[00015] In another aspect, an apparatus for processing a semiconductor substrate is provided where, the apparatus includes: (a) a processing chamber having a support for the semiconductor substrate and an inlet for introduction of one or more reactants into the processing chamber; and (~~c~~b) a controller comprising program instructions for: (i) causing passivation a silicon-containing layer on a semiconductor substrate towards a tin oxide etch chemistry; (ii) causing etching of a tin oxide on a semiconductor substrate; and (iii) causing a repeating, in an alternating fashion of (i) and (ii). In some embodiments (i) includes causing treatment of the semiconductor substrate with a plasma-activated oxygen-containing reactant (e.g., plasma-activated O_2). In some embodiments (ii) includes causing etching of the tin oxide using a chlorine-based chemistry. In some embodiments (ii) includes causing etching of the tin oxide using a hydrogen-based chemistry. In some embodiments the program instructions include instructions for performing (i) and (ii) in an alternating fashion between 2 – 50 times.

[00016] In another aspect an apparatus is provided, where the apparatus includes a process chamber and a controller having program instructions for causing any of the methods provided herein.

[00017] In another aspect, non-transitory computer readable medium is provided containing code configured for performing any of the methods described herein.

[00018] These and other aspects of implementations of the subject matter described in this specification are set forth in the accompanying drawings and the description below.

BRIEF DESCRIPTION OF THE DRAWINGS

[00019] Figures 1A-1F show schematic cross-sectional views of a semiconductor substrate undergoing processing that involves spacer formation.

[00020] Figure 2 is a process flow diagram for a method according to an embodiment provided herein.

exposure dose and/or to prevent photoresist line collapse due to high aspect ratio at small fine pitch. In the described method the CH_x polymer protects the photoresist from being etched. Further this etch can be used to improve the geometry of the photoresist layer. In some embodiments, the tin oxide on a semiconductor substrate is selectively etched using this etch in a presence of a photoresist disposed above the tin oxide layer, and in a presence of a material that underlies tin oxide, with an etch selectivity of at least 10 relative to both photoresist and the material that underlies tin oxide. In some embodiments the material that underlies tin oxide includes one or more of silicon (e.g., amorphous silicon), silicon-containing compound (e.g., SiO_2, SiN, SiC, SiON, SiOC), carbon (e.g., amorphous carbon), and a carbon-containing compound (e.g., carbon tungsten).

[00068] In some embodiments, HBr is used as a hydrogen-containing reactant in the hydrogen-based etch. In one implementation, the etching method involves flowing HBr at a flow rate of ~~100 – 50~~50-100 sccm, and an inert gas (e.g., helium) at a flow rate of 100-500 sccm and forming a plasma in this process gas using RF power of 100 – 500 W (per one 300 mm wafer) corresponding to power densities of 0.14 – 0.71 W/cm^2. This etch can be conducted with or without a substrate bias. For example, substrate bias may be between 0 – 200 Vb, such as 50 – 200 Vb. The process can be performed at a temperature of less than 100 °C and a pressure of 5 – 50 mTorr.

[00069] *Chlorine-based etch.* In some embodiments selective tin oxide etching is performed using a chlorine-based etch. Chlorine-based etch involves exposing tin oxide to a chlorine-containing reactant (typically with plasma activation of the reactant) such that it converts tin oxide to a tin chloride. $SnCl_4$ has a boiling point of 114 °C and can be removed from the process chambers. Examples of suitable chlorine-containing reactants include Cl_2, and BCl_3. Mixture of Cl_2 and BCl_3 is used in one embodiment. Chlorine-based etching involves, in one implementation, forming a plasma in a process gas containing a chlorine-containing reactant, and, optionally, an inert gas, and contacting the substrate with the formed plasma. Chlorine-based etch can selectively remove tin oxide in a presence of the following materials: silicon-containing

residing at the sidewalls of the protruding features. In this example, the etching is conducted using a main (bulk) etch (e.g., Cl_2/BCl_3 plasma etch) followed by overetch, where the overetch may be, for example a hydrogen plasma etch that is used to reduce footing. After etching the method continues by removing the silicon mandrels without removing the tin oxide spacers. It is noted that the silicon oxide passivation layer on the sidewalls can be formed by first conformally depositing silicon oxide over tin oxide (e.g., by PECVD, or ALD), and then selectively etching silicon oxide from horizontal surfaces (e.g., by fluorocarbon plasma). This sequence was experimentally tested using BCl_3/Cl_2 plasma main etch followed by H_2 plasma overetch for tin oxide removal from horizontal surfaces. In this experimentally tested example, after the main etch, the critical dimension loss was zero nm; the footing was about 6 nm, and the amount of etch into silicon oxide ESL is zero nm. After the overetch, the critical dimension loss, the footing, and the amount of etch into silicon oxide ESL were all zero nm.

[000138] In another specific example, tin nitride formed from an outer portion of the tin oxide is used as a passivation material. In some embodiments, it is preferable to passivate the sidewalls of tin oxide using a tin nitride passivation layer during formation of tin oxide spacers, and thereby reduce the variation in the spacer. In some embodiments the method includes: (a) providing a substrate having a silicon oxide layer, and a plurality of silicon protrusions, where the silicon protrusions are covered with native silicon oxide; (b) depositing a tin oxide layer conformally over the substrate (e.g., by ALD); (c) forming a thin tin nitride passivation layer only over tin oxide on the sidewalls of the protruding features; (d) etching tin oxide from horizontal surfaces without completely removing tin oxide residing at the sidewalls of the protruding features (e.g., using a combination of a main (bulk) etch (e.g., Cl_2/BCl_3 etch) and overetch, where the overetch may be, for example hydrogen plasma etch that is used to reduce footing); and (~~d~~e) removing the silicon mandrels without removing the tin oxide spacers. The tin nitride passivation layer on the sidewalls can be formed by first conformally forming the passivation layer over the entire tin oxide layer, followed by selectively removing tin nitride from horizontal surfaces. In some embodiments tin nitride layer is formed by treating the

shown in Figure 5B has recessed features formed in layer 55 and 53 and an exposed material of sublayer 51 at the bottoms of the recessed features.

[000144] Next, in operation ~~603~~605 the tin oxide material 55 is removed providing a structure shown in Figure 5C, where a patterned layer 53 resides over sublayer 51. In some embodiments, this sequence is further used to pattern sublayer 51, which is in some embodiments a SiN layer, a metal nitride (e.g., TiN, or TaN), or metal layer. Removal of tin oxide is preferably performed using a chemistry that is selective to both the material of layer 53 and layer 51. For example, when these materials are silicon-containing materials, carbon-containing materials, metal oxides, metal nitrides, or metals a selective hydrogen-based etch (e.g., H_2 plasma etch may be used). Further, in some embodiments when materials of layer 53 and 51 are silicon-containing materials or carbon-containing materials a chlorine-based etch (e.g., BCl_3/Cl_2 in a plasma) may be employed.

[000145] In one specific example of a process flow that uses a tin oxide hardmask, the sublayer 51 is a SiN layer, or a metal layer, and layer 53 is silicon oxide. The process starts by providing a planar substrate having an exposed layer of silicon oxide over the SiN or metal layer 51. Next, a blanket tin oxide layer is deposited over silicon oxide, and tin oxide is then patterned (e.g., using photolithographic patterning), leading to a structure shown in Figure 5A. Next, exposed silicon oxide is selectively etched relative to tin oxide, for example, using fluorocarbon plasma, leading to a structure shown to Figure 5B. Next, tin oxide is stripped (removed), for example, using a hydrogen plasma etch, leading to a structure shown in Figure 5C.

[000146] *Tin Oxide Middle Layer*. In another hardmask implementation, tin oxide is used as an intermediate hardmask (middle layer) for patterning of a carbon layer or another material. In one embodiment, a substrate is provided, where the substrate includes a patterned layer of tin oxide formed on a carbon-containing layer (e.g., on an amorphous carbon layer), wherein the substrate includes a plurality of recessed features having an exposed carbon-containing material at the bottoms of the recessed features. Next the exposed carbon-containing material is selectively etched in a presence of tin oxide to form

wafer 526 may be moved by the front-end robot 532 to one of the FOUPs 534 or to the aligner 544.

[000175] It should be noted that the computer controlling the wafer movement can be local to the cluster architecture, or can be located external to the cluster architecture in the manufacturing floor, or in a remote location and connected to the cluster architecture via a network. A controller as described above with respect to Figure 11 may be implemented with the tool in Figure 12. Machine-readable media containing instructions for controlling process operations in accordance with the present invention may be coupled to the system controller.

[000176] In some embodiments an apparatus is provided, where the apparatus includes a process chamber having a substrate holder configured for holding the semiconductor substrate during etching; a plasma generator configured for generating a plasma in a process gas; and a controller. The controller includes program instructions for implementing any of the methods describing herein.

[000177] In another aspect a non-transitory computer machine-readable medium is provided, where it includes code for causing the performance of any of the methods described herein.

[000178] In another aspect, a system for forming spacers or hardmasks on a semiconductor substrate is provided. The system includes one or more deposition chambers; one or more etch chambers; and a controller. The controller includes program instructions for implementing any methods described herein. In another aspect, the system includes any of the apparatuses and systems described herein and a stepper. In another aspect, a system for processing a semiconductor substrate is provided. In one embodiment the system includes: one or more deposition chambers; one or more etch chambers; and a system controller comprising program instructions for: (i) causing a deposition of a tin oxide layer over horizontal surfaces and sidewalls of a plurality of protruding features on the semiconductor substrate; (ii) causing a formation of a passivation layer on the tin oxide layer at the sidewalls of the protruding features, and ~~(ii)~~(iii) causing a removal of the tin oxide layer from horizontal surfaces of the protruding features, without causing a removal of the tin oxide layer over the sidewalls of the protruding features.

passivation, the process chamber was purged with argon, and tin oxide was etched at 40 degrees C, and 10 mTorr by exposing the substrate to a plasma formed in a process gas that consisted of 10 sccm BCl_3 (provided at 10 sccm), 190sccm Cl_2 (provided at 190 sccm) and helium (provided at 200 sccm). The plasma was formed using 13.56MHz RF frequency and 400 W power per one 300 mm substrate. The process chamber was then purged and the passivation and etch steps (each followed by purging) were repeated in an alternating fashion until the spacer footing of tin oxide was removed.

[000186] In another aspect, an apparatus is provided (e.g., any of the etching tools described herein), where the apparatus includes: (a) a processing chamber having a support for the semiconductor substrate and an inlet for introduction of one or more reactants into the processing chamber; and (~~e~~b) a controller comprising program instructions for: (i) causing passivation a silicon-containing layer on a semiconductor substrate towards a tin oxide etch chemistry; (ii) causing etching of a tin oxide on a semiconductor substrate; and (iii) causing a repeating, in an alternating fashion of (i) and (ii). The controller may be further programmed to perform any of the methods described herein.

FURTHER IMPLEMENTATIONS

[000187] The apparatus and processes described herein may be used in conjunction with lithographic patterning tools or processes, for example, for the fabrication or manufacture of semiconductor devices, displays, LEDs, photovoltaic panels, and the like. Typically, though not necessarily, such apparatus and processes will be used or conducted together in a common fabrication facility. Lithographic patterning of a film typically comprises some or all of the following steps, each step enabled with a number of possible tools: (1) application of photoresist on a work piece, i.e., a substrate, using a spin-on or spray-on tool; (2) curing of photoresist using a hot plate or furnace or UV curing tool; (3) exposing the photoresist to visible or UV or x-ray light with a tool such as a wafer stepper; (4) developing the resist so as to selectively remove resist and thereby pattern it using a tool such as a wet bench; (5) transferring the resist pattern into an underlying film or work piece by using a

CLAIMS

~~*What is claimed is:*~~

1. A method of processing a semiconductor substrate, the method comprising:

(a) providing a semiconductor substrate having a plurality of protruding features over a silicon-containing layer, wherein the semiconductor substrate comprises an exposed tin oxide at the protruding features and an exposed silicon-containing material of the silicon-containing layer;

(b) passivating the exposed silicon-containing material towards a tin oxide etch chemistry;

(c) etching the exposed tin oxide using the tin oxide etch chemistry; and

(d) repeating operations (b) and (c) such that operations (b) and (c) are performed in an alternating fashion.

2. The method of claim 1, wherein the exposed silicon-containing material is selected from the group consisting of amorphous silicon, silicon oxide, SiON, SiOC, SiONC, SiC, and SiN.

3. The method of claim 1, wherein (c) comprises etching tin oxide using a chlorine-based etch chemistry that comprises exposing the semiconductor substrate to a plasma-activated chlorine-containing reactant selected from the group consisting of Cl_2, BCl_3, and combinations thereof.

4. The method of claim 1, wherein (c) comprises etching the tin oxide using a hydrogen-based etch chemistry that results in a formation of a tin hydride.

5. The method of claim 1, wherein (c) comprises etching the tin oxide using a hydrogen-based etch chemistry, by contacting the semiconductor substrate with a plasma-activated hydrogen-containing reactant selected from the group consisting of H_2, HBr, NH_3, H_2O, a hydrocarbon, and combinations thereof.

6. The method of claim 1, wherein (c) comprises etching tin oxide using a chlorine-based etch chemistry that comprises exposing the semiconductor substrate to

a plasma-activated process gas comprising a chlorine-containing reactant selected from the group consisting of Cl_2, BCl_3, and combinations thereof, and a diluent gas selected from the group consisting from helium, neon, argon, and xenon and combinations thereof.

7. The method of claim 1, wherein (b) comprises treating the substrate with an oxygen-containing reactant.

8. The method of claim 1, wherein (b) comprises treating the substrate with a plasma-activated oxygen-containing reactant.

9. The method of claim 1, wherein (b) comprises treating the substrate with a plasma formed in a process gas comprising a gas selected from the group consisting of O_2, O_3, SO_2, and CO_2.

10. The method of claim 1, wherein (b) is performed before (c).

11. The method of claim 1, wherein (c) is performed before (b).

12. The method of claim 1, wherein operations (b) and (c) are performed between 2 - 50 times.

13. The method of claim 1, wherein the protruding features comprise horizontal surfaces and sidewalls and wherein the method reduces a tin oxide footing at the sidewalls of the protruding features.

14. The method of claim 1, wherein the silicon-containing material is selected from the group consisting of amorphous silicon, silicon oxide, SiON, SiOC, SiONC, SiC, and SiN, wherein the passivating in (b) comprises treating the substrate with a plasma-activated oxygen-containing reactant, and wherein (c) comprises etching the tin oxide using a chlorine-based etch chemistry that comprises exposing the semiconductor substrate to a plasma-activated chlorine-containing reactant selected from the group consisting of Cl_2, BCl_3, and combinations thereof.

15. The method of claim 1, wherein (b) comprises treating the semiconductor substrate with a nitrogen-containing reactant.

16. An apparatus for processing a semiconductor substrate, the apparatus comprising:

(a) a processing chamber having a support for the semiconductor substrate and an inlet for introduction of one or more reactants into the processing chamber; and

(~~c~~b) a controller comprising program instructions for:

(i) causing passivation a silicon-containing layer on a semiconductor substrate towards a tin oxide etch chemistry;

(ii) causing etching of a tin oxide on a semiconductor substrate; and

(iii) causing a repeating, in an alternating fashion of (i) and (ii).

17. The apparatus of claim 16, wherein (i) comprises causing treatment of the semiconductor substrate with a plasma-activated oxygen-containing reactant.

18. The apparatus of claim 16, wherein (i) comprises causing treatment of the semiconductor substrate with a plasma-activated O_2.

19. The apparatus of claim 16, wherein (ii) comprises causing etching of the tin oxide using a chlorine-based chemistry.

20. The apparatus of claim 16, wherein (ii) comprises causing etching of the tin oxide using a hydrogen-based chemistry.

21. The apparatus of claim 16, wherein the program instructions comprise instructions for performing (i) and (ii) in an alternating fashion between 2 – 50 times.