DESCRIPTION

METHODS OF FORMING A PHOSPHORUS DOPED SILICON DIOXIDE COMPRISING LAYER, AND METHODS OF FORMING TRENCH ISOLATION IN THE FABRICATION OF INTEGRATED CIRCUITRY

TECHNICAL FIELD

This invention relates to methods of forming phosphorus doped silicon dioxide comprising layers, and to methods of forming trench isolation in the fabrication of integrated circuitry.

BACKGROUND ART

One commonly used material in the fabrication of integrated circuitry is silicon dioxide. Such might be utilized as essentially 100% pure, or in combination with other materials, including property-modifying dopants. Accordingly, silicon dioxide might be utilized as a mixture with other materials in forming a layer or layers and may or may not constitute a majority of the given layer. Exemplary materials are borophosphosilicate glass (BPSG), phosphosilicate glass (PSG), and borosilicate glass (BSG). Typically, such materials have anywhere from 1% to 4% atomic concentration of each of boron and/or phosphorus atoms, although atomic percent concentrations in excess of 5% have also been used.

As semiconductor devices continue to shrink geometrically, such has had a tendency to result in greater shrinkage in the horizontal dimension than in the vertical dimension. In some instances, the vertical dimension increases. Regardless, increased aspect ratios (height to width) of the devices result, making it increasingly important to develop processes that enable dielectric and other materials to fill high aspect or increasing aspect ratio trenches, vias and other steps or structures. A typical dielectric material of choice has been doped and/or undoped silicon dioxide comprising materials, for example those described above. Dopants such as boron and phosphorus can facilitate a reflowing of the deposited layer at a higher temperature to facilitate more completely filling openings on a substrate. Various reactant precursors can be utilized in forming silicon dioxide layers, for example the silanols disclosed in U.S. Patent No. 6,300,219.

SUMMARY

This invention includes methods of forming a phosphorus doped silicon dioxide comprising layers, and methods of forming trench isolation in the fabrication of integrated circuitry. In one implementation, a method of forming a phosphorus doped silicon dioxide comprising layer includes positioning a substrate within a deposition chamber. First and second vapor phase reactants are introduced in alternate and temporally separated pulses to the substrate within the chamber in a plurality of deposition cycles under conditions effective to deposit a phosphorus doped silicon dioxide comprising layer on the substrate. One of the first and second vapor phase reactants is $PO(OR)_3$ where R is hydrocarbyl, and an other of the first and second vapor phase reactants is $Si(OR)_3OH$ where R is hydrocarbyl.

In one implementation, a method of forming a phosphorus doped silicon dioxide comprising layer includes positioning a substrate within a deposition chamber. A first species is chemisorbed to a surface of the substrate to form a first species monolayer onto the surface within the chamber from a first vapor phase reactant comprising $PO(OR)_3$, where R is hydrocarbyl. The chemisorbed first species is contacted with a second vapor phase reactant comprising $Si(OR)_3OH$, where R is hydrocarbyl, to form a monolayer comprising Si and O. Chemisorbing with the first species and contacting the chemisorbed first species with the second reactant are successively repeated under conditions effective to deposit a phosphorus doped silicon dioxide comprising layer on the substrate.

Other aspects and implementations are contemplated.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a diagrammatic sectional view of a semiconductor wafer fragment in process in accordance with an aspect of the invention.

Fig. 2 is a view of the Fig. 1 wafer fragment at a processing step subsequent to that shown by Fig. 1.

Fig. 3 is a view of the Fig. 2 wafer fragment at a processing step subsequent to that shown by Fig. 2.

Fig. 4 is a diagrammatic sectional view of a semiconductor wafer fragment in process in accordance with an aspect of the invention.

Fig. 5 is a view of the Fig. 4 wafer fragment at a processing step subsequent to that shown by Fig. 4.

Fig. 6 is a view of the Fig. 5 wafer fragment at a processing step subsequent to that shown by Fig. 5.

Fig. 7 is a view of the Fig. 6 wafer fragment at a processing step subsequent to that shown by Fig. 6.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In one implementation, a method of forming a phosphorus doped silicon dioxide comprising layer includes positioning a substrate to be deposited upon within a deposition chamber. First and second vapor phase reactants are introduced in alternate and temporally separated pulses to the substrate within the chamber in a plurality of deposition cycles under conditions effective to deposit a phosphorus doped silicon dioxide comprising layer on the substrate. One of the first and second vapor phase reactants is $PO(OR)_3$, where R is hydrocarbyl. An other of the first and second vapor phase reactants is $Si(OR)_3OH$, where R is hydrocarbyl. Such might be conducted by atomic layer deposition (ALD) methods (for example including chemisorbing and contacting methods), by chemical vapor deposition (CVD) methods, and by other methods, as well as by combinations of these and other methods. CVD and ALD are used herein as referred to in the co-pending U.S. Patent Application Serial No. 10/133,947, filed on April 25, 2002, entitled "Atomic Layer Deposition Methods and Chemical Vapor Deposition Methods", and listing Brian A. Vaartstra as the inventor. This 10/133,947 application filed on April 25, 2002 is hereby fully incorporated by reference as if presented in its entirety herein. Preferred and understood reduction-to-practice examples provided herein are understood to be primarily by atomic layer deposition.

The R hydrocarbyl of the $PO(OR)_3$ and the R hydrocarbyl of the $Si(OR)_3OH$ may be the same or different, and regardless in one preferred embodiment the R hydrocarbyl of each contains only from one to five carbon atoms. One preferred and reduction-to-practice $PO(OR)_3$ material comprises triethyl phosphate. One preferred exemplary and reduction-to-practice $Si(OR)_3OH$ material comprises tristertbutylsilanol. Exemplary preferred conditions comprise a temperature of from about 50°C to about 500°C, and more preferably at from about 100°C to about 300°C.

Exemplary pressure conditions are subatmospheric, preferably being from about 10^{-7} Torr to about 10 Torr, and more preferably from about 10^{-4} Torr to about 1 Torr. The conditions might comprise plasma generation of at least one of the first and second reactants, or be void of plasma generation of the first and second reactants. If plasma generation is utilized, such might occur within the chamber of deposition, and/or externally thereof. Most preferred are believed to be conditions which are void of plasma generation of the first and second reactants.

The conditions might be effective to form the silicon dioxide comprising layer to have very low phosphorus content, for example to have no more than 0.5 atomic percent phosphorus, including lesser amounts. Alternately, the conditions might be effective to form the silicon dioxide comprising layer to have at least 1.0 atomic percent phosphorus including, for example, 5.0 and greater atomic percent phosphorus.

The method might be void of introducing any vapor phase reactant to the chamber other than the first and second vapor phase reactants in the forming of the phosphorus doped silicon dioxide comprising layer. Alternately, the method might include introducing another vapor phase reactant, different from the first and second vapor phase reactants, intermediate at least some of the separated pulses of the first and second vapor phase reactants. By way of example only, an exemplary another vapor phase reactant is oxygen containing, for example O_2, O_3 and/or any vapor phase oxygen containing compound. Ozone pulses, for example as a mixture of O_2 and O_3, in addition to the $PO(OR)_3$ flows have been determined to facilitate greater phosphorus incorporation, for example above 5 atomic percent, if such is desired.

Another exemplary vapor phase reactant would be boron containing, and whereby the phosphorus doped silicon dioxide comprising layer would also then comprise boron, for example in fabricating a BPSG or BPSG-like material. An exemplary boron containing material reactant is $B(OR)_3$.

The alternate and temporally separated pulses might include one or a combination of chamber pump down and/or purging of the chamber with an inert gas (i.e., N_2 and/or any noble gas) intermediate the separated pulses to remove unreacted precursor/reactant.

One prior art technique of forming a silicon dioxide comprising layer is described in Hausmann et al., *Rapid Vapor Deposition of Highly Conformal*

Silica Nanolaminates, SCIENCE MAGAZINE, Vol. 298, pp. 402-406 (2002). Such a process initially utilizes a methyaluminum reactant precursor, for example triethyl aluminum or aluminum dimethylamide, which forms an initial aluminum containing layer on the substrate. An alkoxysilanol, for example tris(tert-butoxy)silanol, is thereafter flowed to the substrate. Apparently, the aluminum presence provides a self-limited catalytic reaction whereby a silicon dioxide comprising layer deposits to some self-limiting thickness anywhere from 100 Angstroms to 700 Angstroms. In other words, continued exposure to the alkoxysilanol does not result in continuing growth of the silicon dioxide comprising layer. Apparently, the silicon dioxide layer self-limited growth occurs in some catalytic manner, as opposed to a simple ALD-like manner due to significantly more than a few monolayers being formed by the silanol exposure/pulsing. Regardless, aluminum is incorporated in the resultant layer, which may not be desired.

While the invention disclosed herein does not preclude its use with the Hausmann et al.-like process, most preferably the inventive process is void of introducing any vapor phase aluminum containing reactant to the chamber in the forming of the phosphorus doped silicon dioxide comprising layer. Further preferably in accordance with the invention, the substrate is void of aluminum in the forming of the phosphorus doped silicon dioxide comprising layer.

In one implementation, a method of forming a phosphorus doped silicon dioxide comprising layer includes at least some ALD processing. By way of example only, an exemplary such process is described with reference to Figs. 1-3. Referring to Fig. 1, a substrate 10 is positioned within any suitable deposition chamber (not shown). In one exemplary embodiment, substrate 10 is a semiconductor substrate, for example comprising some material 12 which preferably includes at least some semiconductive material, and may, of course, include multiple materials and layers. In the context of this document, the term "semiconductor substrate" or "semiconductive substrate" is defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to,

the semiconductive substrates described above. Substrate 10 has a surface 14 which is provided to be hydroxylated (having pending OH groups) as shown. Other surface termination is also contemplated to be effective in the process herein described. If hydroxylated, such surface might by hydroxylated prior to provision within the deposition chamber, or hydroxylated within the deposition chamber. An exemplary technique for hydroxylating surface 14 includes exposure of the surface to water vapor. Further, the surface might be naturally hydroxylated simply from exposure to ambient atmosphere.

Referring to Fig. 2, a first species is chemisorbed to form a first species monolayer 16 onto the hydroxylated surface within the chamber from a first vapor phase reactant comprising $PO(OR)_3$, where R is hydrocarbyl, for example as described above. Such is depicted as being comprised of a variable "A" as constituting at least a part of layer 16 in Fig. 2. Preferred conditions and other attributes are as described above with respect to the first described implementation.

Referring to Fig. 3, the chemisorbed first species has been contacted with a second vapor phase reactant comprising $Si(OR)_3OH$, where R is hydrocarbyl, to form a monolayer 18 which will comprise Si and O. Again, conditions are preferably as described above with respect to the first implementation. Fig. 3 depicts layer 18 as comprising a variable "B", with the chemisorbed first species monolayer being depicted as A' exemplary of some modification of the A species in the chemisorbing of B with A, with the exact preferred and typical species A and B not having been determined. Regardless, chemisorbing with the first species and contacting the chemisorbed first species with the second reactant is successively repeated under conditions effective to deposit a phosphorus doped silicon dioxide comprising layer on the substrate. Typically and preferably, such chemisorbings and contactings are conducted in alternate and temporally separated pulses to the substrate, for example as described above in the first described implementation.

The immediately above-described implementation was relative to the chemisorbing of a surface with $PO(OR)_3$ followed by a second vapor phase reactant exposure comprising $Si(OR)_3OH$, and by which an aspect of the invention was reduced-to-practice, although aspects of the invention are not necessarily so limited.

Regardless, aspects of the invention might preferably be utilized in methods of forming trench isolation in the fabrication of integrated circuitry, for example as shown and described with reference to Figs. 4-7. Fig. 4 shows a semiconductor substrate 26 comprising a bulk monocrystalline silicon or other semiconductive material substrate 28. A masking layer 30 is formed over semiconductor substrate 28. Such is depicted as comprising a pad oxide layer 32 and an overlying nitride comprising layer 34, for example silicon nitride.

Referring to Fig. 5, isolation trenches 36 and 38 have been etched through masking layer 30 into the semiconductive material of substrate 28/26. A thermal oxide layer or other layer, for example silicon nitride (not shown), might be provided now or subsequently, for example with respect to silicon dioxide by exposing substrate 26 to thermal oxidizing conditions.

Referring to Fig. 6, a phosphorus doped silicon dioxide comprising layer 40 has been formed within semiconductive material isolation trenches 36 and 38. Exemplary techniques for doing so include introducing first and second vapor phase reactants in alternate and temporally separated pulses to the substrate within the chamber in a plurality of deposition cycles, as described above, and also for example, by the chemisorbings and contacting methods as described above. As depicted, the depositing is effective to deposit phosphorus doped silicon dioxide comprising layer 40 onto masking layer 30, and also is depicted as not being effective to selectively deposit phosphorus doped silicon dioxide layer 40 within isolation trenches 36 and 38. In the context of this document, a "selective/selectively deposit" is one which deposits a material over one region of a substrate as compared to another at a deposition thickness ratio of at least 2:1.

The depositing might be effective to completely fill isolation trenches 36 and 38, or to not fill such isolation trenches for example as shown in Fig. 6. Deposition processing, for example as described in any of the above, could continue to completely fill such trenches, for example as shown in Fig. 7. Alternately by way of example only, the Fig. 6 construction could be filled with another material before or after removing the material from over masking layer 30.

An exemplary reduction-to-practice example utilized triethyl phosphate and tris(tert-butoxy)silanol as first and second respective vapor phase reactants. A 650 Angstrom conformal layer of PSG (8 atomic percent phosphorus) was deposited over a silicon nitride lined trench using respective two second reactive pulses of each reactant, with a one second argon purge followed by a three second pump down without flowing argon between the reactant pulses. This was conducted for 600 complete cycles at 300°C. No ozone was utilized. Respective bubbler/ampoule temperatures for feeding the triethyl phosphate and tris(tert-butoxy)silanol were 50°C and 40°C.

Such processing was also conducted with the triethyl phosphate having a temperature of 60°C and with tris(tert-butoxy)silanol at 70°C. One (1) second and 0.5 second respective pulses of such triethyl phosphate and of the tris(tert-butoxy)silanol yielded a 650 Angstrom film after 300 complete cycles, providing an approximate 2.2 Angstrom per cycle rate of deposition. This was somewhat higher than the first reduction-to-practice example deposition, which was at 1.1 Angstroms per cycle. The deposited film was substantially carbon-free, and the phosphorus content was below 0.5 atomic percent. Longer triethyl phosphate exposure at such reactant temperature is expected to yield higher growth rates and increase phosphorus content in the deposited film.

In another reduction-to-practice example, triethyl phosphate from a 60°C bubbler/ampoule was fed to a substrate within a deposition chamber for one second. This was followed by the flow of 30 sccm Ar for one second, followed by three seconds of pumping down the chamber without flowing any gas thereto. Thereafter, 25 sccm of a combined stream of O_2/O_3 (5% to 12% O_3 by volume) was flowed to the chamber for two seconds. This was followed by a 30 sccm flow of Ar for one second, followed by three seconds of pump down while feeding no gas to the chamber. Then, tris(tert-butoxy)silanol was flowed to the chamber from a 60°C bubbler/ampoule for two seconds. This was followed by one second of Ar flow at 30 sccm, again followed by three seconds of pump down while no gas flowed to the chamber. This was conducted for 400 complete cycles, with pressure during all of the processing varying from 0.24 Torr to 10^{-6} Torr. Such resulted in a 1000 Angstrom thick layer having 5.7 atomic percent phosphorus incorporated therein.

CLAIMS

What is claimed is:

1. A method of forming a phosphorus doped silicon dioxide comprising layer, comprising:

positioning a substrate within a deposition chamber; and

introducing first and second vapor phase reactants in alternate and temporally separated pulses to the substrate within the chamber in a plurality of deposition cycles under conditions effective to deposit a phosphorus doped silicon dioxide comprising layer on the substrate, one of the first and second vapor phase reactants being $PO(OR)_3$ where R is hydrocarbyl, and an other of the first and second vapor phase reactants being $Si(OR)_3OH$ where R is hydrocarbyl.

2. The method of claim 1 wherein the conditions comprise atomic layer deposition.

3. The method of claim 1 wherein the conditions are effective to form the silicon dioxide comprising layer to have no more than 0.5 atomic percent phosphorus.

4. The method of claim 1 wherein the conditions are effective to form the silicon dioxide comprising layer to have at least 1.0 atomic percent phosphorus.

5. The method of claim 1 being void of introducing any vapor phase reactant to the chamber other than said first and second vapor phase reactants in said forming of the phosphorus doped silicon dioxide comprising layer.

6. The method of claim 1 comprising introducing another vapor phase reactant different from the first and second vapor phase reactants intermediate at least some of said separated pulses of the first and second vapor phase reactants.

7. The method of claim 6 wherein the another vapor phase reactant is oxygen containing.

8. The method of claim 7 wherein the another vapor phase reactant comprises O_3.

9. The method of claim 6 wherein the another vapor phase reactant is boron containing, the phosphorus doped silicon dioxide comprising layer comprising boron.

10. The method of claim 1 wherein the R hydrocarbyl of the $PO(OR)_3$ contains only from one to five carbon atoms.

11. The method of claim 1 wherein the R hydrocarbyl of the $Si(OR)_3OH$ contains only from one to five carbon atoms.

12. The method of claim 1 wherein the $PO(OR)_3$ comprises triethyl phosphate.

13. The method of claim 1 wherein the $Si(OR)_3OH$ comprises tris(tert-butoxy)silanol.

14. The method of claim 1 wherein the $PO(OR)_3$ comprises triethyl phosphate, and wherein the $Si(OR)_3OH$ comprises tris(tert-butoxy)silanol.

15. The method of claim 1 wherein the conditions comprise a temperature from about 50°C to about 500°C.

16. The method of claim 15 wherein the conditions comprise a temperature from about 100°C to about 300°C.

17. The method of claim 1 wherein the conditions comprise a pressure from about 10^{-7} Torr to about 10 Torr.

18. The method of claim 1 wherein the conditions comprise plasma generation of at least one of the first and second reactants.

19. The method of claim 1 wherein the conditions are void of plasma generation of the first and second reactants.

20. The method of claim 1 comprising purging the chamber with an inert gas intermediate the separated pulses.

21. The method of claim 1 being void of aluminum on the substrate in said forming of the phosphorus doped silicon dioxide comprising layer.

22. The method of claim 1 being void of introducing any vapor phase aluminum containing reactant to the chamber in said forming of the phosphorus doped silicon dioxide comprising layer.

23. A method of forming a phosphorus doped silicon dioxide comprising layer, comprising:

positioning a substrate within a deposition chamber;

chemisorbing a first species to a surface of the substrate to form a first species monolayer onto the surface within the chamber from a first vapor phase reactant comprising $PO(OR)_3$, where R is hydrocarbyl;

contacting the chemisorbed first species with a second vapor phase reactant comprising $Si(OR)_3OH$, where R is hydrocarbyl, to form a monolayer comprising Si and O; and

successively repeating chemisorbing with the first species and contacting the chemisorbed first species with the second reactant under conditions effective to deposit a phosphorus doped silicon dioxide comprising layer on the substrate.

24. The method of claim 23 wherein the substrate surface to which the first species is at least first chemisorbed is provided to be an hydroxylated surface.

25. The method of claim 23 wherein the conditions are effective to form the silicon dioxide comprising layer to have no more than 0.5 atomic percent phosphorus.

26. The method of claim 23 wherein the conditions are effective to form the silicon dioxide comprising layer to have at least 1.0 atomic percent phosphorus.

27. The method of claim 24 being void of introducing any vapor phase reactant to the chamber other than said first and second vapor phase reactants at least after providing the hydroxylated surface in said forming of the phosphorus doped silicon dioxide comprising layer.

28. The method of claim 23 comprising introducing another vapor phase reactant different from the first and second vapor phase reactants intermediate at least some of said repeated chemisorbings and contactings.

29. The method of claim 28 wherein the another vapor phase reactant is oxygen containing.

30. The method of claim 29 wherein the another vapor phase reactant comprises O_3.

31. The method of claim 28 wherein the another vapor phase reactant is boron containing, the phosphorus doped silicon dioxide comprising layer comprising boron.

32. The method of claim 23 wherein the R hydrocarbyl of the $PO(OR)_3$ contains only from one to five carbon atoms.

33. The method of claim 23 wherein the R hydrocarbyl of the $Si(OR)_3OH$ contains only from one to five carbon atoms.

34. The method of claim 23 wherein the $PO(OR)_3$ comprises triethyl phosphate.

35. The method of claim 23 wherein the $Si(OR)_3OH$ comprises tris(tert-butoxy)silanol.

36. The method of claim 23 wherein the $PO(OR)_3$ comprises triethyl phosphate, and wherein the $Si(OR)_3OH$ comprises tris(tert-butoxy)silanol.

37. The method of claim 23 comprising purging the chamber with an inert gas intermediate said repeated chemisorbings and contactings.

38. The method of claim 23 being void of aluminum on the substrate in said forming of the phosphorus doped silicon dioxide comprising layer.

39. The method of claim 23 being void of introducing any vapor phase aluminum containing reactant to the chamber in said forming of the phosphorus doped silicon dioxide comprising layer.

40. The method of claim 23 comprising depositing the phosphorus doped silicon dioxide comprising layer within semiconductive material isolation trenches formed in the substrate.

41. A method of forming trench isolation in the fabrication of integrated circuitry, comprising:

forming a masking layer over a semiconductor substrate;

etching isolation trenches through the masking layer into semiconductive material of the semiconductor substrate; and

after etching the isolation trenches, introducing first and second vapor phase reactants in alternate and temporally separated pulses to the substrate within the chamber in a plurality of deposition cycles effective to deposit a phosphorus doped silicon dioxide comprising layer within the isolation trenches, one of the first and second vapor phase reactants being $PO(OR)_3$ where R is hydrocarbyl, and an other of the first and second vapor phase reactants being $Si(OR)_3OH$ where R is hydrocarbyl.

42. The method of claim 41 wherein the deposit is effective to fill the isolation trenches.

43. The method of claim 41 wherein the deposit does not fill the isolation trenches.

44. The method of claim 41 wherein the deposition cycles are effective to deposit the phosphorus doped silicon dioxide comprising layer on the masking layer.

45. The method of claim 41 wherein the deposition cycles are not effective to selectively deposit the phosphorus doped silicon dioxide comprising layer within the isolation trenches.

46. The method of claim 41 wherein the conditions are effective to form the silicon dioxide comprising layer to have no more than 0.5 atomic percent phosphorus.

47. The method of claim 41 wherein the conditions are effective to form the silicon dioxide comprising layer to have at least 1.0 atomic percent phosphorus.

48. The method of claim 41 being void of introducing any vapor phase reactant to the chamber other than said first and second vapor phase reactants in said forming of the phosphorus doped silicon dioxide comprising layer.

49. The method of claim 41 comprising introducing another vapor phase reactant different from the first and second vapor phase reactants intermediate at least some of said separated pulses of the first and second vapor phase reactants.

50. The method of claim 49 wherein the another vapor phase reactant is oxygen containing.

51. The method of claim 50 wherein the another vapor phase reactant comprises O_3.

52. The method of claim 49 wherein the another vapor phase reactant is boron containing, the phosphorus doped silicon dioxide comprising layer comprising boron.

53. The method of claim 41 wherein the $PO(OR)_3$ comprises triethyl phosphate.

54. The method of claim 41 wherein the Si(OR)30H comprises tris(tert-butoxy)silanol.

55. The method of claim 41 wherein the PO(OR)3 comprises triethyl phosphate, and wherein the Si(OR)30H comprises tris(tert-butoxy)silanol.

56. The method of claim 41 comprising purging the chamber with an inert gas intermediate the separated pulses.

57. The method of claim 41 being void of aluminum on the substrate in said forming of the phosphorus doped silicon dioxide comprising layer.

58. The method of claim 41 being void of introducing any vapor phase aluminum containing reactant to the chamber in said forming of the phosphorus doped silicon dioxide comprising layer.

59. The method of claim 1 comprising forming said phosphorus doped silicon dioxide-comprising layer to be homogeneous.

60. The method of claim 23 comprising forming said phosphorus doped silicon dioxide-comprising layer to be homogeneous.