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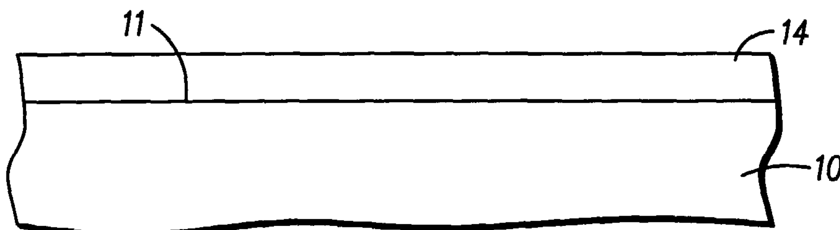
(54) Title: SINGLE CRYSTALLINE OXIDE ON A SEMICONDUCTOR SUBSTRATE



(57) Abstract: A method of forming single crystalline oxides on the surface of a semiconductor substrate includes placing the semiconductor substrate (10) in a vacuum chamber and depositing a thin layer of material (12) including a II metal on the surface (11). At a minimum the layer is thick enough to passivate the surface. An alternative oxidation agent is introduced into the chamber at a partial vapor pressure and at a temperature so as to form a layer (14) of single crystal oxide from the thin layer of material with the layer of single crystal oxide lattice matched to the semiconductor substrate. The surface is monitored by reflection high energy electron diffraction (RHEED) during the oxide growth. In a preferred embodiment single crystal BaO or (Ba,Sr)O is grown on and lattice matched to a silicon substrate.

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SINGLE CRYSTALLINE OXIDE ON A SEMICONDUCTOR SUBSTRATE

Field of the Invention

This invention relates to a method for forming single crystal oxides.

More particularly, the present invention relates to apparatus and method for forming single crystal oxides on semiconductor substrates.

Background of the Invention

In the fabrication of various semiconductor devices there is generally a need for layers of oxide as insulating layers. As a typical example, gate oxides are used in field effect transistors (FETs) to separate a gate terminal or contact from the gate area within the transistor. For high density arrays of devices, such as DRAMs, FeRAMs, SOIs, and the like, it is highly desirable to grow single crystalline oxides directly on the semiconductor substrate. However, this procedure is very difficult to achieve.

A major problem with using oxygen molecules (O_2) to form an oxide directly on a semiconductor substrate is that the oxidation generally proceeds very fast so that some oxidation and other damage of the substrate occurs. Oxidation or any other alterations occurring in the semiconductor substrate will very radically affect any semiconductor devices formed in the substrate. In the prior art, single crystalline BaO and (Ba, Sr)O thin oxide layers have been grown on a cubic $BaSi_2$ or (Ba, Sr) Si_2 template on a Si substrate using oxygen molecules (O_2) by MBE techniques. While this procedure provides some protection for the semiconductor substrate, it does not result in the oxide being formed directly on the semiconductor substrate.

Accordingly it is highly desirable to provide a method of forming single crystalline oxide directly on the surface of a semiconductor substrate.

It is an object of the present invention to provide a method of forming single crystalline oxide on the surface of a semiconductor substrate.

It is another object of the present invention to provide a method of forming single crystalline oxide on the surface of a semiconductor substrate which does not
5 damage the substrate and which is inexpensive and easy to use.

Brief Description of the Drawings

Referring to the drawings, FIGS. 1 through 3 are simplified sectional views of
10 sequential steps in a method of forming single crystalline oxide on the surface of a semiconductor substrate in accordance with the present invention.

Description of the Preferred Embodiment

15 Turning now to FIG. 1, a simplified sectional view of a semiconductor substrate 10 having a surface 11 is illustrated. Semiconductor substrate 10 includes any of the well known semiconductor materials, such as silicon, germanium, etc. or any of the compound semiconductor materials. In the preferred embodiment substrate 10 is silicon. Also, surface 11 is a clean surface with no
20 oxidation or other foreign materials thereon.

Semiconductor substrate 10 is placed in an epitaxial chamber, such as a molecular beam epitaxy (MBE) chamber at a base pressure generally in a low 10^{-10} Torr range. A metal from group II of the periodic table (hereinafter a II metal) is chosen for an oxide formation. Preferably, the metal is barium, barium, strontium,
25 or some combination including one of these metals. A very thin layer 12 of the II metal is deposited on surface 11 of semiconductor substrate 10, as illustrated in FIG. 2. Generally, the thickness of layer 12 will be in a range of 1 to 5 monolayers of the II metal. In a specific example, barium and strontium beams can be generated from resistively heated effusion cells. Layer 12 is formed with a

thickness at least sufficient to passivate the material (i.e., terminate all loose bonds or links) and protect surface 11 from oxygen introduced into the epitaxial chamber.

With layer 12 in place on surface 11, a controlled amount of alternative oxidation agent is introduced into the chamber. Generally, the alternative oxidation
5 agent is a material other than molecular oxygen (O_2), such as one of pure H_2O, NO, and N_2O, including activated species, such as a plasma of any of these oxidation agents. The alternative oxidation agent is introduced into the epitaxial chamber at a partial vapor pressure and at a temperature high enough to enhance the formation of the II metal in layer 12 into an oxide and to prevent unwanted by-
10 product formation, such as hydroxides of the II metal. Also, the temperature should be low enough to prevent unwanted metal-semiconductor interactions and interdiffusion of the II metal into semiconductor substrate 10. Generally, a controlled amount of the alternative oxidation agent is introduced into the epitaxial chamber through a leak valve, or other convenient device, at a partial vapor
15 pressure in a range of approximately 10^{-8} Torr to 10^{-5} Torr and at a temperature in a range of approximately 300°C to 800°C. The alternative oxidation agent may be introduced in pulses or continuously.

Depending upon the thickness of the II metal layer 12, and the desired thickness of the final II metal oxide layer 14, additional molecular II metal can be
20 introduced into the epitaxial chamber with the alternative oxidation agent. Generally, sufficient amounts of the alternative oxidation agent are introduced to completely oxidize layer 12 and then a combination of alternative oxidation agent and molecular II metal is introduced to grow layer 14 to the desired thickness.

During the oxide growth step, the surface of the formation on semiconductor
25 substrate 10 is monitored continuously by reflection high energy electron diffraction (RHEED). Generally, a streaky (1x1) RHEED pattern represents a single crystalline surface of a II metal oxide closely lattice-matched to semiconductor substrate 10. The result is a single crystalline layer 14 of II metal oxide formed on surface 11 of

semiconductor substrate 10 and lattice-matched to the semiconductor material, as illustrated in FIG. 3.

In a specific example, a silicon substrate is provided and introduced into an MBE chamber. 1 to 5 monolayers of barium are deposited on the surface of the
5 silicon substrate at a base pressure in the low 10^{-10} Torr. A controlled amount of ultra-pure H_2O is introduced into the epitaxial chamber through a leak valve at a partial vapor pressure in a range of approximately 10^{-8} Torr to 10^{-5} Torr and at a temperature in a range of approximately 300°C to 800°C. A single crystalline layer of BaO is grown on the surface of the silicon substrate and lattice-matched to the
10 silicon.

Basically, two slightly different embodiments or methods can be used. In each method, sufficient II metal is initially deposited in the semiconductor surface to passivate the surface, this is generally a sub-monolayer to a monolayer of material. In one method additional II metal is deposited to increase the thickness of layer 12
15 to 1 to 5 monolayers. The controlled amount of alternative oxidation agent is then introduced, as described above, to oxidize layer 12. In this method, additional II metal oxide can be added if desired by simultaneously introducing the II metal and the oxidation agent. In another method, after the deposition of the sub-monolayer to one monolayer, molecular II metal and the oxidation agent are introduced
20 simultaneously to grow the II metal oxide layer 14 to the desired thickness.

Thus, a new and improved method of growing single crystalline oxide layers lattice-matched on semiconductor substrates is disclosed. The new method prevents the formation of unwanted by-products, such as hydroxides of the II metal. Also, the new method prevents unwanted metal-semiconductor interactions and
25 interdiffusion of the II metal into a semiconductor substrate. Further, the new method is simple and can be used in an MBE chamber during normal processing procedures.

While we have shown and described specific embodiments of the present invention, further modifications and improvements will occur to those skilled in the

art. We desire it to be understood, therefore, that this invention is not limited to the particular forms shown and we intend in the appended claims to cover all modifications that do not depart from the spirit and scope of this invention.

5

What is claimed is:

1. A method of forming single crystalline oxides on a semiconductor substrate comprising the steps of:

5 providing a semiconductor substrate having a surface to be oxidized;

placing the semiconductor substrate in a vacuum chamber;

depositing a thin layer including a II metal on the surface to be oxidized;

introducing an alternative oxidation agent into the chamber at a partial vapor pressure and at a temperature such that it is high enough to enhance oxide

10 formation and to prevent unwanted by-product formation and low enough to prevent unwanted metal-semiconductor interactions and interdiffusion.

2. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 1 wherein the step of depositing a thin layer including

15 the II metal includes passivating the surface to be oxidized with a sub-monolayer to a monolayer of the II metal and the step of introducing the alternative oxidation agent includes simultaneously introducing molecular II metal.

3. A method of forming single crystalline oxides on a semiconductor

20 substrate as claimed in claim 1 further including a step of introducing additional material including barium during the step of introducing the alternative oxidation agent.

4. A method of forming single crystalline oxides on a semiconductor

25 substrate as claimed in claim 1 wherein the step of providing the semiconductor substrate includes providing a substrate including silicon.

5. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 1 wherein the step of placing the semiconductor substrate in the vacuum chamber includes placing the substrate in a molecular beam epitaxy chamber.

5

6. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 1 wherein the step of depositing the thin layer includes depositing a layer with a thickness in a range of approximately 1 to 5 monolayers.

10

7. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 1 wherein the step of depositing the thin layer including the II metal includes a step of depositing a metal including one of barium and barium-strontium.

15

8. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 1 wherein the step of introducing the alternative oxidation agent includes introducing one of pure H_2O, NO, and N_2O, including activated species of any of H_2O, NO, and N_2O.

20

9. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 1 wherein the step of placing the semiconductor substrate in the vacuum chamber includes reducing pressure within the vacuum chamber to a base pressure in a 10^{-10} Torr range.

25

10. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 9 wherein the step of introducing the alternative oxidation agent includes introducing the agent at a partial vapor pressure in a range of approximately 10^{-8} Torr to 10^{-5} Torr.

11. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 10 wherein the step of introducing the alternative oxidation agent includes introducing the agent at a temperature in a range of approximately 300°C to 800°C.

5

12. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 1 further including a step of monitoring the surface by reflection high energy electron diffraction (RHEED) during oxide growth.

10 13. A method of forming single crystalline oxides on a semiconductor substrate comprising the steps of:

providing a semiconductor substrate having a surface to be oxidized;

placing the semiconductor substrate in a vacuum chamber;

depositing a thin layer of material including barium on the surface to be

15 oxidized;

introducing an alternative oxidation agent into the chamber at a partial vapor pressure and at a temperature so as to form a layer of single crystal oxide from the thin layer of material with the layer of single crystal oxide lattice matched to the semiconductor substrate.

20

14. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 13 wherein the step of providing the semiconductor substrate includes providing a substrate including silicon.

25 15. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 13 wherein the step of placing the semiconductor substrate in the vacuum chamber includes placing the substrate in an MBE chamber.

16. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 13 wherein the step of depositing the thin layer includes depositing a layer with a thickness in a range of approximately 1 to 5 monolayers.

5

17. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 13 wherein the step of depositing the thin layer including barium includes a step of depositing one of barium and barium-strontium.

10 18. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 13 wherein the step of introducing the alternative oxidation agent includes introducing one of pure H_2O, NO, and N_2O, including activated species of any of H_2O, NO, and N_2O.

15 19. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 13 wherein the step of placing the semiconductor substrate in the vacuum chamber includes reducing pressure within the vacuum chamber to a base pressure in a 10^{-10} Torr range.

20 20. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 13 wherein the step of introducing the alternative oxidation agent includes introducing the agent at a partial vapor pressure in a range of approximately 10^{-8} Torr to 10^{-5} Torr.

25 21. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 20 wherein the step of introducing the alternative oxidation agent includes introducing the agent at a temperature in a range of approximately 300°C to 800°C.

22. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 13 further including a step of monitoring the surface by reflection high energy electron diffraction (RHEED) during oxide growth.

5 23. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 13 wherein the step of depositing a thin layer of material including barium includes passivating the surface to be oxidized with a sub-monolayer to a monolayer of material including barium and the step of introducing the alternative oxidation agent includes simultaneously introducing
10 molecular material including barium.

24. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 13 further including a step of introducing additional material including barium during the step of introducing the alternative oxidation
15 agent.

25. A method of forming single crystalline oxides on a semiconductor substrate comprising the steps of:

providing a semiconductor substrate including silicon having a surface to be
20 oxidized;

placing the semiconductor substrate in a vacuum chamber at a base pressure in a 10^{-10} Torr range;

depositing a thin layer of material including barium on the surface to be oxidized; and

25 introducing an alternative oxidation agent into the chamber at a partial vapor pressure in a range of approximately 10^{-8} Torr to 10^{-5} Torr and at a temperature in a range of approximately 300°C to 800°C so as to form a layer of single crystal oxide from the thin layer of material with the layer of single crystal oxide lattice matched to the semiconductor substrate.

26. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 25 wherein the step of placing the semiconductor substrate in the vacuum chamber includes placing the substrate in an MBE chamber.

5

27. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 25 wherein the step of depositing the thin layer includes depositing a layer with a thickness in a range of approximately 1 to 5 monolayers.

10

28. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 25 wherein the step of depositing the thin layer including barium includes a step of depositing one of barium and barium-strontium.

15 29. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 25 wherein the step of introducing the alternative oxidation agent includes introducing one of pure H_2O, NO, and N_2O, including activated species of any of H_2O, NO, and N_2O.

20 30. A method of forming single crystalline oxides on a semiconductor substrate as claimed in claim 25 further including a step of monitoring the surface by reflection high energy electron diffraction (RHEED) during oxide growth.

31. A method of forming single crystalline oxides on a semiconductor

25 substrate as claimed in claim 25 further including a step of introducing additional material including barium during the step of introducing the alternative oxidation agent.

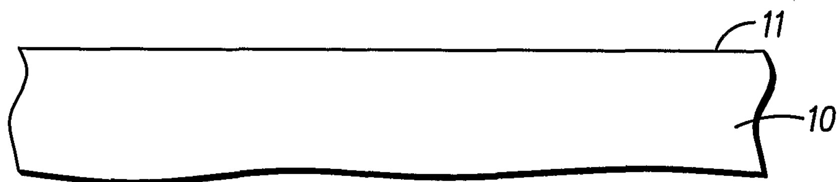

FIG. 1

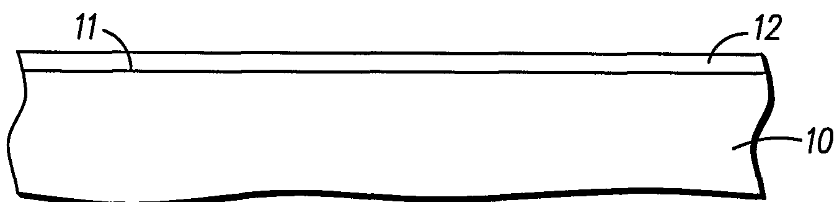

FIG. 2

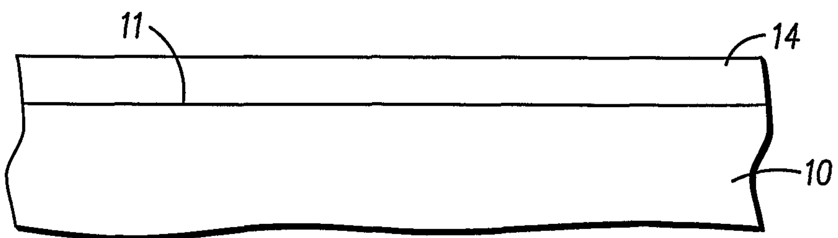

FIG. 3