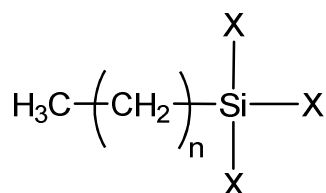


CLAIMS

1. An apparatus for processing semiconductor substrates, the apparatus comprising:
a process chamber comprising a pedestal for holding a substrate;
at least one outlet for coupling to a vacuum; and
a controller for controlling operations in the apparatus including machine-readable instructions for:
causing delivery of a semiconductor substrate to the pedestal of the process chamber,
causing introduction of a blocking reagent to the process chamber,
causing introduction of a silicon-containing precursor to the process chamber and
causing introduction of a nitrogen-containing reactant without igniting a plasma.
2. The apparatus of claim 1, wherein the controller further comprises machine-readable instructions for causing introduction of hydrogen prior to introduction of the blocking reagent.
3. The apparatus of claim 1, further comprising a remote plasma generator for generation of the plasma.
4. The apparatus of claim 1, further comprising a plasma generator for generation of the plasma in the process chamber.
5. A method of depositing silicon nitride on a semiconductor substrate, the method comprising:
providing the semiconductor substrate having an exposed silicon oxide surface and an exposed silicon surface;
exposing the semiconductor substrate to a blocking reagent to block one of the exposed silicon oxide surface and the exposed silicon surface by forming an organic moiety on the one of the exposed silicon oxide surface and the exposed silicon surface while the other of the exposed silicon oxide surface and the exposed silicon surface remains unblocked; and
selectively depositing silicon nitride on the other of the exposed silicon oxide surface and the exposed silicon surface by one or more thermal atomic layer deposition cycles, each cycle comprising:
exposing the semiconductor substrate having the blocked and unblocked surfaces to a

- silicon-containing precursor to adsorb the silicon-containing precursor to the unblocked surface; and
- exposing the semiconductor substrate to a nitrogen-containing reactant without igniting a plasma to form silicon nitride selectively on the unblocked surface relative to the blocked surface.
6. The method of claim 5, wherein the exposed silicon oxide surface comprises hydroxyl groups.
 7. The method of claim 5, further comprising, after selectively depositing the silicon nitride, removing the organic moiety by igniting a plasma.
 8. The method of any of claims 5-7, further comprising, prior to exposing the semiconductor substrate to the blocking reagent, exposing the semiconductor substrate to hydrogen to form hydrogenated groups on the exposed silicon surface.
 9. The method of any of claims 5-6, wherein the silicon-containing precursor is selected from the group consisting of silicon halides and aminosilanes.
 10. The method of any of claims 5-6, wherein the nitrogen-containing reactant is ammonia, nitrogen, a hydrazine, or a combination thereof.
 11. A method of depositing silicon nitride on a semiconductor substrate, the method comprising:
 - providing the semiconductor substrate having a blocked surface and an unblocked surface, the blocked surface comprising an organic moiety having an Si-C bond; and
 - selectively depositing silicon nitride on the unblocked surface by one or more thermal atomic layer deposition cycles, each cycle comprising:
 - exposing the semiconductor substrate having the blocked and unblocked surfaces to a silicon-containing precursor to adsorb the silicon-containing precursor to the unblocked surface; and
 - exposing the semiconductor substrate to a nitrogen-containing reactant without igniting a plasma to form silicon nitride selectively on the unblocked surface relative to the blocked surface.

12. The method of claim 11, wherein the unblocked surface is a non-silicon surface.
13. The method of claim 11, wherein the unblocked surface is a non-silicon-oxide surface.
14. The method of claim 11, wherein the unblocked surface comprises hydroxyl groups.
15. The method of any of claims 11, 12, and 14, further comprising preparing the blocked surface by exposing the semiconductor substrate to an alkene.
16. The method of any of claims 11 and 13, further comprising preparing the blocked surface by exposing the semiconductor substrate to an alkylsilylhalide having a chemical structure



wherein X is a halogen, and n is an integer between and including 1 and 20.

17. The method of any of claims 7 or 16, wherein the plasma is ignited in a remote plasma generator.
18. The method of any of claims 7 or 16, wherein the plasma is ignited in situ.
19. The method of any of claims 5 or 11, further comprising, after selectively depositing the silicon nitride, removing the organic moiety.
20. A method of depositing silicon nitride on a semiconductor substrate, the method comprising:
 - providing the semiconductor substrate having an exposed hydroxyl-terminated silicon-containing surface and an exposed hydrogen-terminated silicon-containing surface;
 - exposing the semiconductor substrate to a blocking reagent to block one of the exposed hydroxyl-terminated silicon-containing surface and the exposed hydrogen-terminated silicon-containing surface by forming an organic moiety on

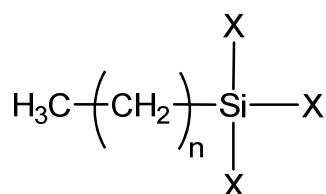
the one of the exposed hydroxyl-terminated silicon-containing surface and the exposed hydrogen-terminated silicon-containing surface while the other of the exposed hydroxyl-terminated silicon-containing surface and the exposed hydrogen-terminated silicon-containing surface remains unblocked; and selectively depositing silicon nitride on the other of the exposed hydroxyl-terminated silicon-containing surface and the exposed hydrogen-terminated silicon-containing surface by one or more thermal atomic layer deposition cycles, each cycle comprising:

exposing the semiconductor substrate having the blocked and unblocked surfaces to a silicon-containing precursor to adsorb the silicon-containing precursor to the unblocked surface; and

exposing the semiconductor substrate to a nitrogen-containing reactant without igniting a plasma to form silicon nitride selectively on the unblocked surface relative to the blocked surface.

21. The method of any of claims 5 or 20, wherein the blocking reagent is an alkene.

22. The method of any of claims 5 or 20, wherein the blocking reagent is an alkylsilylhalide having a chemical structure



wherein X is a halogen, and n is an integer between and including 1 and 20.

23. The method of any of claims 5, 7 or 20-22, further comprising, prior to exposing the semiconductor substrate to the blocking reagent, performing an operation selected from the group consisting of:

exposing the semiconductor substrate to hydrogen to form the exposed hydrogen-terminated silicon-containing surface;

exposing the semiconductor substrate to ambient air to form the exposed hydroxyl-terminated silicon-containing surface; and

exposing the semiconductor substrate to 1% hydrofluoric acid diluted in water to form the exposed hydroxyl-terminated silicon-containing surface.