REMOVING AN AMORPHOUS OXIDE FROM A MONOCRYSTALLINE SURFACE

Related Applications

This application is a continuation-in-part of United States Patent Application Serial No. 09/502,023 filed on 10 February 2000, which application is incorporated herein by reference.

Field of the Invention

This invention relates generally to a method for preparing a monocrystalline surface for deposition of a monocrystalline oxide thereon, and more particularly to a method for removing an amorphous oxide from a monocrystalline surface.

Background of the Invention

Single crystal oxides, such as perovskites, are attractive materials due to their simple crystal structures and unique ferroelectric, dielectric, and optical properties. The high quality epitaxial growth of single crystal oxides on monocrystalline substrates, such as silicon, is desirable for numerous device applications, such as optical waveguides, ferroelectrics, non-volatile high density memory devices, MOS devices and the like.

For many years, attempts to grow monocrystalline oxides on monocrystalline substrates have proven difficult because of the easily-formed amorphous oxide layer that forms on the substrate surface in an oxygen atmosphere. This amorphous oxide layer prevents high quality growth of monocrystalline oxides on monocrystalline substrates. Because an ordered and stable substrate surface is needed to facilitate the growth of high quality monocrystalline oxide layers, it is desirable to remove the amorphous oxide layer from the surface of the substrate before depositing the monocrystalline oxide layer.

Accordingly, a method of removing an amorphous oxide layer from a monocrystalline substrate is needed. In addition, a method for forming an ordered and stable surface on a monocrystalline substrate for subsequent growth of a monocrystalline oxide layer is needed.

Brief Description of the Drawings

The present invention is illustrated by way of example and not limitation in the accompanying figures, in which like references indicate similar elements, and in which:

FIG. 1 illustrates, in cross section, a semiconductor structure having a monocrystalline substrate and a native amorphous oxide formed thereon;

FIG. 2 illustrates, in cross section, a passivation material layer formed overlying the native amorphous oxide layer of the semiconductor structure of FIG. 1;

FIG. 3 illustrates, in cross section, the semiconductor structure of FIG. 2 in which voids have formed in the native amorphous oxide layer;

FIG. 4 illustrates, in cross section, the semiconductor structure of FIG. 3 wherein the material of the passivation layer has passivated exposed portions of the monocrystalline substrate;

FIG. 5 illustrates, in cross section, the semiconductor structure of FIG. 4 wherein the native amorphous oxide layer has been removed and the monocrystalline substrate has been passivated by the passivation layer; and

FIG. 6 illustrates, in cross section, the semiconductor structure of FIG. 5 wherein a monocrystalline oxide has been grown overlying the monocrystalline substrate.

Skilled artisans will appreciate that elements in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the dimensions of some of the elements in the figures may be exaggerated relative to other elements to help to improve understanding of embodiments of the present invention.

Detailed Description of the Drawings

A method for removing an amorphous oxide from the surface of a monocrystalline substrate and producing an ordered surface on the substrate for subsequent growth of a monocrystalline oxide is illustrated in FIGS. 1 - 6. FIG. 1 illustrates schematically, in cross section, a portion of a semiconductor structure 20 that includes a monocrystalline substrate 22 having an amorphous oxide layer 24. In this context, the term "monocrystalline" shall have the meaning commonly used within the semiconductor industry. The term shall refer to materials that are a single crystal or that are substantially a single crystal and shall include those materials having a relatively

small number of defects such as dislocations and the like as are commonly found in substrates of silicon or germanium or mixtures of silicon and germanium and epitaxial layers such materials commonly found in the semiconductor industry.

Substrate 22, in accordance with an embodiment of the invention, is a monocrystalline semiconductor or compound semiconductor material, such as, for example, materials from Group IV of the periodic table. Examples of Group IV semiconductor materials include silicon, germanium, mixed silicon and germanium, mixed silicon and carbon, mixed silicon, germanium and carbon, and the like. Preferably, substrate 22 is a wafer containing silicon or germanium, and most preferably is a high quality monocrystalline silicon wafer having a (100) orientation, as used in the semiconductor industry. The substrate is oriented on axis or, at most, about 6° off axis.

At least a portion of the semiconductor substrate 22 has a bare surface, although other portions of the substrate may encompass other structures. The term "bare" in this context means that the surface in the portion of the substrate has been cleaned to remove any oxides, contaminants, or other foreign material. As is well known, bare substrates such as silicon may be highly reactive and may readily form native amorphous oxide layer 24. The term "bare" is intended to encompass such a native oxide layer. A thin oxide may also be intentionally grown on the semiconductor substrate, although such a grown oxide is not essential to the process in accordance with the invention. In order to epitaxially grow a monocrystalline oxide layer overlying the monocrystalline substrate, the native amorphous oxide layer 24 must first be removed to expose the crystalline structure of the underlying substrate.

The following process is preferably carried out by ultra high vacuum (UHV) molecular beam epitaxy (MBE), although other epitaxial processes may also be used in accordance with the present invention. In one exemplary embodiment of the invention, monocrystalline substrate 22 is positioned with a processing chamber of an UHV MBE. Monocrystalline substrate 22 may then be heated below the sublimation temperature of the amorphous oxide layer 24, preferably to a temperature of about 500°C, although it will be appreciated that heating monocrystalline substrate 22 at this point in the process is not essential to the present invention. Referring to FIG. 2, a passivation material layer 26 is deposited overlying the amorphous oxide layer 24 by MBE. The passivation

material layer 26 may comprise alkali or alkaline earth metals, combinations of alkali and/or alkaline earth metals, the oxides of alkali or alkaline earth metals or the combinations of oxides of alkali and/or alkaline earth metals. Examples of materials suitable for passivation material layer 26 include strontium, strontium oxide, barium, barium oxide, a combination of strontium and barium, and the like. The MBE process is initiated by opening shutters in the MBE apparatus to expose one or more sources of the passivation material, creating a flux of the passivation material. The flux of the passivation material may be set depending on the melting point and vapor pressure of the passivation material. Typically, the flux of the material is in the range of about 1 Angstrom/minute to about 10 Angstroms/minute. In a preferred embodiment of the invention, the flux of the passivation material may be terminated when passivation material layer 26 has grown to its desired thickness. Alternatively, a continuous flux of the passivation material may be provided during the process. If a continuous flux of the passivation material is provided during processing, it may be desirable to provide in situ monitoring of the thickness of passivation material layer 26, such as by a reflection high energy electron diffraction (RHEED) crystal oscillation thickness monitor, so that the thickness of passivation material layer 26 does not reach a thickness that would prevent or otherwise adversely affect removal of amorphous oxide layer 24. Preferably, about one to five monolayers of passivation material layer 26, and more preferably about one to 2 monolayers of passivation material layer 26, is deposited overlying the amorphous oxide layer 24, although it will be appreciated that passivation material layer 26 may be of any thickness suitable for facilitating the removal of amorphous oxide layer 24.

The substrate is then heated to a temperature in the range of from about 700°C to about 900°C. FIG. 3 illustrates, in cross section, structure 20 upon being heated to about 700°C or higher. At this temperature, molecules from the amorphous oxide layer 24 are liberated from the surface of monocrystalline substrate 22, forming voids 28 in amorphous oxide layer 24. The passivation material layer 26 overlying amorphous oxide layer 24 facilitates liberation of the amorphous oxide layer from the surface of the monocrystalline substrate 22, thus increasing the rate of removal of the amorphous oxide layer. The passivation material serves as a catalyst that promotes the ejection of electrons from one or both of the passivation material and the amorphous oxide. This

results in a dipole field between the passivation material and the amorphous oxide which causes the amorphous oxide to be in an activated state. Accordingly, the amorphous oxide more readily decomposes into volatile species that are liberated from the monocrystalline substrate surface. In addition, portions of the monocrystalline substrate 22 exposed during formation of the voids 28 are passivated by the passivation material of passivation material layer 26, as illustrated in FIG. 4. Without the presence of the passivation material from passivation material layer 26, the voids would continue to grow into the monocrystalline substrate 22, forming pits in monocrystalline substrate 22. As the process continues, the amorphous oxide layer 24 continues to be liberated from the surface of monocrystalline substrate 22, which in turn continues to be passivated by the passivation material of passivation material layer 26. FIG. 5 illustrates, in cross section, structure 30, which results from the above-described process. At conclusion of the process, substantially all of amorphous oxide layer 24 has been liberated from monocrystalline substrate 22 and passivation material layer 26 provides an ordered and stable surface overlying monocrystalline substrate 22.

Following the removal of the amorphous oxide layer 24 from the surface of the substrate, the substrate may be cooled to a temperature in the range of about 200-800°C, preferably 350-450°C, and a monocrystalline oxide layer 42, as illustrated in FIG. 6, may then be epitaxially grown overlying passivation material layer 26 to form structure 40. Monocrystalline oxide layer 42 is preferably selected for its crystalline compatibility with the underlying monocrystalline substrate 22. Materials that are suitable for monocrystalline oxide 42 include metal oxides such as the alkaline earth metal titanates, alkaline earth metal zirconates, alkaline earth metal hafnates, alkaline earth metal tantalates, alkaline earth metal ruthenates, alkaline earth metal niobates, alkaline earth metal vanadates, alkaline earth metal tin-based perovskites, lanthanum aluminate, lanthanum scandium oxide, and gadolinium oxide. Most of these materials are insulators, although strontium ruthenate, for example is a conductor. Generally, these materials are metal oxides or metal nitrides, and more particularly, these metal oxide or nitrides typically include at least two different metallic elements.

Structure 40 may also include an amorphous interface layer 44, which is preferably an oxide formed by the oxidation of the surface of substrate 22 during or after

the growth of monocrystalline oxide layer 42. The thickness of layer 44 may be sufficient to relieve strain attributed to mismatches between the lattice constants of monocrystalline substrate 22 and monocrystalline oxide layer 42. Typically, layer 44 has a thickness in the range of approximately 0.5 – 5 nm.

The following example illustrates a process, in accordance with one embodiment of the invention, for fabricating a semiconductor structure such as the structure depicted in FIG. 6. The process starts by providing a monocrystalline semiconductor substrate comprising silicon or germanium. In accordance with a preferred embodiment of the invention, the semiconductor substrate is a silicon wafer having a (100) orientation. The substrate is oriented on axis or, at most, about 6° off axis. At least a portion of a silicon substrate has a native amorphous silicon oxide layer. In order to epitaxially grow a monocrystalline oxide layer overlying the monocrystalline silicon substrate, the native amorphous silicon oxide layer must first be removed to expose the crystalline structure of the underlying silicon substrate. The process is preferably performed in an UHV MBE apparatus, although other epitaxial processes may also be used in accordance with the present invention. The silicon substrate is positioned within the processing chamber of an UHV MBE unit and heated to a temperature below the sublimation temperature of silicon oxide, preferably about 500°C. Shutters in the MBE apparatus are then opened to expose one or more strontium sources to produce a flux of strontium preferably in the range of about 1 Angstrom/minute to about 10 Angstroms/minute and more preferably about 4 Angstroms/minute. One to two monolayers of strontium is then deposited overlying the native amorphous oxide layer. Alternatively, three to four monolayers of strontium oxide may be deposited on the silicon substrate surface by exposing one or more strontium sources in an atmosphere having an oxygen partial pressure in the range of from about 1×10^{-8} torr to 1×10^{-7} torr.

The silicon substrate is then heated to a temperature of at least 720°C. The strontium (or strontium oxide) serves as a catalyst that increases the rate of removal of the silicon oxide from the surface of the silicon substrate. The strontium promotes the ejection of electrons from one or both of the strontium layer and the silicon oxide layer. This results in a dipole field between the strontium layer and the silicon oxide layer. The dipole field weakens the Si-O bonds of the silicon oxide layer which causes the silicon

oxide layer to be in an activated state. Accordingly, the silicon oxide more readily decomposes into a volatile species that is liberated from the monocrystalline silicon substrate surface according to the following reaction:

$$SiO_2 + Sr \text{ (or SrO)} \rightarrow SiO(g) + O^+ + e^- + Sr \text{ (or SrO)}.$$

As the silicon oxide is liberated from the silicon substrate surface, voids, such as voids 28 illustrated in FIG. 3, begin to form in the native amorphous silicon oxide layer. Without strontium (or strontium oxide) overlying the silicon oxide layer, the voids would continue to grow into the silicon substrate, resulting in pits in the silicon surface. However, the strontium serves to passivate the exposed silicon substrate surface so further etching of the silicon substrate will be reduced or eliminated. Accordingly, a strontium-terminated silicon (100) substrate with an ordered 2x1 structure results. If an ordered (2x1) structure has not been achieved at this stage of the process, the structure may be exposed to additional strontium until an ordered (2x1) structure is obtained. If strontium oxide is used to passivate the silicon substrate surface, the process may be continued so that the strontium oxide reacts with the silicon substrate to form volatile SiO, leaving a strontium-terminated silicon substrate. This strontium layer forms a template for the subsequent growth of an ordered monocrystalline oxide layer.

Following the removal of the amorphous silicon oxide from the surface of the silicon substrate, in accordance with one embodiment of the invention, the substrate is cooled to a temperature in the range of about 200-800°C, preferably 350-450°C, and a monocrystalline oxide layer of strontium titanate is grown on the template layer by MBE. The MBE process is initiated by opening shutters in the MBE apparatus to expose strontium, titanium and oxygen sources. The ratio of strontium and titanium is approximately 1:1. The partial pressure of oxygen is initially set at a minimum value to grow stoichiometric strontium titanate at a growth rate of about 0.1 – 0.8 nm per minute, preferably about 0.3 – 0.5 nm per minute. After initiating growth of the strontium titanate, the partial pressure of oxygen is increased above the initial minimum value. The stoichiometry of the strontium titanate can be controlled during growth by monitoring RHEED patterns and adjusting the fluxs. The overpressure of oxygen causes

the growth of an amorphous silicon oxide interface layer at the interface between the underlying substrate and the strontium titanate layer. This step may be applied either during or after the growth of the $SrTiO_3$ layer. The growth of the silicon oxide interface layer results from the diffusion of oxygen through the strontium titanate layer to the interface where the oxygen reacts with silicon at the surface of the underlying substrate. The strontium titanate grows as an ordered (100) monocrystal with the (100) crystalline orientation rotated by 45° with respect to the underlying silicon substrate. Strain that otherwise might exist in the strontium titanate layer because of the small mismatch in lattice constant between the silicon substrate and the growing crystal is relieved in the amorphous silicon oxide interface layer.

The method described above illustrates a method for removing an amorphous silicon oxide from a silicon substrate and for forming a semiconductor structure including a silicon substrate and an overlying monocrystalline oxide layer comprising strontium titanate by the process of molecular beam epitaxy. The process can also be carried out by chemical vapor deposition (CVD), metal organic chemical vapor deposition, (MOCVD), migration enhanced epitaxy (MEE), atomic layer epitaxy (ALE), physical vapor deposition (PVD), chemical solution deposition (CSD), pulsed laser deposition (PLD), or the like. Further, by a similar process, native amorphous oxides may be removed from other monocrystalline substrates such as germanium, mixed silicon and germanium, mixed silicon and carbon, mixed germanium and carbon, mixed silicon, germanium and carbon, and the like. In addition, by a similar process other monocrystalline oxide layers such as alkaline earth metal titanates, zirconates, hafnates, tantalates, vanadates, ruthenates, and niobates, alkaline earth metal tin-based perovskites, lanthanum aluminate, lanthanum scandium oxide, and gadolinium oxide, can also be grown.

In the foregoing specification, the invention has been described with reference to specific embodiments. However, one of ordinary skill in the art appreciates that various modifications and changes can be made without departing from the scope of the present invention as set forth in the claims below. Accordingly, the specification and figures are to be regarded in an illustrative rather than a restrictive sense, and all such modifications are intended to be included within the scope of present invention.

Benefits, other advantages, and solutions to problems have been described above with regard to specific embodiments. However, the benefits, advantages, solutions to problems, and any element(s) that may cause any benefit, advantage, or solution to occur or become more pronounced are not to be construed as a critical, required, or essential features or elements of any or all the claims. As used herein, the terms "comprises," "comprising," or any other variation thereof, are intended to cover a non-exclusive inclusion, such that a process, method, article, or apparatus that comprises a list of elements does not include only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus.

We Claim:

1. A method of removing an amorphous oxide from a surface of a monocrystalline substrate, the method comprising:

depositing a passivation material overlying said amorphous oxide; and

heating said surface so that said amorphous oxide layer decomposes into at least one volatile species that is liberated from said surface.

2. The method of claim 1, wherein said heating is performed after said depositing.

3. The method of claim 1, wherein said heating is performed during said depositing.

4. The method of claim 1, further comprising epitaxially growing a monocrystalline oxide layer overlying said surface of said monocrystalline substrate.

5. The method of claim 4, further comprising forming an amorphous oxide interface layer overlying said monocrystalline substrate and underlying said monocrystalline oxide layer.

6. The method of claim 1, further comprising heating said monocrystalline substrate to a temperature below the sublimation temperature of said amorphous oxide layer before said depositing.

7. The method of claim 1, wherein said monocrystalline substrate comprises one of silicon, germanium, a combination of silicon and germanium, a combination of silicon and carbon, and a combination of silicon, germanium and carbon.

8. The method of claim 1, wherein said passivation material comprises at least one of an alkali earth metal, an alkali earth metal oxide, an alkaline earth metal, and an alkaline earth metal oxide.

9. The method of claim 8, wherein said passivation material comprises one of strontium and strontium oxide.

10. The method of claim 4, wherein said monocrystalline oxide comprises at least one of alkaline earth metal titanates, alkaline earth metal zirconates, alkaline earth metal hafnates, alkaline earth metal tantalates, alkaline earth metal ruthenates, alkaline earth metal niobates, alkaline earth metal vanadates, alkaline earth metal tin-based perovskites, lanthanum aluminate, lanthanum scandium oxide, and gadolinium oxide.

11. The method of claim 1, wherein said heating comprises heating to a temperature in the range of from about 700°C to about 900°C.

12. The method of claim 1, further comprising heating said surface so that said passivation material passivates said monocrystalline substrate and forms an ordered layer thereon.

13. The method of claim 1, wherein said depositing is performed by the process of ultra high vacuum molecular beam epitaxy.

14. A method of fabricating a semiconductor structure utilizing a monocrystalline substrate having an amorphous oxide formed thereon, the method comprising:

depositing a passivation material overlying said substrate and said amorphous oxide;

heating said monocrystalline substrate so that said amorphous oxide layer decomposes into at least one volatile species that is liberated from said monocrystalline substrate; and

depositing a monocrystalline oxide overlying said monocrystalline substrate.

15. A method of removing an amorphous oxide from a monocrystalline substrate, the method comprising:

depositing a passivation material overlying said monocrystalline surface; and

heating said monocrystalline substrate,

wherein said passivation material promotes the ejection of electrons from at least one of the passivation material and the amorphous oxide, said ejection of electrons producing a dipole field between said passivation material and the amorphous oxide facilitating the decomposition of the amorphous oxide into volatile species and resulting in the passivation of the monocrystalline substrate by the passivation material.