adsorbs to the surface of the oxide in (a) at a first temperature, and wherein the water is removed in (d) by raising the temperature of the substrate to a second temperature that is higher than the first temperature.

14. The method of claim 11, wherein the flow of the anhydrous HF into the process chamber is ceased before (d).

15. The method of claim 1, wherein (d) comprises removing water by a method selected from the group consisting of: (i) raising the temperature of the substrate, (ii) lowering pressure in the process chamber, (iii) treating the substrate with a plasma, (iv) treating the substrate with an electron beam, (v) irradiating the substrate with an electromagnetic radiation, and combinations thereof.

16. The method of claim 1, wherein operations (a) - (d) remove 0.5 – 10 atomic layers of oxide from the substrate.

17. The method of claim 1, comprising performing at least 2 cycles comprising operations (a) – (d).

18. The method of claim 1, wherein operations (a) – (d) are performed at a single temperature of at least about 80 °C.

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19. The method of claim 1, further comprising:

applying photoresist to the substrate;

exposing the photoresist to light;

patterning the photoresist and transferring the pattern to the

20 substrate;

and selectively removing the photoresist from the substrate.

20. An etching apparatus for controllably etching an oxide on a substrate, the apparatus comprising:

(a) a process chamber having an inlet for introduction of process gases;

(b) a substrate support in the process chamber configured for holding the substrate in position during etching of the oxide on the substrate; and

5 (c) a controller comprising program instructions for:

(i) contacting the substrate housed in the process chamber with an active hydrogen-containing species to modify the surface of the oxide on the substrate, wherein the active hydrogen-containing species is a compound containing one or more OH groups, or a hydrogen-containing species generated in a hydrogen containing plasma, and wherein the oxide is selected from the group consisting of silicon oxide, germanium oxide and combinations thereof;

(ii) removing non surface-bound active hydrogen species from the process chamber after the surface of the oxide is modified;

15 (iii) flowing an anhydrous HF into the process chamber after (ii), wherein the anhydrous HF reacts with the modified surface of the oxide and wherein the reaction generates water;

(iv) removing the water generated in (iii) from the surface of the substrate.

20 21. A method of controllably etching an oxide layer on a substrate, the method comprising:

(a) contacting the substrate housed in a process chamber with an anhydrous HF to adsorb a layer of HF on the oxide layer on the substrate, wherein the oxide is selected from the group consisting of silicon oxide, germanium oxide, and combinations thereof;

25 (b) removing non surface-bound HF from the process chamber after the HF has adsorbed;