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1 03 JUL 2000

METHOD FOR FABRICATING A SEMICONDUCTOR STRUCTURE
INCLUDING A METAL OXIDE INTERFACE WITH SILICON

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Field of Invention

10 The present invention relates in general to a method
for fabricating a semiconductor structure including a
crystalline metal oxide interface between a silicon
substrate and metal oxides, and more particularly to a
method for fabricating an interface including a seed
15 layer and a high dielectric constant oxide.

Background of the Invention

20 An ordered and stable silicon (Si) surface is most
desirable for subsequent epitaxial growth of single
crystal thin films on silicon for numerous device
applications, e.g., ferroelectrics or high dielectric
constant oxides for non-volatile high density memory and
25 next generation MOS devices. It is pivotal to establish
an ordered transition layer on the Si surface, especially
for subsequent growth of single crystal oxides, e.g.,
perovskites.

Some reported growth of these oxides, such as BaO
30 and BaTiO₃ on Si (100) were based on a BaSi₂ (cubic)

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template by depositing one fourth monolayer of Ba on Si (100) using molecular beam epitaxy at temperatures greater than 850°C. See for example: R. McKee et al., *Appl. Phys. Lett.* 59(7), pp. 782-784 (12 August 1991); R. McKee et al., *Appl. Phys. Lett.* 63(20), pp. 2818-2820 (15 November 1993); R. McKee et al., *Mat. Res. Soc. Symp. Proc.*, Vol. 21, pp. 131-135 (1991); U.S. Patent No. 5,225,031, issued July 6, 1993, entitled "PROCESS FOR DEPOSITING AN OXIDE EPITAXIALLY ONTO A SILICON SUBSTRATE AND STRUCTURES PREPARED WITH THE PROCESS"; and U.S. Patent No. 5,482,003, issued January 9, 1996, entitled "PROCESS FOR DEPOSITING EPITAXIAL ALKALINE EARTH OXIDE ONTO A SUBSTRATE AND STRUCTURES PREPARED WITH THE PROCESS". A strontium silicide (SrSi_2) interface model with a $c(4 \times 2)$ structure was proposed. See for example: R. McKee et al., *Phys. Rev. Lett.* 81(14), 3014 (5 October, 1998). However, atomic level simulation of this proposed structure indicates that it likely is not stable at elevated temperatures.

Growth of SrTiO_3 on silicon (100) using an SrO buffer layer has been accomplished. See for example: T. Tambo et al., *Jpn. J. Appl. Phys.*, Vol. 37 (1998), pp. 4454-4459. However, the SrO buffer layer was thick (100 Å), thereby limiting application for transistor films, and crystallinity was not maintained throughout the growth.

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Furthermore, SrTiO_3 has been grown on silicon using thick oxide layers (60-120 Å) of SrO or TiO_x . See for example: B. K. Moon et al., *Jpn. J. Appl. Phys.*, Vol. 33 (1994), pp. 1472-1477. These thick buffer layers would
5 limit the application for transistors.

Therefore, a method for fabricating a thin, stable crystalline silicate interface with silicon is needed.

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Summary of the Invention

The above problems and others are at least partially solved and the above purposes and others are realized in a method of fabricating a semiconductor structure
15 including the steps of providing a silicon substrate having a surface, forming on the surface of the silicon substrate a seed layer comprising a silicate crystalline material and forming one or more layers of a high dielectric constant oxide on the seed layer.

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Brief Description of the Drawings

Referring to the drawings:

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FIG. 1 illustrates a cross-sectional view of a clean semiconductor substrate having a plurality of oxide

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layers formed thereon and in accordance with the present invention;

FIG. 2 illustrates a cross-sectional view of a semiconductor substrate having an interface seed layer
5 formed of a crystalline silicate layer in accordance with the present invention; and

FIG. 3 illustrates a cross-sectional view of a high dielectric constant metal oxide layer formed on the structure illustrated in FIG. 2 in accordance with the
10 present invention.

Detailed Description of the Preferred Embodiment

15 This disclosure teaches a method of fabricating a high dielectric constant (high-k) metal oxide having an interface with a silicon substrate. The process is based on the solid state reaction of a metal oxide, such as strontium oxide (SrO), barium oxide (BaO), calcium oxide
20 (CaO), zirconium oxide (ZrO_2), hafnium oxide (HfO_2), or the like, with SiO_2 , to form a stable silicate seed layer necessary for the subsequent growth of alkaline-earth metal oxide layers. Accordingly, disclosed is a new method of growing perovskite oxides such as SrTiO_3 ,
25 BaTiO_3 , SrBaTiO_3 , CaTiO_3 , or the like.

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To form the novel interface between a silicon (Si) substrate and one or more layers of a high dielectric constant (high-k) metal oxide, various approaches may be used. Several examples will be provided for starting
5 with a Si substrate having silicon dioxide (SiO_2) on the surface. The silicon dioxide is disclosed as formed as a native oxide, or by utilizing thermal, or chemical techniques. SiO_2 is amorphous rather than single crystalline and it is desirable for purposes of growing
10 additional single crystal material on the substrate that a single crystal oxide layer be provided as the interface.

Turning now to the drawings in which like elements are designated with like numbers throughout the FIGs.,
15 FIG. 1 illustrates a Si substrate 10 having a surface 12, and a layer 14 of SiO_2 thereupon. In this particular embodiment, layer 14 of SiO_2 naturally exists (native oxide) once the silicon substrate 10 is exposed to air (oxygen). Alternatively, layer 14 of SiO_2 may be formed
20 purposely in a controlled fashion well known in the art, e.g., thermally by applying oxygen onto the surface 12 at a high temperature, or chemically using a standard chemical etch process. Layer 14 is formed with a thickness in a range of 5-100Å thick, and more
25 particularly with a thickness in a range of 10-25Å.



The novel seed layer (discussed presently) is formed by depositing an amorphous metal oxide such as SrO, BaO or the like 18 to the surface 16 of SiO₂ layer 14 at 0-900°C . More specifically, the Si substrate 10 and the
5 amorphous SiO₂ layer 14 are heated to a temperature below the sublimation temperature of the SiO₂ layer 14 (generally below 900°C). This can be accomplished in a molecular beam epitaxy chamber or in a chemical or physical vapor deposition chamber under inert ambient
10 conditions.

Once the substrate 10 is properly heated and the surface 12 of the substrate 10 having SiO₂ layer 14 thereon is exposed to a beam of metal 18, such as strontium (Sr), barium (Ba), calcium (Ca), zirconium
15 (Zr), hafnium (Hf), or the like in an oxygen atmosphere under O₂ pressure equal to or less than 1×10^{-4} mBar to form an amorphous oxide onto the SiO₂ oxide 14 as illustrated in FIG. 1. In a preferred embodiment, the beam is Ba or Sr which is generated by resistively
20 heating effusion cells or from e-beam evaporation sources. In a specific example, substrate 10 and SiO₂ layer 14 are exposed to a beam of Sr and Oxygen O₂. The SrO joins the SiO₂ and converts the SiO₂ layer 14 into a

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seed layer 20 comprised of SrSiO_4 or SrSiO_3 , or the like, in a crystalline form as illustrated in FIG. 2.

This step provides for the formation of a stable silicate on the silicon substrate, more particularly the formation of seed layer 20. The thickness of metal oxide layer 20 is approximately the same thickness of the SiO_2 oxide layer 14, more specifically in the range of 5-100Å, with a preferred thickness in the range of 10-25Å. This silicate layer is crystalline and ordered showing a 2x1 reconstruction.

In this particular embodiment, the application of the Sr and oxygen to the surface 16 of layer 14 and subsequent heating causes a chemical reaction, forming SrSiO_3 or SrSiO_4 , or the like as the seed layer 20. During fabrication, this growth is monitored using reflection high energy electron diffraction (RHEED) techniques which are well documented in the art and which can be used in situ, i.e., while performing the exposing step within the growth chamber. The RHEED techniques are used to detect or sense surface crystalline structures and in the present process change rapidly to strong and sharp streaks by the forming of a few atomic layers of the SrSiO_4 , SrSiO_3 , or the like. It will of course be understood that once a specific manufacturing process is provided and followed, it may not be necessary to perform

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the RHEED techniques on every substrate. Alternatively, monitoring of the crystalline structure can be accomplished utilizing any surface sensitive technique, such as reflection difference spectroscopy, spectroscopic
5 ellipsometry, or the like wherein the surface is monitored by in situ techniques.

It should be understood by those skilled in the art that the temperatures and pressures given for these processes are recommended for the particular embodiment
10 described, but the invention is not limited to a particular temperature or pressure range. As taught, seed layer 20 comprises rows of strontium, silicon, and oxygen atoms in a 2x1 configuration on a (001) surface of silicon substrate 10, 1x in the <110> direction and 2x in
15 the orthogonal <110> direction.

Referring to FIG. 3, the formation of high dielectric constant oxide layer 22 may be accomplished by either the simultaneous or alternating supply to a surface 21 of the seed layer 20 of a crystalline silicate
20 at less than or equal to 800°C, more particularly at a temperature in a range of 350-650°C and under O₂ partial pressure less than or equal to 1×10^{-4} mBar.

Single crystal high dielectric constant oxide layer 22, more particularly a perovskite, is formed on surface
25 21 of the seed layer 20 by either the simultaneous or alternating supply of alkaline metal (Sr, Ba etc),



oxygen, and a transition metal, such as titanium, at less than or equal to 800°C under an oxygen partial pressure less than or equal to 1×10^{-4} mBar. This single crystal oxide layer 22 may, for example, comprise a thickness of 5 50-1000Å and will be substantially lattice matched with the underlying seed layer 20.

Accordingly, disclosed is a method for fabricating a thin, crystalline seed layer 20 with silicon 10 as been described herein. The interface, or seed layer, 20 may 10 comprise a single atomic layer. This forcing of the formation of a silicate layer is necessary for the subsequent growth of a perovskite film thereon. Better transistor applications are achieved by the interface being thin, in that the electrical coupling effects of 15 the overlying high dielectric constant oxide layers are not compromised, and in that the seed layer 20 is more stable since the atoms will more likely maintain their crystallinity in processing.

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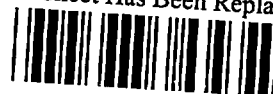
What is claimed is:

1. A method of fabricating a semiconductor structure comprising the steps of:
providing a silicon substrate having a surface;
5 forming on the surface of the silicon substrate a seed layer comprising a silicate crystalline material;
and
forming one or more layers of a high dielectric constant oxide on the seed layer.

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2. The method of fabricating a semiconductor structure of claim 1 wherein the forming the seed layer step includes forming a 2x1 reconstruction.
- 15 3. The method of fabricating a semiconductor structure of claim 1 wherein the step of forming a seed layer includes forming the seed layer in UHV environment.
4. The method of fabricating a semiconductor
20 structure of claim 1 wherein the step of forming a seed layer includes forming the seed layer in a chemical vapor deposition system.
5. The method of fabricating a semiconductor
25 structure of claim 1 wherein the step of forming a seed

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layer includes forming in a physical vapor deposition system.

6. The method of fabricating a semiconductor structure of claim 1 wherein the step of forming a seed layer comprises forming at least a single monolayer of silicon, oxygen, and a metal.

7. The method of fabricating a semiconductor structure of claim 6 wherein the metal is selected from the group of strontium, barium, calcium, zirconium, and hafnium.

8. The method of fabricating a semiconductor structure of claim 1 wherein the step of forming a seed layer further comprises the steps of:

forming a silicon oxide layer having a surface;

depositing a metal oxide on the surface of the silicon oxide layer; and

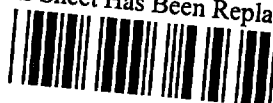
20 heating the silicon oxide layer and the metal oxide to form a silicate crystalline material seed layer.

9. A method of fabricating a semiconductor structure comprising the steps of:

25 providing a silicon substrate having a surface;

forming amorphous silicon dioxide on the surface of the silicon substrate;

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providing a metal oxide on the amorphous silicon dioxide; and

heating the semiconductor structure to form an interface comprising a seed layer adjacent the surface of
5 the silicon substrate.

10. The method of fabricating a semiconductor structure of claim 9 wherein the heating step includes forming the interface with a 2x1 reconstruction.

10

11. The method of fabricating a semiconductor structure of claim 9 wherein the steps of providing a metal oxide and heating the semiconductor structure are accomplished in an ultra-high-vacuum system.

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12. The method of fabricating a semiconductor structure of claim 9 wherein the steps of providing a metal oxide and heating the semiconductor structure are accomplished in a chemical vapor deposition system.

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13. The method of fabricating a semiconductor structure of claim 9 wherein the steps of providing metal oxide and heating the semiconductor structure are accomplished in a physical vapor deposition system.

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14. The method of fabricating a semiconductor structure of claim 9 wherein the heating step includes

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forming an interface including a seed layer of silicon, oxygen, and a metal.

15. The method of fabricating a semiconductor
5 structure of claim 14 wherein the metal oxide is selected from the group of barium, strontium, calcium, zirconium, and hafnium.

16. The method of fabricating a semiconductor
10 structure of claim 9 wherein the heating step to form the seed layer comprises the steps of:

forming a silicon oxide layer having a surface;

depositing a metal oxide on the surface of the silicon oxide layer; and

15 heating the silicon oxide layer and the metal oxide to form a silicate crystalline material seed layer.

17. A method of fabricating a semiconductor structure comprising the steps of:

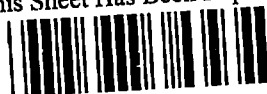
20 providing a silicon substrate having a surface;

forming amorphous silicon dioxide on the surface of the silicon substrate;

providing a metal oxide on the amorphous silicon dioxide;

25 heating the semiconductor structure to form an interface comprising a seed layer adjacent the surface of the silicon substrate; and

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forming one or more layers of a high dielectric constant oxide on the seed layer.

18. The method of fabricating a semiconductor
5 structure of claim 17 wherein the step of forming the seed layer includes forming an interface having a 2x1 reconstruction.

19. The method of fabricating a semiconductor
10 structure of claim 17 wherein the step of providing a metal oxide is accomplished in an ultra-high-vacuum system.

20. The method of fabricating a semiconductor
15 structure of claim 17 wherein the step of providing a metal oxide is accomplished in a chemical vapor deposition system.

21. The method of fabricating a semiconductor
20 structure of claim 17 wherein the step of providing a metal oxide is accomplished in a physical vapor deposition system.

22. The method of fabricating a semiconductor
25 structure of claim 17 wherein the metal oxide on the amorphous silicon dioxide is selected from the group of

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barium oxide, strontium oxide, calcium oxide, zirconium oxide, and hafnium oxide.

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