CLAIMS

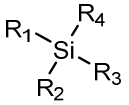
1. A method for depositing a silicon- and oxygen-containing layer on a substrate, the method comprising:

(a) introducing a substrate into a reaction zone of a deposition chamber;

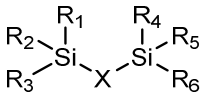
(b) heating or cooling the reaction zone to about 0 °C to about 150 °C; and

(c) performing a thermal atomic layer deposition process on the substrate to form a silicon- and oxygen-containing layer on the substrate by alternately exposing the substrate to at least one silicon-containing compound and low-water content hydrogen peroxide until a desired layer thickness is obtained.

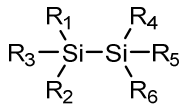
2. The method according to claim 1, wherein the at least one silicon-containing compound has Formula 1, Formula 2, Formula 3, Formula 4, or Formula 5:



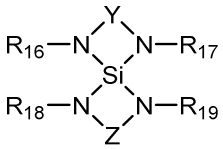
Formula 1



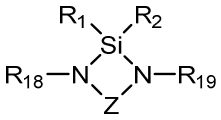
Formula 2



Formula 3



Formula 4



Formula 5

wherein R_1, R_2, R_3, R_4, R_5, R_6, R_{26}, R_{27}, R_{29}, and R_{30} are independently selected from hydrogen, halogen, OR_7 or $N(R_8)(R_9)$; X is O or $N(R_{10})$; Y and Z are $-C(R_{20})(R_{21})$, $-C(R_{20})(R_{21})-C(R_{22})(R_{23})-$, $-C(R_{20})(R_{21})-C(R_{22})(R_{23})-C(R_{24})(R_{25})-$ or $-Si(R_{26})(R_{27})-N(R_{28})-Si(R_{29})(R_{30})-$, Y and Z are optionally bidentate and form a ring with the adjacent nitrogen atoms; R_7 is a linear or branched (C_1-C_8) alkyl group, or $-Si(R_{11})(R_{12})(R_{13})$, R_{11}, R_{12} and R_{13} are independently selected from hydrogen, halide, linear or branched (C_1-C_8)alkoxy, or $-N(R_{14})(R_{15})$, R_{14} and R_{15} are independently hydrogen or linear or branched (C_1-C_8)alkyl; R_8, R_9, R_{10}, R_{16}, R_{17}, R_{18}, R_{19} and R_{28} are independently hydrogen, linear or branched (C_1-C_8) alkyl groups or $Si(R_{31})(R_{32})(R_{33})$, R_{31}, R_{32} and R_{33} are hydrogen, (C_1-C_8)alkyl, or $N(R_{34})(R_{35})$, R_{34} and R_{35} are hydrogen or (C_1-C_8)alkyl; R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, and R_{25} are hydrogen, vinyl, allyl, or linear or branched (C_1-C_4) alkyl; and wherein at least half of the bonds to silicon atoms comprise Si-N bonds or silicon halide bonds.

3. The method according to claim 2, wherein the at least one silicon-containing compound is tris(dimethylamino)silane, tris(dimethylamino)chlorosilane, tris(diethylamino)silane, tris(ethylamino)silane, or tris(isopropylamino)silane.

4. The method according to claim 1, wherein a temperature of the reaction zone in step (b) is below about 50 °C.

5. The method according to claim 1, wherein the hydrogen peroxide contains less than about 10 weight percent water.

6. The method according to any of claims 1 to 5, wherein a deposition rate of the silicon- and oxygen-containing layer is greater than about 0.5 angstroms per cycle and a cycle time is less than about 60 seconds.

7. The method according to any of claims 1 to 5, wherein the substrate comprises a semiconductor device, an active pharmaceutical ingredient, a drug product, a polymer, or a polymer film.

8. A method for depositing a silicon- and carbon-containing layer on a substrate, the method comprising:

(f) introducing a substrate into a reaction zone of a deposition chamber;

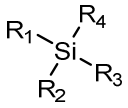
(g) heating or cooling the reaction zone to about 0 °C to about 150 °C; and

(h) performing a thermal atomic layer deposition process on the substrate to form a silicon- and carbon-containing layer on the substrate by alternately exposing the substrate to two or more silicon-containing compounds and low-water content hydrogen peroxide; wherein at least one of the two or more silicon-containing compounds has Formula 1, Formula 2, Formula 3, Formula 4, or Formula 5, and at least one of the two or more silicon-containing compounds has Formula 6, Formula 7, Formula 8, Formula 9, or Formula 10; wherein at least two of the two or more silicon-containing compounds are:

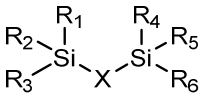
delivered to the substrate simultaneously; or

delivered to the substrate sequentially, optionally separated by purges of the reaction zone, optionally separated by exposures to low-water content hydrogen peroxide, and

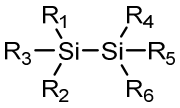
(i) repeating step (h) until a desired layer thickness is obtained:



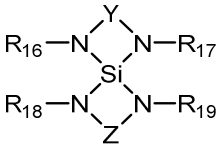
Formula 1



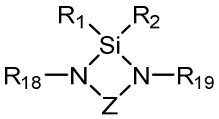
Formula 2



Formula 3

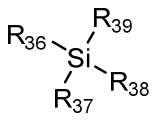


Formula 4

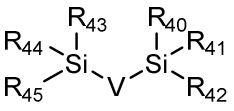


Formula 5

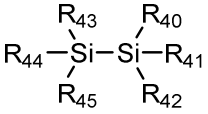
wherein R_1, R_2, R_3, R_4, R_5, R_6, R_{26}, R_{27}, R_{29}, and R_{30} are independently selected from hydrogen, halogen, OR_7 or $N(R_8)(R_9)$; X is O or $N(R_{10})$; Y and Z are $-C(R_{20})(R_{21})$, $-C(R_{20})(R_{21})-C(R_{22})(R_{23})-$, $-C(R_{20})(R_{21})-C(R_{22})(R_{23})-C(R_{24})(R_{25})-$ or $-Si(R_{26})(R_{27})-N(R_{28})-Si(R_{29})(R_{30})-$, Y and Z are optionally bidentate and form a ring with the adjacent nitrogen atoms; R_7 is a linear or branched (C_1-C_8) alkyl group, or $-Si(R_{11})(R_{12})(R_{13})$, R_{11}, R_{12} and R_{13} are independently selected from hydrogen, halide, linear or branched (C_1-C_8)alkoxy, or $-N(R_{14})(R_{15})$, R_{14} and R_{15} are independently hydrogen or linear or branched (C_1-C_8)alkyl; R_8, R_9, R_{10}, R_{16}, R_{17}, R_{18}, R_{19} and R_{28} are independently hydrogen, linear or branched (C_1-C_8) alkyl groups or $Si(R_{31})(R_{32})(R_{33})$, R_{31}, R_{32} and R_{33} are hydrogen, (C_1-C_8)alkyl, or $N(R_{34})(R_{35})$, R_{34} and R_{35} are hydrogen or (C_1-C_8)alkyl; R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, and R_{25} are hydrogen, vinyl, allyl, or linear or branched (C_1-C_4) alkyl; and wherein at least half of the bonds to silicon atoms comprise Si-N bonds or silicon halide bonds;



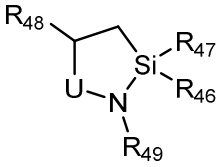
Formula 6



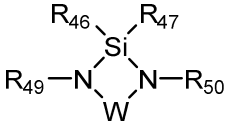
Formula 7



Formula 8



Formula 9



Formula 10

wherein R_{36}, R_{37}, R_{38}, R_{39}, R_{40}, R_{41}, R_{42}, R_{43}, R_{44}, R_{45}, R_{46}, R_{47}, R_{79}, and R_{80} are independently selected from hydrogen, halogen, linear or branched (C_1-C_{18}) alkyl, linear or branched (C_1-C_{18}) alkoxy, vinyl, allyl, butenyl, phenyl, tolyl, cyclohexyl, cyclooctyl, or norbornyl, or $N(R_{51})(R_{52})$; V is optionally bidentate and is O, $N(R_{53})$, $C(R_{73})(R_{74})$, linear or branched (C_1-C_8) alkyl, or $-C(R_{73})(R_{74})-C(R_{75})(R_{76})-$ wherein R_{73}, R_{74}, R_{75} and R_{76} are hydrogen or linear or branched (C_1-C_8)alkyl; R_{49}, R_{50}, R_{51}, R_{52} and R_{53} are hydrogen, a linear or branched (C_1-C_8) alkyl group, or $-Si(R_{54})(R_{55})(R_{56})$; R_{54}, R_{55} and R_{56} are independently selected from hydrogen, linear or branched (C_1-C_8)alkyl, linear or branched (C_1-C_8)alkoxy, or $-N(R_{57})(R_{58})$; R_{57} and R_{58} are independently hydrogen or (C_1-C_8)alkyl; R_{48} is hydrogen or linear or branched (C_1-C_8) hydrocarbon; W is

optionally bidentate and forms a ring with the adjacent nitrogen, silicon, and/or carbon atoms and is a linear or branched (C_1-C_8) alkyl, C(R_{59})(R_{60}), -C(R_{59})(R_{60})-C(R_{61})(R_{62})-, -C(R_{59})(R_{60})-C(R_{61})(R_{62})-C(R_{63})(R_{64})- or -Si(R_{65})(R_{66})-N(R_{67})-Si(R_{68})(R_{69})-; R_{59}, R_{60}, R_{61}, R_{62}, R_{63}, R_{64} are independently hydrogen, linear or branched (C_1-C_8)alkyl; R_{65}, R_{66}, R_{68} and R_{69} are hydrogen, halide, (C_1-C_8) alkyl, O(R_{70}) or N(R_{71})(R_{72}); R_{70} is linear or branched (C_1-C_8)alkyl; U is C(R_{77})(R_{78}) or Si(R_{79})Si(R_{80}); R_{67}, R_{71}, R_{72}, R_{77}, and R_{78} are independently hydrogen or linear or branched (C_1-C_8)alkyl; and wherein the compound having Formula 6, Formula 7, Formula 8, Formula 9, or Formula 10 contains at least one silicon-nitrogen or silicon-halide bond, and at least one silicon-carbon bond.

9. The method according to claim 8, wherein all but a final exposure of the substrate to the two or more silicon-containing compounds covers only a fraction of the available substrate surface or is followed by an exposure to low-water content hydrogen peroxide.

10. The method according to claim 8, wherein at least one of the silicon-containing compounds having Formula 1, Formula 2, Formula 3, Formula 4, or Formula 5 is tris(dimethylamino)silane, tris(dimethylamino)chlorosilane, tris(diethylamino)silane, tris(ethylamino)silane, or tris(isopropylamino)silane.

11. The method according to any of claims 8 to 10, wherein at least one of the silicon-containing compounds having Formula 6, Formula 7, Formula 8, Formula 9, or Formula 10 is tris(dimethylamino)methylsilane, bis(tris(dimethylamino)silyl)methane, n-methyl-aza-2,2,4-trimethylsilacyclopentane or bis(dimethylaminomethylsilyl)methane.

12. The method according to any of claims 8 to 11, wherein a temperature of the reaction zone in step (g) is below about 50°C.

13. The method according to any of claims 8 to 12, wherein the hydrogen peroxide contains less than about 10 weight percent water.

14. The method according to any of claims 8 to 13, wherein a deposition rate of the silicon- and carbon-containing layer is greater than about 0.5 angstroms per cycle and a cycle time is less than about 60 seconds.

15. The method according to any of claims 8 to 14, wherein the substrate comprises a semiconductor device, an active pharmaceutical ingredient, a drug product, a polymer, or a polymer film.

16. A method for selectively depositing a silicon-containing layer on a patterned substrate, the method comprising:

(j) introducing a patterned substrate into a reaction zone of a deposition chamber;

(k) heating or cooling the reaction zone to about 0 °C to about 150 °C;

(l) performing a thermal atomic layer deposition process on the substrate to form a silicon-containing layer on the substrate by alternately exposing the substrate to low-water content hydrogen peroxide and at least one silicon-containing compound having Formula 1, Formula 2, Formula 3, Formula 4, or Formula 5 until a desired layer thickness is obtained; or

(m) performing a thermal atomic layer deposition process on the substrate to form a silicon- and carbon-containing layer on the substrate by alternately exposing the substrate to two or more silicon-containing compounds and low-water content hydrogen peroxide; wherein at least one of the two or more silicon-containing compounds has Formula 1, Formula 2, Formula 3, Formula 4, or Formula 5, and at least one of the two or more silicon-containing compounds has Formula 6, Formula 7, Formula 8, Formula 9, or Formula 10; wherein at least two of the two or more silicon-containing compounds are:

delivered to the substrate simultaneously; or

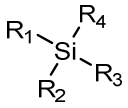
delivered to the substrate sequentially, optionally separated by purges of the reaction zone, optionally separated by exposures to low-water content hydrogen peroxide, and

(n) repeating step (m) until a desired layer thickness is reached;

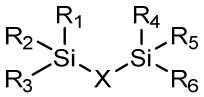
wherein the method further comprises:

prior to step (j): (j2) performing one or more substrate passivation steps; and/or

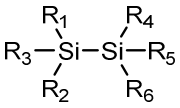
prior to step (k): (k2) performing one or more substrate passivation steps;



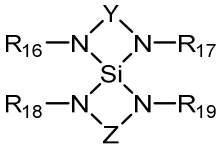
Formula 1



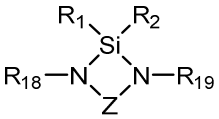
Formula 2



Formula 3

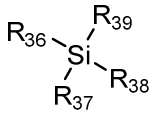


Formula 4

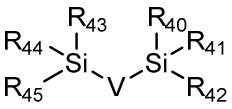


Formula 5

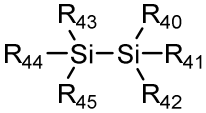
wherein R_1, R_2, R_3, R_4, R_5, R_6, R_{26}, R_{27}, R_{29}, and R_{30} are independently selected from hydrogen, halogen, OR_7 or $N(R_8)(R_9)$; X is O or $N(R_{10})$; Y and Z are $-C(R_{20})(R_{21})$, $-C(R_{20})(R_{21})-C(R_{22})(R_{23})-$, $-C(R_{20})(R_{21})-C(R_{22})(R_{23})-C(R_{24})(R_{25})-$ or $-Si(R_{26})(R_{27})-N(R_{28})-Si(R_{29})(R_{30})-$, Y and Z are optionally bidentate and form a ring with the adjacent nitrogen atoms; R_7 is a linear or branched (C_1-C_8) alkyl group, or $-Si(R_{11})(R_{12})(R_{13})$, R_{11}, R_{12} and R_{13} are independently selected from hydrogen, halide, linear or branched (C_1-C_8)alkoxy, or $-N(R_{14})(R_{15})$, R_{14} and R_{15} are independently hydrogen or linear or branched (C_1-C_8)alkyl; R_8, R_9, R_{10}, R_{16}, R_{17}, R_{18}, R_{19} and R_{28} are independently hydrogen, linear or branched (C_1-C_8) alkyl groups or $Si(R_{31})(R_{32})(R_{33})$, R_{31}, R_{32} and R_{33} are hydrogen, (C_1-C_8)alkyl, or $N(R_{34})(R_{35})$, R_{34} and R_{35} are hydrogen or (C_1-C_8)alkyl; R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, and R_{25} are hydrogen, vinyl, allyl, or linear or branched (C_1-C_4) alkyl; and wherein at least half of the bonds to silicon atoms comprise Si-N bonds or silicon halide bonds;



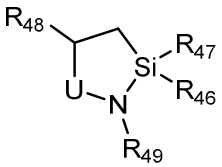
Formula 6



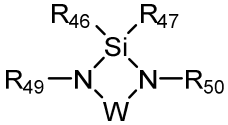
Formula 7



Formula 8



Formula 9



Formula 10

wherein R_{36}, R_{37}, R_{38}, R_{39}, R_{40}, R_{41}, R_{42}, R_{43}, R_{44}, R_{45}, R_{46}, R_{47}, R_{79}, and R_{80} are independently selected from hydrogen, halogen, linear or branched (C_1-C_{18}) alkyl, linear or branched (C_1-C_{18}) alkoxy, vinyl, allyl, butenyl, phenyl, tolyl, cyclohexyl, cyclooctyl, or norbornyl, or $N(R_{51})(R_{52})$; V is optionally bidentate and is O, $N(R_{53})$, $C(R_{73})(R_{74})$, linear or branched (C_1-C_8) alkyl, or $-C(R_{73})(R_{74})-C(R_{75})(R_{76})-$ wherein R_{73}, R_{74}, R_{75} and R_{76} are hydrogen or linear or branched (C_1-C_8)alkyl; R_{49}, R_{50}, R_{51}, R_{52} and R_{53} are hydrogen, a linear or branched (C_1-C_8) alkyl group, or $-Si(R_{54})(R_{55})(R_{56})$; R_{54}, R_{55} and R_{56} are independently selected from hydrogen, linear or branched (C_1-C_8)alkyl, linear or branched (C_1-C_8)alkoxy, or $-N(R_{57})(R_{58})$;

R_{57} and R_{58} are independently hydrogen or (C_1-C_8)alkyl; R_{48} is hydrogen or linear or branched (C_1-C_8) hydrocarbon; W is optionally bidentate and forms a ring with the adjacent nitrogen, silicon, and/or carbon atoms and is a linear or branched (C_1-C_8) alkyl, C(R_{59})(R_{60}), -C(R_{59})(R_{60})-C(R_{61})(R_{62})-, -C(R_{59})(R_{60})-C(R_{61})(R_{62})-C(R_{63})(R_{64})- or -Si(R_{65})(R_{66})-N(R_{67})-Si(R_{68})(R_{69})-; R_{59}, R_{60}, R_{61}, R_{62}, R_{63}, R_{64} are independently hydrogen, linear or branched (C_1-C_8)alkyl; R_{65}, R_{66}, R_{68} and R_{69} are hydrogen, halide, (C_1-C_8) alkyl, O(R_{70}) or N(R_{71})(R_{72}); R_{70} is linear or branched (C_1-C_8)alkyl; U is C(R_{77})(R_{78}) or Si(R_{79})Si(R_{80}); R_{67}, R_{71}, R_{72}, R_{77}, and R_{78} are independently hydrogen or linear or branched (C_1-C_8)alkyl; and wherein the compound having Formula 6, Formula 7, Formula 8, Formula 9, or Formula 10 contains at least one silicon-nitrogen or silicon-halide bond, and at least one silicon-carbon bond.

17. The method according to claim 16, wherein all but a final exposure of the substrate to the two or more silicon-containing compounds covers only a fraction of the available substrate surface or is followed by an exposure to low-water content hydrogen peroxide.

18. The method according to claim 16 or 17, wherein at least one passivation step (j2) or (k2) meets the following criteria:

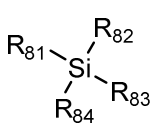
(i) when the substrate comprises silicon dioxide, silicon oxycarbide, silicon oxynitride, silicon carboxynitride, or germanium dioxide, exposing the patterned substrate to a compound having Formula 11 or Formula 12 to selectively passivate regions of the substrate; or

(ii) when the substrate comprises silicon nitride, titanium nitride, tantalum nitride, or germanium nitride, exposing the patterned substrate to a compound containing an aldehyde functional group to selectively passivate regions of the substrate; or

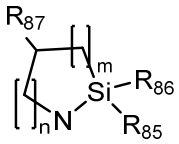
(iii) when the substrate comprises copper, cobalt, molybdenum, ruthenium, and/or tungsten, exposing the patterned substrate to an N-heterocyclic carbene or a chemical compound containing sulfur or phosphorus to selectively passivate regions of the substrate; or

(iv) when the substrate comprises silicon, germanium, copper, cobalt, molybdenum, ruthenium, or tungsten, exposing the patterned substrate to a chemical compound of Formula 13 to selectively passivate regions of the substrate; or

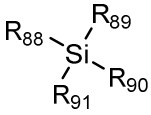
(v) when the substrate comprises aluminum oxide, exposing the patterned substrate to a chemical compound of Formula 11, Formula 12, Formula 14, or Formula 15 to selectively passivate regions of the substrate:



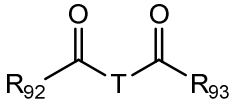
Formula 11



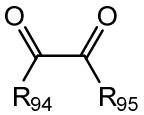
Formula 12



Formula 13



Formula 14



Formula 15

wherein R_{81}, R_{82}, R_{83}, and R_{84} are independently hydrogen, halogen, linear or branched (C_1-C_8)alkyl, linear or branched (C_1-C_8)alkoxy, or N(R_{96})(R-$_{97}$), wherein R_{96} and R_{97} are independently hydrogen or (C_1-C_8)alkyl, and at least one of R_{81}, R_{82}, R_{83}, and R_{84} is a linear or branched (C_1-C_8)alkyl and at least one is N(R_{96})(R_{97}); R_{85} and R_{86} are hydrogen, halogen, linear or branched (C_1-C_8)alkyl, linear or branched (C_1-C_8)alkoxy, or N(R_{96})(R_{97}); R_{88}, R_{89}, R_{90} and R_{91} are independently hydrogen or (C_1-C_{18})alkyl, and at least one of R_{88}, R_{89}, R_{90}, or R_{91} is hydrogen and at least one is (C_1-C_{18})alkyl; T is linear or branched (C_1-C_4)alkyl; and R_{92}, R_{93}, R_{94} and R_{95} are hydrogen or (C_1-C_4)alkyl; wherein R_{87} is hydrogen or linear or branched (C_1-C_4)alkyl; and wherein n and m are 1, 2, or 3.

19. The method according to any of claims 16 to 18, wherein the silicon-containing compound having Formula 1, Formula 2, Formula 3, Formula 4, or Formula 5 is tris(dimethylamino)silane, tris(dimethylamino)chlorosilane, tris(diethylamino)silane, tris(ethylamino)silane, or tris(isopropylamino)silane.

20. The method according to claim 19, wherein the silicon-containing compound having Formula 6, Formula 7, Formula 8, Formula 9, or Formula 10 is tris(dimethylamino)methylsilane, bis(tris(dimethylamino)silyl)methane, n-methyl-aza-2,2,4-trimethylsilacyclopentane or bis(dimethylaminomethylsilyl)methane.

21. The method according to any of claims 16 to 20, wherein a temperature of the reaction zone in step (k) is below about 50 °C.

22. The method according to any of claims 16 to 21, wherein the hydrogen peroxide comprises less than about 10 weight percent water.

23. The method according to any of claims 16 to 22, wherein a deposition rate of the silicon- or silicon- and carbon-containing layer is greater than about 0.5 angstroms per cycle and a cycle time is less than about 60 seconds.

24. The method according to any of claims 16 to 23, wherein the patterned substrate has growth and non-growth surfaces, and wherein a selectivity ratio between the growth and the non-growth surfaces is at least about 2:1.

25. The method according to claim 24, wherein the selectivity ratio between the growth and the non-growth surfaces is at least about 10:1.

26. The method according to any of claims 16 to 25, wherein the substrate comprises a semiconductor device, an active pharmaceutical ingredient, a drug product, a polymer, or a polymer film.