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(54) **METHODS OF FORMING RESISTIVE MEMORY ELEMENTS**

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CPC *H01L 45/08* (2013.01); *H01L 45/1233* (2013.01); *H01L 45/145* (2013.01); *H01L 45/1641* (2013.01)

(58) **Field of Classification Search**
USPC 257/2, 296, E27.085; 427/569, 533; 438/240, 706, 104, 471, 474, 475, 758, 438/775
See application file for complete search history.

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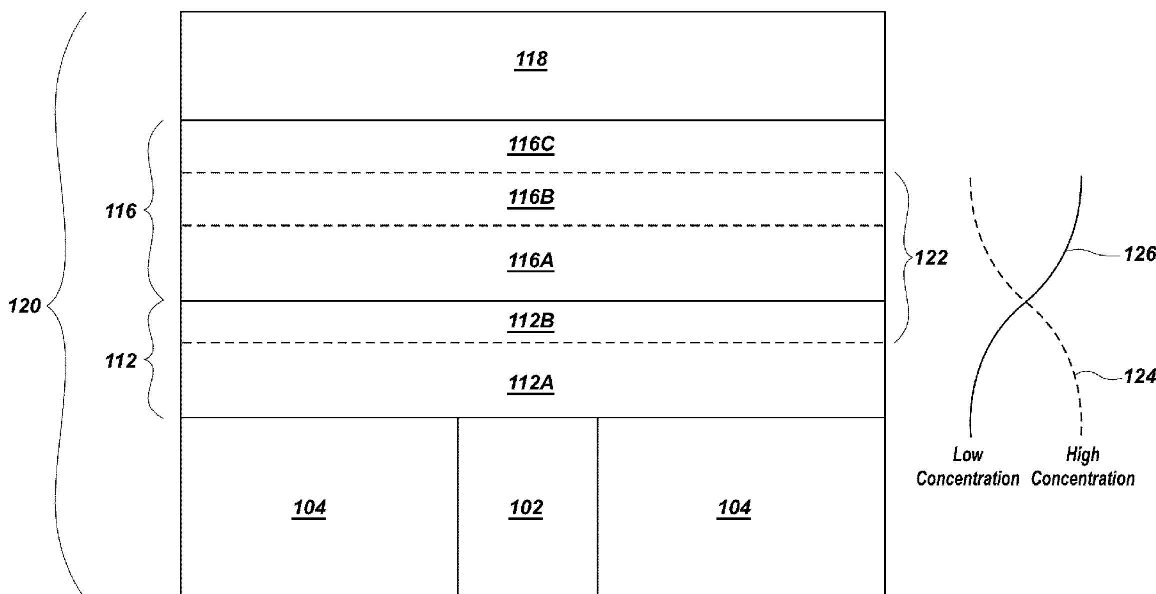
(57) **ABSTRACT**

A method of forming a resistive memory element comprises forming an oxide material over a first electrode. The oxide material is exposed to a plasma process to form a treated oxide material. A second electrode is formed on the treated oxide material. Additional methods of forming a resistive memory element, as well as related resistive memory elements, resistive memory cells, and resistive memory devices are also described.

17 Claims, 6 Drawing Sheets



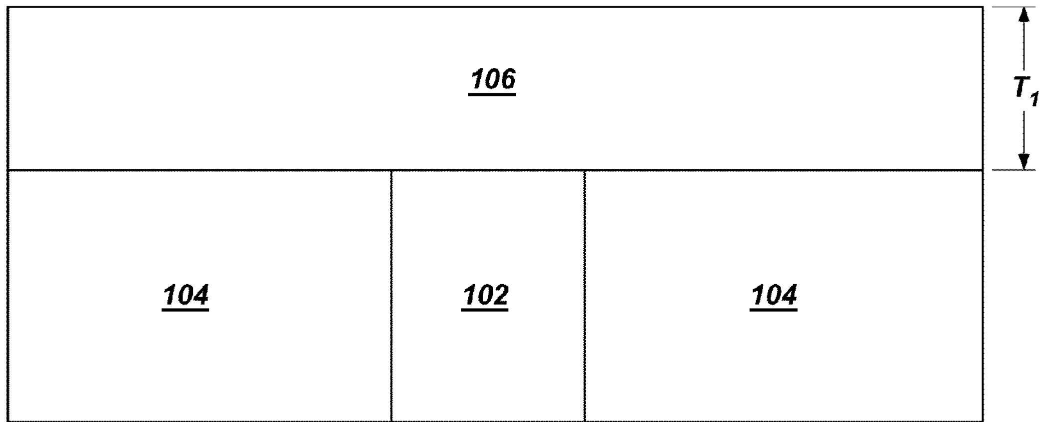


FIG. 1A

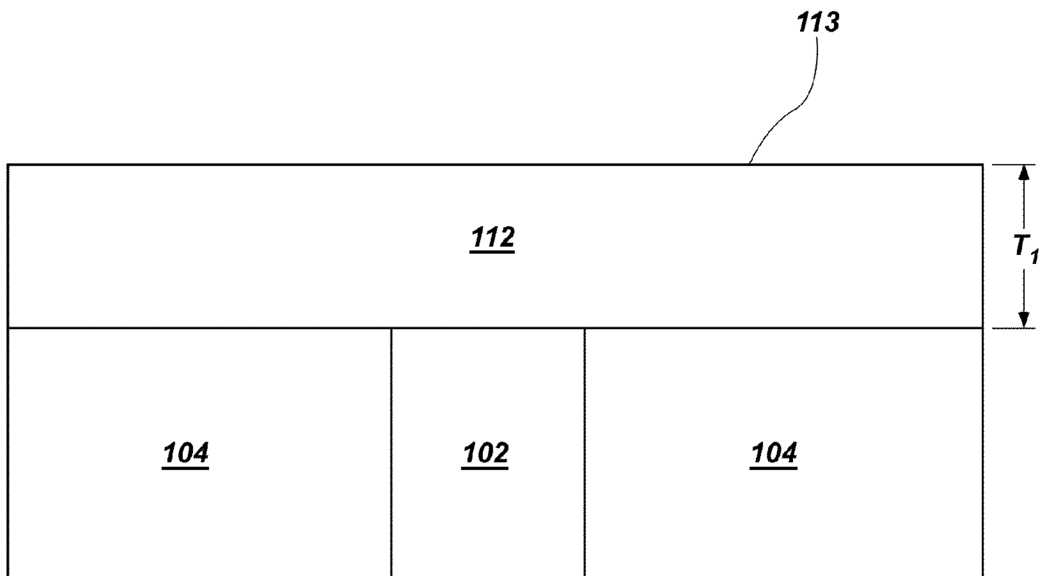


FIG. 1B

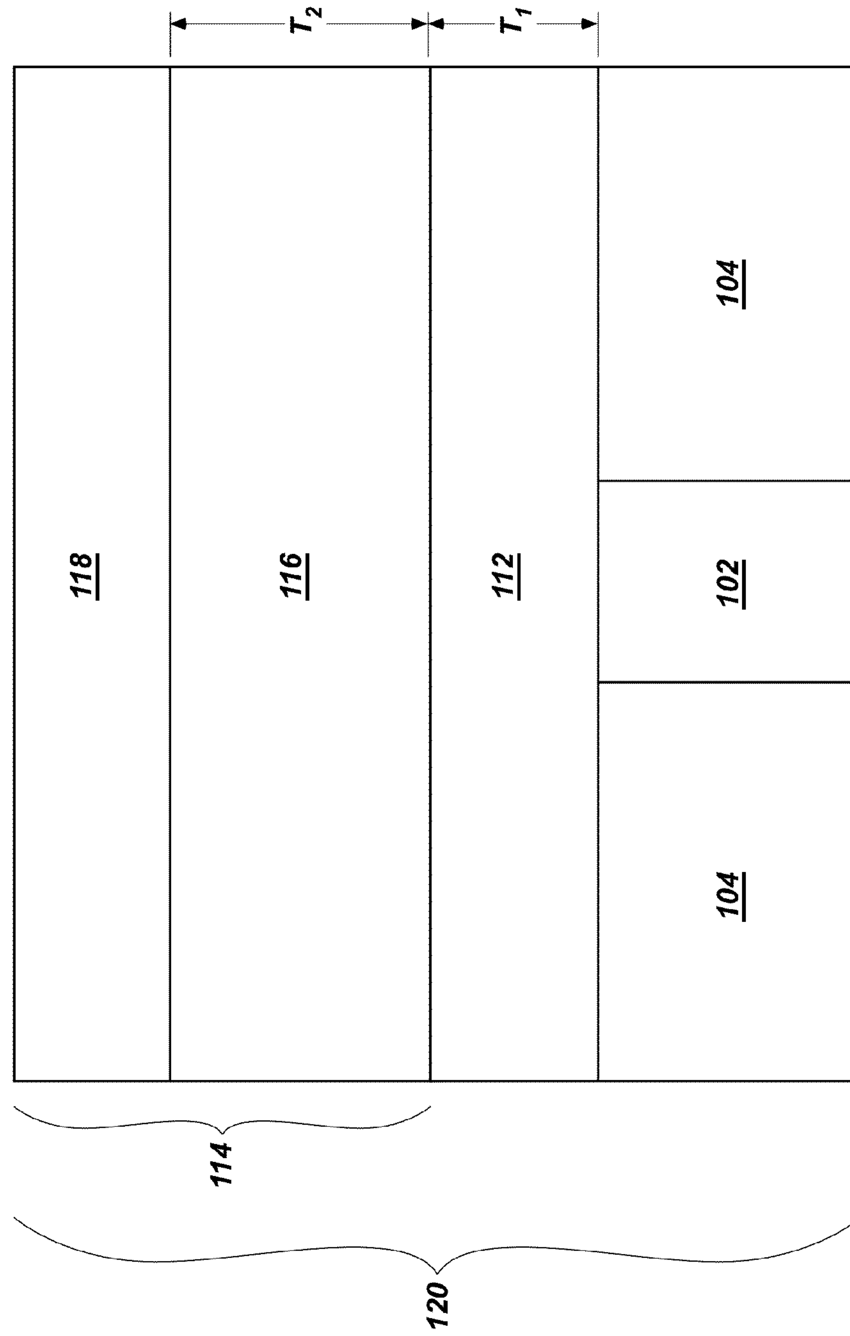


FIG. 1C

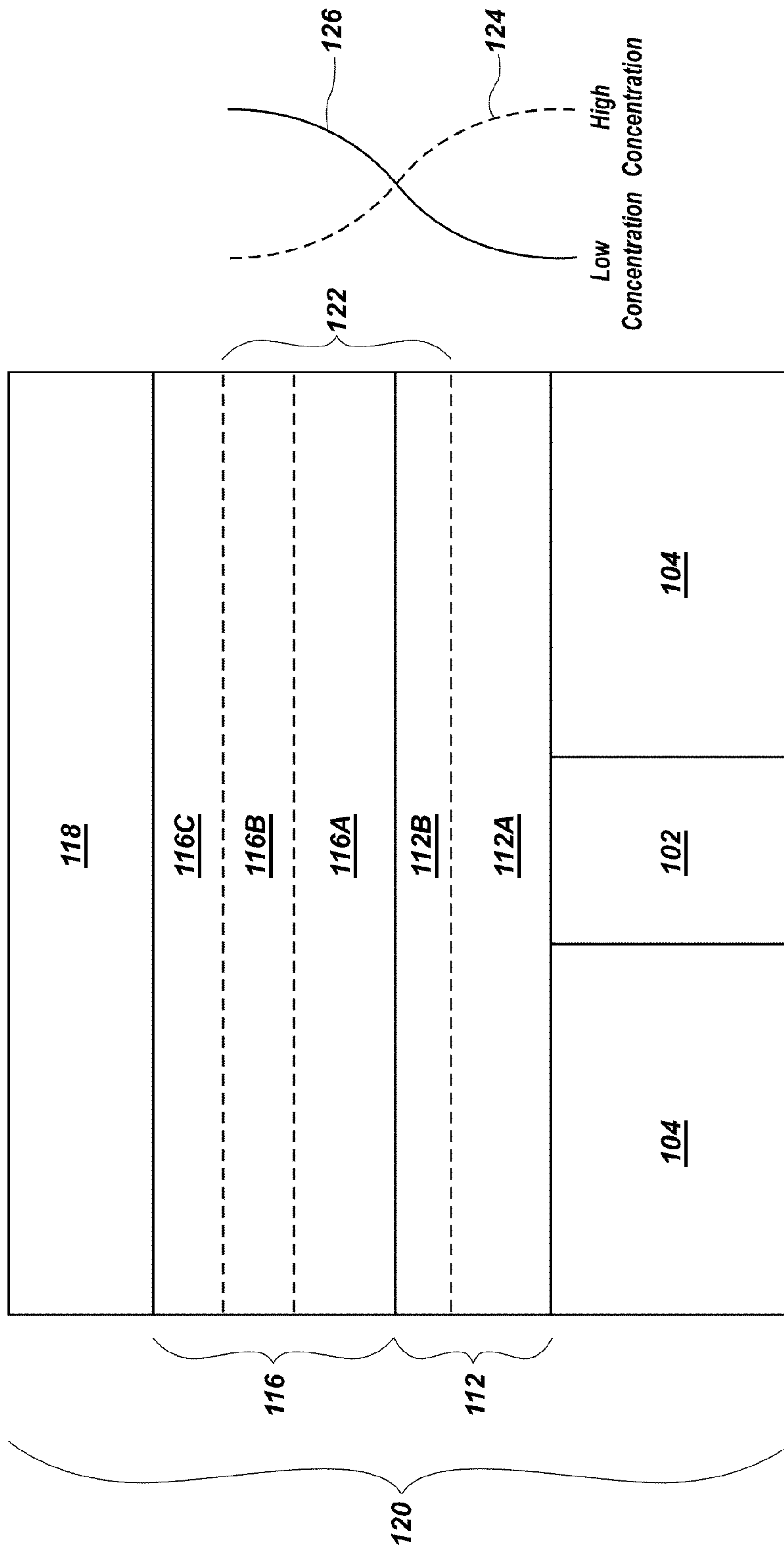


FIG. 1D

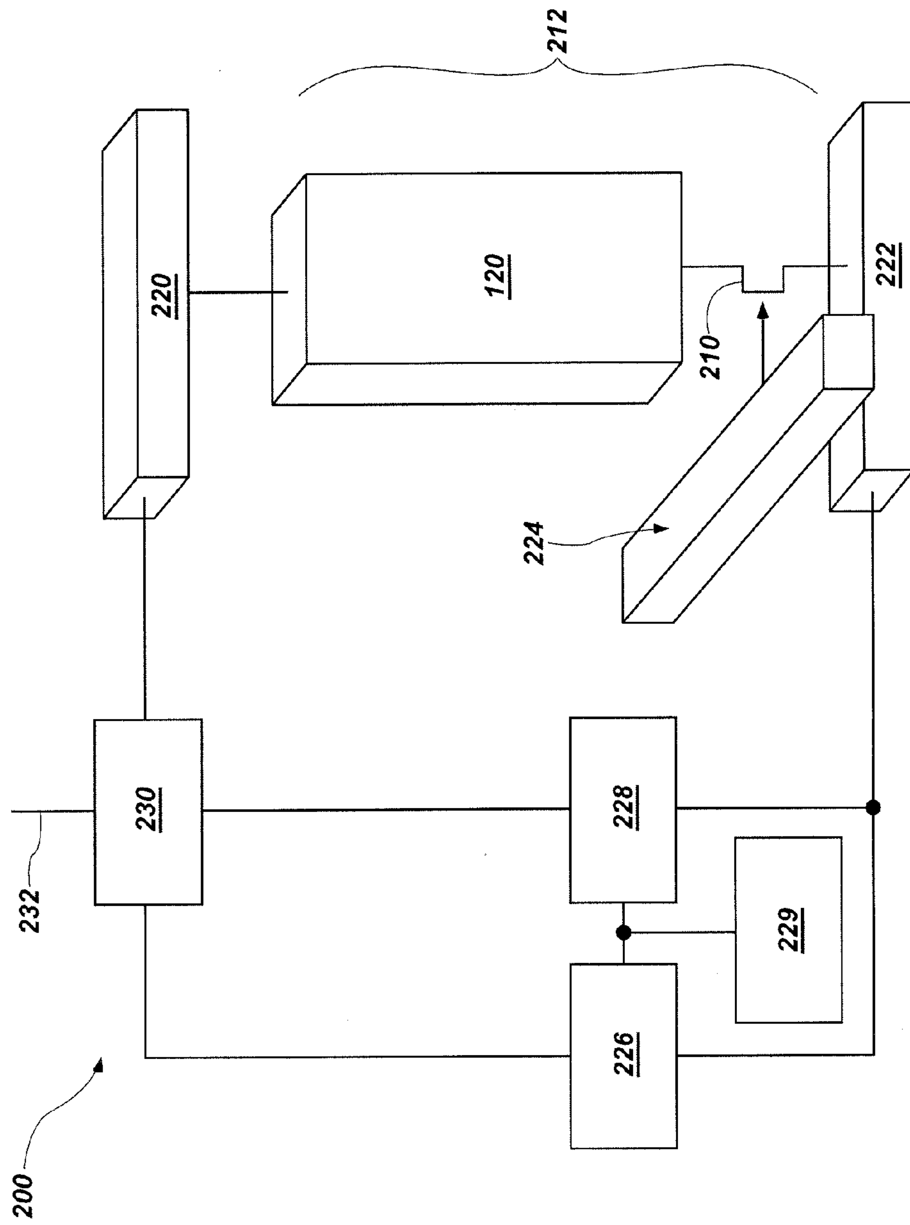


FIG. 2

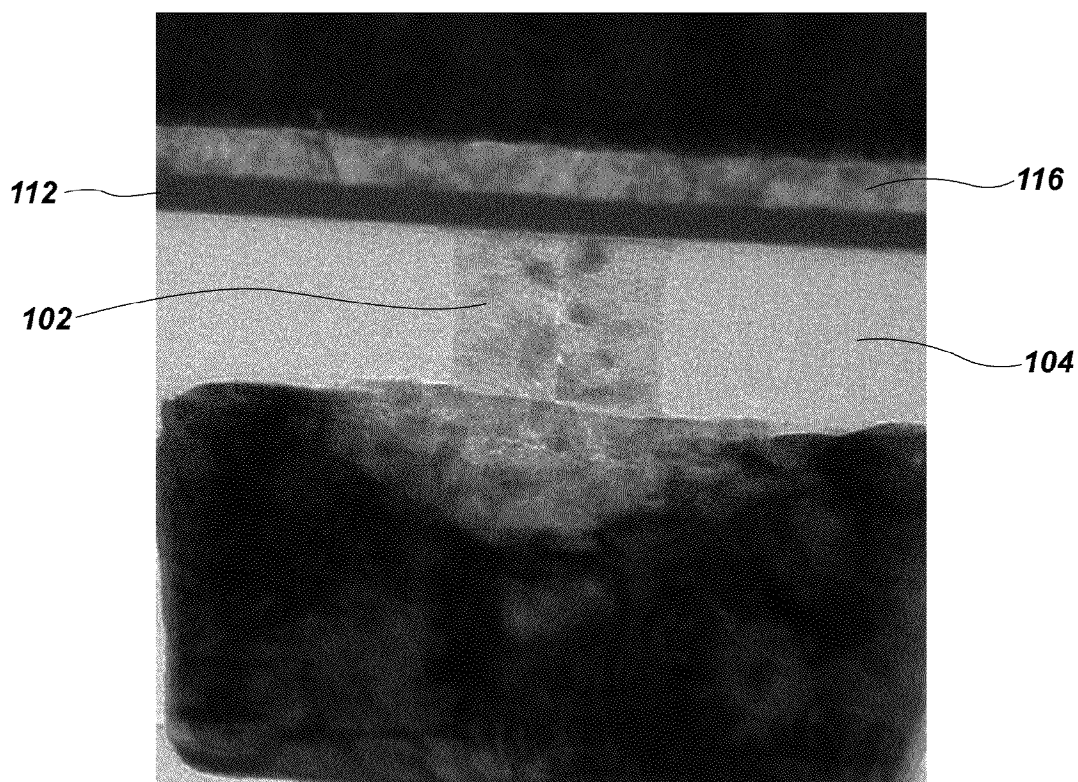


FIG. 3A

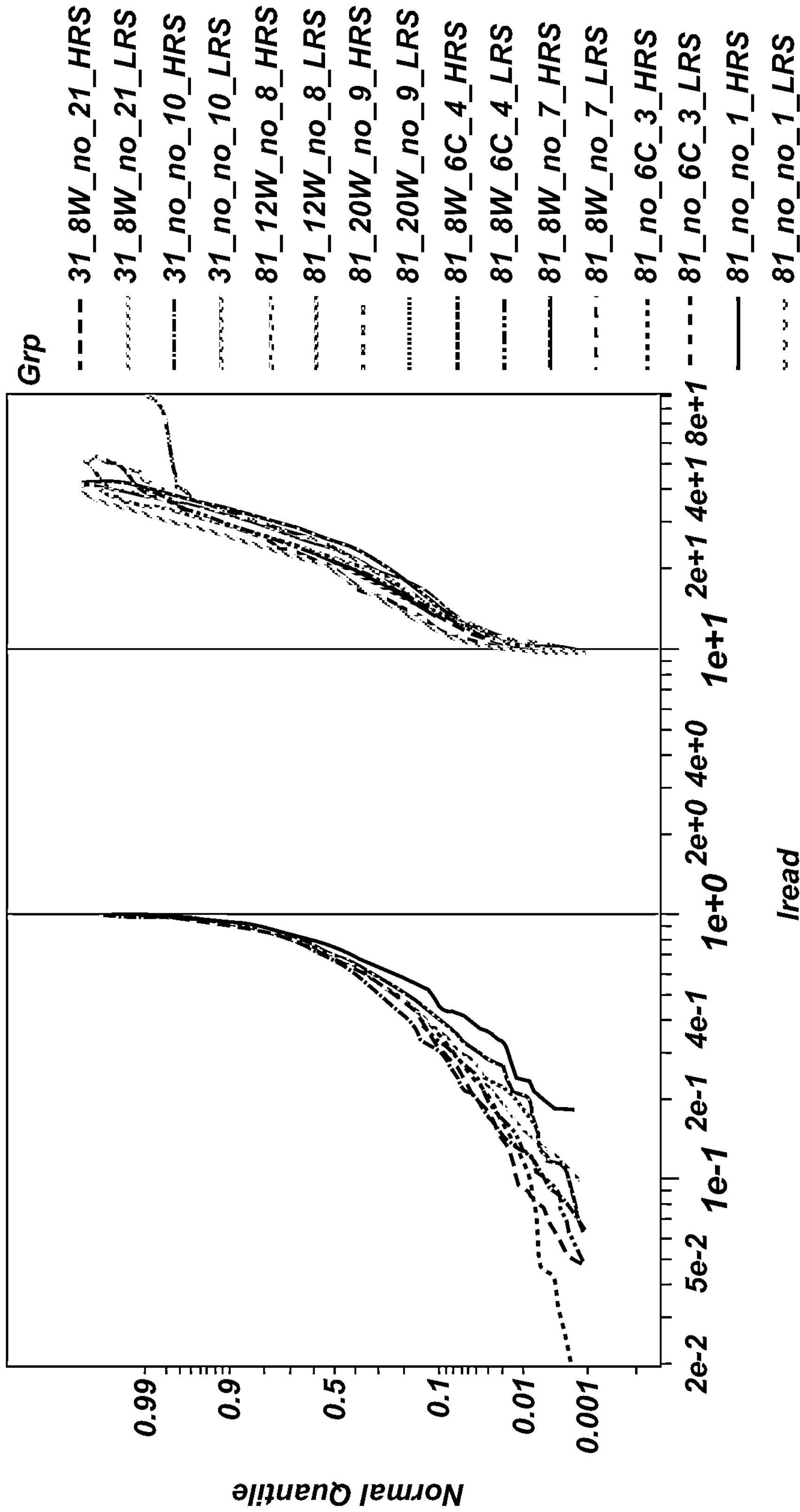


FIG. 3B

METHODS OF FORMING RESISTIVE MEMORY ELEMENTS

TECHNICAL FIELD

Embodiments of the present disclosure relate generally to methods of forming resistive memory elements for resistive memory cells. More specifically, embodiments of the present disclosure relate to methods of forming resistive memory elements using plasma treatment processes, such as a plasma nitridation process, and to related resistive memory elements, resistive memory cells, and resistive memory devices.

BACKGROUND

Non-volatile resistive memory devices are an important element of integrated circuit devices due to their ability to store data absent a power supply. Resistive memory cells, such as resistive random access memory (RRAM) cells, store data by switching between resistance states. For example, for binary data storage, a high-resistance state of the resistive memory cell may be read as logical "1," while a low-resistance state of the resistive memory cell may be read as logical "0." Switching between resistance states may be achieved by applying different physical signals (e.g., voltage, current, etc.) across the resistive memory cell to form, at least partially remove, or repair conductive filaments in a resistive memory element therein. Forming the conductive filaments can decrease the resistance of the memory cell, removing the conductive filaments can increase the resistance of the memory cell, and repairing the conductive filaments can decrease the resistance of the memory cell once again. Conventionally, the initial formation of the conductive filaments is referred to as "forming," the at least partial removal of the conductive filaments is referred to as "resetting," and the repair of the conductive filaments is referred to as "setting."

Oxide-based resistive memory cells, in particular, are attractive because of their simple structure and method of operation. In conventional oxide-based resistive memory cells, the resistive memory element includes a switchable resistance material, such as a dielectric metal oxide, between a first electrode and a second electrode. Conductive filaments in formed by removing oxygen atoms from the switchable resistance material to form oxygen vacancies therein. The conductive filaments can be reset by inserting oxygen atoms back into the switchable resistance material to fill the oxygen vacancies. The conductive filaments can be set by again removing oxygen atoms from the switchable resistance material to reform the oxygen vacancies. However, problems such as instability of operational parameters, poor yield, poor on/off resistance ratio, and unsatisfactory switching endurance resulting from deficiencies in conventional methods of forming resistive memory elements have limited the commercial potential of resistive memory cells and resistive memory cell devices.

It would, therefore, be desirable to have an improved method of forming resistive memory elements for resistive memory cells to overcome one or more of the above problems.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

FIGS. **1**A through **1**D are cross-sectional views illustrating different process stages and structures for a method of foaming a resistive memory element in accordance with embodiments of the present disclosure;

FIG. **2** is a functional block diagram of a resistive memory device in accordance with embodiments of the present disclosure;

FIG. **3**A is a transmission electron micrograph (TEM) showing a partial cross-sectional view of a resistive memory element, as described in Example 1; and

FIG. **3**B is a graph illustrating a low-resistance state and a high-resistance state for a variety of resistive memory devices formed using embodiments of the method of the present disclosure, as described in Example 1.

DETAILED DESCRIPTION

Methods of forming at least one resistive memory element, a resistive memory cell, and a resistive memory device are disclosed. In some embodiments, forming at least one resistive memory element includes forming an oxide material over a contact plug extending through an insulation material. The oxide material may be exposed to a plasma treatment process, such as a plasma process (e.g., a plasma nitridation process), to break chemical bonds between oxygen atoms and at least some other atoms of oxide material and form a treated oxide material. Dangling bonds resulting from plasma damage may be passivated during or after the plasma treatment process. A reactive material may be formed over the treated oxide material to getter oxygen from the treated oxide material. A capping material may be formed over the reactive material to form the at least one resistive memory element. By exposing the oxide material to the plasma treatment process, oxygen atoms may be more easily removed from and inserted into the treated oxide material during forming, reset, and set operations, facilitating high yield, a high on/off resistivity ratio, and excellent switching endurance as compared to conventional resistive memory cells.

The following description provides specific details, such as material types, material thicknesses, and processing conditions in order to provide a thorough description of embodiments of the present disclosure. However, a person of ordinary skill in the art will understand that the embodiments of the present disclosure may be practiced without employing these specific details. Indeed, the embodiments of the present disclosure may be practiced in conjunction with conventional fabrication techniques employed in the industry. In addition, the description provided herein does not form a complete process flow for forming a resistive memory cell, and each of the resistive memory elements, resistive memory cells, and resistive memory devices described below do not form a complete semiconductor device. Only those process acts and structures necessary to understand the embodiments of the present disclosure are described in detail below. Additional acts to form the complete semiconductor device may be performed by conventional fabrication techniques. Also note, any drawings accompanying the present application are for illustrative purposes only, and are thus not drawn to scale. Additionally, elements common between figures may retain the same numerical designation.

As used herein, the term "substrate" means and includes a base material or construction upon which additional materials are formed. The substrate may be a semiconductor substrate, a base semiconductor layer on a supporting structure, a metal electrode or a semiconductor substrate having one or more layers, structures or regions formed thereon. The substrate may be a conventional silicon substrate, or other bulk substrate comprising a layer of semiconductive material. As used herein, the term "bulk substrate" means and includes not only silicon wafers, but also silicon-on-insulator (SOI) substrates, such as silicon-on-sapphire (SOS) substrates and silicon-on-

glass (SOG) substrates, epitaxial layers of silicon on a base semiconductor foundation, and other semiconductor or opto-electronic materials, such as silicon-germanium, germanium, gallium arsenide, gallium nitride, and indium phosphide. The substrate may be doped or undoped.

As used herein, relational terms, such as "first," "second," "top," "bottom," "upper," "lower," "over," "under," etc., are used for clarity and convenience in understanding the disclosure and accompanying drawings and do not connote or depend on any specific preference, orientation, or order, except where the context clearly indicates otherwise.

As used herein, the term "yield" means and includes the number of memory cells that are validly programmable and erasable as a percentage of the total number of memory cells in a given batch. As used herein, the term "validly programmable" means and includes that correct logic is read for a particular physical signal (e.g., set voltage, reset voltage, etc.) applied to a memory cell.

As used herein, the term "on/off resistance ratio" means and includes the ratio between a resistance value at a time when a memory cell is in a low-resistivity state (ON state), and a resistance value at a time when the memory cell is in a high-resistivity state (OFF state).

As used herein, the term "switching endurance" means and includes the number of times a memory cell is able to be switched between resistance states before operability of the memory cell is compromised.

FIGS. **1**A through **1**D are simplified partial cross-sectional views illustrating embodiments of a method of forming at least one resistive memory element. With the description as provided below, it will be readily apparent to one of ordinary skill in the art that the methods described herein may be used in various applications. In other words, the methods of the present disclosure may be used whenever it is desired to enhance the switchable resistivity of a material through the removal and insertion of oxygen atoms.

Referring to FIG. **1**A, an oxide material **106** may be formed on or over at least a first electrode **102**. The first electrode **102**, which may also be referred to as a contact plug, may extend through an electrically insulative material **104**, such as a silicon nitride material. The first electrode **102** may be formed of and include an electrically conductive material including, but not limited to, a metal, a metal alloy, a conductive metal oxide, or combinations thereof. The first electrode **102** may be formed of, for example, an oxidation-resistant metal material, such as tungsten nitride (WN), titanium nitride (TiN), tantalum nitride (TaN), titanium aluminum nitride (TiAlN), platinum (Pt), iridium (Ir), iridium oxide (IrO_x), ruthenium (Ru), or ruthenium oxide (RuO_x). In at least some embodiments, the first electrode **102** includes TiN. The first electrode **102** may be in electrical contact with at least one of a conductive structure (not shown) and a semiconductive structure (not shown) in, on, or over a substrate (not shown). Each of the insulation material **104** and the first electrode **102** may be formed using conventional techniques and processing equipment, which are not described in detail herein.

The oxide material **106**, which may also be referred to as a switchable resistivity material, may include an oxide dielectric material, such as a metal oxide dielectric material, formulated to be switched from one resistance state to another resistance state upon application of a physical signal (e.g., at least one of energy, voltage, current, or other physical phenomena). The oxide material **106** may be switchable from one resistance state to another resistance state, such as from a high-resistance state to a low-resistance state, upon application of a first physical signal, and may be switchable from the low-resistance state to the high-resistance state upon application of a second physical signal. As used herein, the term "metal" means and includes a refractory metal, an alkali metal, an alkaline earth metal, a transition metal, a post-transition metal, or a metalloid. If, for example, the oxide material **106** is a metal oxide dielectric material, a metal component of the oxide material **106** may at least one of chromium (Cr), cobalt (Co), hafnium (Hf), molybdenum (Mo), niobium (Nb), tantalum (Ta), titanium (Ti), tungsten (W), vanadium (V), zirconium (Zr), lanthanum (La), manganese (Mn), calcium (Ca), praseodymium (Pr), europium (Eu), silicon (Si), germanium (Ge), aluminum (Al), and nickel (Ni). By way of non-limiting example, the oxide material **106** may be at least one of silicon dioxide (SiO_2), a hafnium oxide (HfO_x), a hafnium silicon oxide ($HfSi_yO_x$), a zirconium oxide (ZrO_x), a zirconium silicon oxide ($ZrSi_yO_x$), a titanium oxide (TiO_x), a titanium silicon oxide ($TiSi_yO_x$), a tantalum oxide (TaO_x), a tantalum silicon oxide ($TaSi_yO_x$), a niobium oxide (NbO_x), a niobium silicon oxide ($NbSi_yO_x$), a vanadium oxide (VO_X), a vanadium silicon oxide (VSi_yO_x), a tungsten oxide (WO_x), a tungsten silicon oxide (WSi_yO_x), a molybdenum oxide (MoO_x), a molybdenum silicon oxide ($MoSi_yO_x$), a chromium oxide (CrO_x), and a chromium silicon oxide ($CrSi_yO_x$). In at least some embodiments, the oxide material **106** is $HfSi_yO_x$. Formulae including at least one of "x" and "y" above (e.g., HfO_x, $HfSi_yO_x$, ZrO_x, $ZrSi_yO_x$, TiO_x, $TiSi_yO_x$, etc.) represent a composite material that on average contains x atoms of oxygen and y atoms of silicon for every one atom of the metal component. As the formulae are representative of relative atomic ratios and not strict chemical structure, the oxide material **106** may be a stoichiometric compound or a non-stoichiometric compound, and values of x and y may be integers or may be non-integers. As used herein, the term "non-stoichiometric compound" means and includes a chemical compound with an elemental composition that cannot be represented by a ratio of well-defined natural numbers and is in violation of the law of definite proportions. If, for example, the oxide material **106** includes silicon, a ratio of metal atoms to silicon atoms in the oxide material **106** may be within a range of from about 200:1 to about 1:200, such as from about 8:1 to about 3:1.

The oxide material **106** may be selected at least partially based on a number of oxygen vacancies expected to be formed in the oxide material **106** following additional processing (e.g., plasma treatment, exposure to a reactive material, etc.), as described in further detail below. In one or more embodiments, the oxide material **106** may be a material that exhibits a comparatively larger number of oxygen vacancies when subjected to the additional processing (e.g., SiO_2, HfO_x, ZrO_x, TiO_x, TaO_x, NbO_x, VO_x, WO_x, MoO_x, or CrO_x). In additional embodiments, the oxide material **106** may be a material that exhibits a comparatively smaller number of oxygen vacancies (i.e., a smaller ratio of metal atoms to oxygen atoms) when subjected to the additional processing (e.g., $HfSi_yO_x$, $ZrSi_yO_x$, $TiSi_yO_x$, $TaSi_yO_x$, $NbSi_yO_N$, VSi_yO_x, WSi_yO_x, $MoSi_yO_x$, or $CrSi_yO_x$).

The oxide material **106** may have any suitable thickness. By way of non-limiting example, a thickness T_1 of the oxide material **106** may be within a range of from about 5 Angstroms (Å) to about 200 Å, such as from about 10 Å to about 100 Å, or from about 20 Å to about 80 Å. In at least some embodiments, the thickness T_1 of the oxide material **106** is about 50 Å.

The oxide material **106** may be formed on or over at least the first electrode **102** using conventional techniques, such as physical vapor deposition ("PVD"), chemical vapor deposition ("CVD"), or atomic layer deposition ("ALD"). PVD includes, but is not limited to, sputtering, evaporation, or

ionized PVD. Such deposition techniques are known in the art and, therefore, are not described in detail herein.

Referring to FIG. **1**B, the oxide material **106** (FIG. **1**A) may be subjected to a plasma nitridation process, such as a decoupled plasma nitridation (DPN) process, to damage and passivate the oxide material **106** and form a treated oxide material **112**. The plasma nitridation process may simultaneously break chemical bonds between oxygen atoms and other atoms of the oxide material **106** while implanting nitrogen atoms into the lattice. Passivation of dangling bonds may also occur simultaneously. If, for example, the oxide material **106** is SiO_2, HfO_x, $HfSi_yO_x$, ZrO_x, $ZrSiO_x$, TiO_x, $TiSi_yO_x$, TaO_x, $TaSi_yO_x$, NbO_x, $NbSi_yO_x$, VO_x, VSi_yO_x, WO_x, WSi_yO_x, MoO_x, $MoSi_yO_x$, CrO_x, or $CrSi_yO_x$, at least a portion of the treated oxide material **112** may include a hafnium oxy-nitride (HfO_xN_m), a hafnium silicon oxy-nitride ($HfSi_yO_xN_m$), a zirconium oxy-nitride (ZrO_xN_m), a zirconium silicon oxy-nitride ($ZrSi_yO_xN_m$), a titanium oxy-nitride (TiO_xN_m), a titanium silicon oxy-nitride ($TiSi_yO_xN_m$), a tantalum oxy-nitride (TaO_xN_m), a tantalum silicon oxy-nitride ($TaSi_yO_xN_m$), a niobium oxy-nitride (NbO_xN_m), a niobium silicon oxy-nitride ($NbSi_yO_xN_m$), a vanadium oxy-nitride (VO_xN_m), a vanadium silicon oxy-nitride ($VSi_yO_xN_m$), a tungsten oxy-nitride (WO_xN_m), a tungsten silicon oxy-nitride ($WSi_yO_xN_m$), a molybdenum oxy-nitride (MoO_xN_m), a molybdenum silicon oxy-nitride ($MoSi_yO_xN_m$), a chromium oxy-nitride (CrO_xN_m), and a chromium silicon oxy-nitride ($CrSi_yO_xN_m$), respectively. Formulae including at least one of "y," "x," and "m" above (e.g., HfO_xN_m, $HfSi_yO_xN_m$, ZrO_zN_m, $ZrSi_yO_xN_m$, TiO_xN_m, $TiSi_yO_xN_m$, etc.) represent a composite material that, on average, contains x atoms of oxygen, y atoms of silicon, and m atoms of nitrogen for every one atom of the metal component. The treated oxide material **112** may be a stoichiometric compound or a non-stoichiometric compound, and values of y, x, and m may be integers or may be non-integers. The values of y, x, and m and may at least partially depend on the metal (e.g., Hf, Zr, Ti, Ta, Nb, V, W, Mo, Cr, etc.) used in the oxide material **106**.

In one or more embodiments, the plasma used in the plasma nitridation process may include at least one non-nitrogen component. By way of non-limiting example, the plasma may include nitrogen and at least one dopant component (e.g., boron, oxygen, carbon, arsenic, silicon, germanium, etc.). If, for example, the plasma includes a dopant component, the dopant component and nitrogen may be provided as single chemical species (e.g., a compound including dopant component atoms and nitrogen atoms), or may be provided as different chemical species (e.g., a first chemical species including dopant component atoms and a separate chemical species including nitrogen atoms). In at least some embodiments, non-nitrogen components are substantially absent from the plasma used in the plasma nitridation process.

The treated oxide material **112** may include nitrogen up to the thickness T_1 of the treated oxide material **112**. By way of non-limiting example, if the thickness T_1 of the treated oxide material **112** is about 50 Å, nitrogen may be included to a depth within a range of from about 1 Å to about 50 Å, such from about 1 Å to about 20 Å, from an exposed surface **113** of the treated oxide material **112**. In one or more embodiments, the treated oxide material **112** includes nitrogen to a depth less than the thickness T_1 of the treated oxide material **112**. In additional embodiments, nitrogen may be substantially limited to a location proximate the exposed surface **113** of the treated oxide material **112**. A concentration of nitrogen throughout the thickness T_1 of the treated oxide material **112** may be varied from about 0 atomic percent to about 80 atomic percent. The concentration of nitrogen may vary throughout the thickness T_1 of the treated oxide material **112**. By way of non-limiting example, the concentration of nitrogen throughout the thickness T_1 may decrease, may increase, may decrease and then increase, or may increase and then decrease in a direction extending away from the exposed surface **113** of the treated oxide material **112**. Nitrogen may have, for example, a linear concentration distribution, a stepwise concentration distribution, or a Gaussian concentration distribution throughout the thickness T_1 of the treated oxide material **112**.

The depth of nitrogen penetration and the concentration of nitrogen throughout the thickness T_1 of the treated oxide material **112** may be controlled and may be a function of a power applied during the plasma nitridation process and a duration of the plasma nitridation process. For example, an increase in the power applied during the plasma nitridation process may increase the depth of nitrogen penetration into the oxide material **106** (FIG. **1**A), and an increase in the duration of the plasma nitridation process may increase the concentration of nitrogen throughout the depth. A power applied during the plasma nitridation process (e.g., DPN process) may be within a range of from about 200 watts (W) to about 2500 W, such as from about 400 W to about 2000 W, or from about 800 W to about 2000 W. In addition, a duration of the plasma nitridation process may be within a range of from about 10 seconds to about 300 seconds, such as from about 30 seconds to about 240 seconds, or from about 30 seconds to about 180 seconds. In at least some embodiments, the power applied during the plasma nitridation process is about 800 W and the duration of the plasma nitridation process is about 60 seconds.

The plasma nitridation process may be performed without performing an annealing process (e.g., a thermal anneal) prior to further processing. Conventionally, an annealing process is used to repair damage (e.g., broken bonds) to the structure subjected to the plasma nitridation process before performing additional processing. Omitting such an annealing process may maintain at least some damage to the treated oxide material **112**, facilitating enhanced oxygen atom removal from the treated oxide material **112** during subsequent processing, as described in further detail below. In further embodiments, such as where at least some repair to the treated oxide material **112** is desirable, an annealing process may be employed prior to performing additional processing. The treated oxide material **112** may be damaged up to the thickness T_1 of the treated oxide material **112**. By way of non-limiting example, if the thickness T_1 of the treated oxide material **112** is about 50 Å, the treated oxide material **112** may be damaged to a depth within a range of from about 1 Å to about 50 Å from the exposed surface **114** of the treated oxide material **112**.

In additional embodiments, the oxide material **106** (FIG. **1**A) may be subjected to a plasma treatment process other than a plasma nitridation process. By way of non-limiting example, the oxide material **106** may be exposed to a plasma including elements other than nitrogen, such as at least one element selected from the group consisting of hydrogen, deuterium, noble gas elements (e.g., argon, krypton, xenon, etc.), other non-metal elements (e.g., phosphorus, etc.), and metalloid elements (e.g., boron, arsenic, tellurium, etc.). The at least one element and conditions for generating and maintaining the plasma (e.g., temperature, pressure, power, duration, etc.) may be selected based on at least one of a desired depth of penetration into the oxide material **106**, a desired concentration of the at least one element, and a desired amount of plasma damage to the oxide material **106**. As the oxide material **106** is bombarded with the plasma, chemical bonds between oxygen atoms and other atoms of the oxide material

106 may be broken. The plasma treatment process may substantially simultaneously break chemical bonds of the oxide material **106** and passivate dangling bonds, or the plasma treatment process may break chemical bonds of the oxide material **106** without substantially simultaneously passivating dangling bonds. If, for example, the plasma treatment process does not substantially simultaneously passivate dangling bonds, the treated oxide material **112** may be subsequently exposed to at least one passivation material (e.g., hydrogen, nitrogen, fluorine, deuterium, etc.) to passivate at least some dangling bonds, or the treated oxide material **112** may be left substantially unpassivated such that dangling bonds substantially remain in the treated oxide material **112**.

Referring to FIG. **1**C, a second electrode **114** may be formed on or over the treated oxide material **112** to form a resistive memory element **120** including the first electrode **102**, the treated oxide material **112**, and the second electrode **114**. The second electrode **114** may include a reactive material **116** and a capping material **118**. The reactive material **116** may be formed on or over the treated oxide material **112**, and the capping material **118** may be formed on or over the reactive material **116**. The reactive material **116**, which may also be referred to as a gettering material, may be any material formulated to remove or getter oxygen atoms from the treated oxide material **112**. The reactive material **116** may, for example, facilitate the breaking of chemical bonds between oxygen atoms and other atoms of the treated oxide material **112**, and may facilitate the migration of unbonded oxygen atoms from the treated oxide material **112** into the reactive material **116**. As a non-limiting example, the reactive material **116** may be a metal included in the treated oxide material **112**, or may be a metal not included in the treated oxide material **112**. If, for example, the treated oxide material **112** includes Hf (e.g., HfO_x, $HfSi_yO_x$, HfO_xN_m, $HfSi_yO_xN_m$, etc.), Zr (e.g., ZrO_x, $ZrSi_yO_x$, ZrO_xN_m, $ZrSi_yO_xN_m$, etc.), Ti (e.g., TiO_x, $TiSi_yO_x$, TiO_xN_m, $TiSi_yO_xN_m$, etc.), Ta (e.g., TaO_x, $TaSi_yO_x$, TaO_xN_m, $TaSi_yO_xN_m$), Nb (NbO_x, $NbSi_yO_x$, NbO_xN_m, $NbSi_yO_xN_m$, etc.), V (VO_x, VSi_yO_x, VO_xN_m, $VSi_yO_xN_m$), W (WO_x, WSi_yO_x, WO_xN_m, $WSi_yO_xN_m$, etc.), Mo (MoO_x, $MoSi_yO_x$, MoO_xN_m, $MoSi_yO_xN_m$, etc.), or Cr (e.g., CrO_x, $CrSi_yO_x$, CrO_xN_m, $CrSi_yO_xN_m$, etc.), the reactive material **116** may be Hf, Zr, Ti, Ta, Nb, V, W, Mo, or Cr. In at least some embodiments, the reactive material **116** is Ti.

A thickness T_2 of the reactive material **116** may be selected at least partially based on the thickness T_1 of the treated oxide material **112** and the ease of oxygen removal from the treated oxide material **112** (e.g., as facilitated through the plasma nitridation process, or another process). The thickness T_2 of the reactive material **116** may be selected such that neither too little oxygen nor too much oxygen is removed from the treated oxide material **112** by the reactive material **116**. As a non-limiting example, thickness T_2 of the reactive material **116** may be less than or equal to the thickness T_1 of the treated oxide material **112**, such as within a range of from about 10 Angstroms up to the thickness T_1 of the treated oxide material **112**.

The reactive material **116** may be formed on or over the treated oxide material **112** shortly after the formation of the treated oxide material **112** to substantially limit a loss of oxygen atoms to the environment surrounding the treated oxide material **112** and enhance the amount of oxygen atoms gettered into the reactive material **116**. The reactive material **116** may be formed on or over the treated oxide material **112** using known methods, such as PVD, CVD, or ALD, which are not described in detail herein. In at least some embodiments, the reactive material **116** is formed using PVD.

The capping material **118** may be fondled of and include any suitable conductive material including, but not limited to, a metal, a metal alloy, a conductive metal oxide, or combinations thereof. The capping material **118** may substantially limit or prevent the reactive material **116** from reacting with ambient oxygen (i.e., oxygen atoms other than those gettered from the treated oxide material **112**). The capping material **118** may be, for example, an oxidation-resistant metal material, such as WN, TiN, TaN, TiAlN, Pt, Ir, IrO_x, Ru, or RuO_x. The capping material **118** may be substantially the same as or may be different than a material of the first electrode **102**. In at least some embodiments, the capping material **118** is WN. The capping material **118** may be formed shortly after the formation of the reactive material **116** to substantially limit or prevent the reactive material **116** from reacting with ambient oxygen. The capping material **118** may be formed on the reactive material **116** using known techniques, such as PVD, CVD, or ALD, which are not described in detail herein.

Accordingly, a method of forming a resistive memory element may comprise forming a switchable resistivity material over a contact plug extending through an insulation material. The switchable resistivity material may be exposed to a plasma treatment process to break chemical bonds between oxygen atoms and other atoms of the switchable resistivity material. A reactive material may be formed on the switchable resistivity material without annealing the switchable resistivity material. A capping material may be formed over the reactive material.

In addition, another method of forming a resistive memory element may comprise forming an oxide material over a first electrode. The oxide material may be exposed to a plasma process to form a treated oxide material. A second electrode may be formed on the treated oxide material.

Referring to FIG. **1**D, forming the reactive material **116** on the treated oxide material **112** enables oxygen atoms to migrate from the treated oxide material **112** into the reactive material **116**. The migration of the oxygen atoms may, for example, form an oxygen-deficient region **112**B and a remaining region **112**A in the treated oxide material **112**. The oxygen-deficient region **112**B may have a lower oxygen concentration than before the removal of the oxygen atoms, and the remaining region **112**A may have a substantially similar oxygen concentration as compared to before the removal of the oxygen atoms. In addition, the migration of the oxygen atoms may, for example, form an insulative oxygen-deficient region **116**A, a conductive oxygen-deficient region **116**B, and an unreacted region **116**C in the reactive material **116**. Each of the insulative oxygen-deficient region **116**A and the conductive oxygen-deficient region **116**B may have an oxygen concentration greater than before the removal of the oxygen atoms from the treated oxide material **112**, and the unreacted region **116**C may have a substantially similar oxygen concentration as compared to before the removal of the oxygen atoms from the treated oxide material **112**. As of formation, the insulative oxygen-deficient region **116**A may be electrically insulative and may have a greater oxygen concentration than the conductive oxygen-deficient region **116**B, which may be electrically conductive. As shown in FIG. **1**D, the oxygen-deficient region **112**B may be located over the remaining region **112**A, the insulative oxygen-deficient region **116**A may be located over the oxygen-deficient region **112**B, the conductive oxygen-deficient region **116**B may be located over the insulative oxygen-deficient region **116**A, and the unreacted region **116**C may be located over the conductive oxygen-deficient region **116**B. In additional embodiments, the unreacted region **116**C of the reactive material **116** may be substantially absent (i.e., substantially all of the reac-

tive material **116** may be oxidized by oxygen gettered from the treated oxide material **112**). A reactive region **122** may include the conductive oxygen-deficient region **112**B of the treated oxide material **112**, the insulative oxygen-deficient region **116**A of the reactive material **116**, and the conductive oxygen-deficient region **116**B of the reactive material **116**. Oxygen atoms may shift locations in the reactive region **122** during forming, resetting, and setting operations, as described in further detail below.

Accordingly, a resistive memory element of the present disclosure may comprise a contact plug extending through a insulation material and comprising an oxidation-resistant material, a treated oxide material over the contact plug and comprising an oxygen-deficient oxide material and an oxy-nitride material, a reactive material over the treated oxide material and comprising metal, and a capping material over the reactive material and comprising another oxidation-resistant material.

In one or more embodiments, an annealing process (e.g., a thermal anneal) may be used to increase the migration of oxygen atoms from the treated oxide material **112** into the reactive material **116**. The annealing process may, for example, enhance the breaking of bonds between oxygen atoms and other atoms of the treated oxide material **112**. In additional embodiments, the plasma treatment process previously described above (e.g., the plasma nitridation process) may facilitate sufficient oxygen atom removal from the treated oxide material **112** so that the annealing process may be omitted.

An oxygen concentration profile throughout each of the treated oxide material **112** and the reactive material **116** upon the initial removal of the oxygen atoms from the treated oxide material **112** is illustrated by the graphic representation **124** on the right side of FIG. **1**D. As shown in FIG. **1**D, oxygen concentration may be highest in the remaining region **112**A of the treated oxide material **112** and may decrease heading in the direction of the capping material **118** (i.e., the oxygen concentration may decrease across the oxygen-deficient region **112**B, the insulative oxygen-deficient region **116**A, the conductive oxygen-deficient region **116**B, and the unreacted region **116**C). Conversely, an oxygen vacancy profile throughout the treated oxide material **112** and the reactive material **116** upon the initial removal of the oxygen atoms from the treated oxide material **112** is illustrated by the graphic representation **126** on the right side of FIG. **1**D. As shown in **1**D, the oxygen vacancy profile may be substantially inversely proportional to the oxygen concentration. Put another way, the number of oxygen vacancies may be lowest in the remaining region **112**A of the treated oxide material **112** and may increase heading in the direction of the capping material **118**.

Following the migration of oxygen atoms from the treated oxide material **112** into the reactive material **116**, the resistive memory element **120** may be subjected to additional processing. By way of non-limiting example, the resistive memory element **120** may be patterned, etched, and passivated. Such additional processing may be performed using conventional techniques and processing equipment, which are not described in detail herein.

FIG. **2** illustrates a functional block diagram of a resistive memory device **200** in accordance with an embodiment of the present disclosure. The resistive memory device **200** may include at least one resistive memory cell **212** between at least one data/sense line, for example, a bit line **220**, and at least one source line **222**. The resistive memory cell **212** may include an access device **210** coupled or connected in series with the resistive memory element **120** previously described above. The access device **210** may act as a switch for enabling and disabling current flow through the resistive memory element **120**. By way of non-limiting example, the access device **210** may be a transistor (e.g., a field-effect transistor, a bipolar junction transistor, etc.) with a gate (not shown) connected to an access line, for example, a word line **224**. The word line **224** may extend in a direction substantially perpendicular to that of the bit line **220**. The bit line **220** and the source line **222** may be connected to logic for programming and reading the resistive memory element **120**. A control multiplexer **230** may have an output connected to the bit line **220**. The control multiplexer **230** may be controlled by a control logic line **232** to select between a first input connected to a pulse generator **226**, and a second input connection to read-sensing logic **228**.

Accordingly, a resistive memory cell of the present disclosure may comprise an access device and a resistive memory element coupled to the access device. The resistive memory element may comprise a first electrode, a treated oxide material on the first electrode and comprising an oxygen-deficient oxide material and an oxy-nitride material, and a second electrode on the treated oxide material.

In addition, a resistive memory device of the present disclosure may comprise a word line, a bit line, a source line, and a resistive memory cell between the bit line and the source line. The resistive memory cell may comprise an access device coupled to the word line, and a resistive memory element between to the access device and the bit line. The resistive memory element may comprise a first electrode, a second electrode and a treated oxide material between the first electrode and the second electrode, the treated oxide material comprising an oxygen-deficient oxide material and an oxy-nitride material.

During a programming operation, a voltage greater than a threshold voltage of the access device **210** may be applied to the word line **224** to turn on the access device **210**. Turning on the access device **210** completes a circuit between the source line **222** and the bit line **220** by way of the resistive memory element **120**. After turning on the access device **210**, a bias generator **229** may establish, by way of the pulse generator **226**, a bias voltage potential difference between the bit line **220** and the source line **222**. Referring to FIG. **1**D, if a forming bias voltage or a set bias voltage is established, oxygen atoms migrate from the treated oxide material **112** into the reactive material **116** (e.g., the insulative oxygen-deficient region **116**A, and the conductive oxygen-deficient region **116**B) to form oxygen-vacancy-based conductive filaments in at least the treated oxide material **112**. The oxygen-vacancy-based conductive filaments reduce the resistivity of the resistive memory element **120**. Conversely, if a reset bias voltage is established, oxygen atoms migrate from the reactive material **116** back into the treated oxide material **112** to remove the oxygen-vacancy-based conductive filaments therein and increase the resistivity of the resistive memory element **120**.

Referring again to FIG. **2**, during a read operation, the bias generator **229** may establish, by way of read-sensing logic **228**, a read bias voltage potential difference between the bit line **220** and the source line **222**. The read bias voltage may be lower than the reset bias voltage. The read bias voltage enables current to flow through the resistive memory element **120** according a resistance state of the treated oxide material **112** (FIG. **1**D). For example, for a given read bias voltage, if the treated oxide material **112** is in a high-resistance state (e.g., a reset state), a relatively smaller current flows through the resistive memory element **120** than if the treated oxide material **112** is in a low-resistance state (e.g., a set state). The amount of current flowing through resistive memory element

120 during the read operation may be compared to a reference input by the read-sensing logic 228 (e.g., a sense amplifier) to discriminate whether the data stored in the resistive memory cell 212 is a logic "1" or a logic "0."

The methods and structures of the present disclosure may advantageously improve resistive memory performance as compared to conventional methods and structures. For example, the plasma nitridation processing described herein may increase migration of oxygen atoms in the resistive memory element (e.g., by breaking O—R bonds, where R is an atom of another element, to enable easier oxygen atom removal by a resistive material) and increase oxygen availability (e.g., by replacing at least some O—R bonds with N—R bonds). The increased oxygen atom availability and migration may, in turn, facilitate high yield (e.g., greater than or equal to 99%), a high on/off resistance ratio (e.g., greater than or equal to 100), and excellent switching endurance (e.g., greater than or equal to 10^6 cycles). The methods and structures of the present disclosure may also facilitate low operation currents, fast switching speed, reliable data retention, and excellent scalability.

The following example serves to explain some embodiments of the present disclosure in more detail. The example is not to be construed as being exhaustive or exclusive as to the scope of the disclosure.

EXAMPLE

A number of sample RRAM devices, each including one hundred RRAM elements formed by different methods, were analyzed. To form the RRAM elements of each device, $HfSi_yO_x$ (Hf:Si ratio of 8:1 or 3:1) was formed on TiN. For some of the sample devices, after forming the $HfSi_yO_x$, the $HfSi_yO_x$ was exposed to at least one of a DPN process and a thermal anneal at 600° C. If utilized, the DPN process employed a power of 800 W, 1200 W, or 2000 W and a duration of 30 seconds. Ti was deposited on the $HfSi_yO_x$ (whether nitrided or unnitrided), and WN was deposited on the Ti. FIG. 3A is a transmission electron micrograph (TEM) showing a partial cross-sectional view an RRAM element that was fowled for one of the sample RRAM devices. The sample RRAM devices were finalized for testing using conventional processes (e.g., masking, etching, passivation).

Upon formation of the sample RRAM devices, each sample RRAM device was switched between a low-resistivity state ("LRS") and a high-resistivity state ("HRS") ten times and then subjected to yield analysis and on/off resistance analysis. Table 1 below briefly summarizes the RRAM element formation details and yield results of some of the sample RRAM devices. The results indicate that, for at least some switchable resistivity materials, employing DPN without a thermal anneal facilitates an improvement in yield, as compared to either not performing DPN (i.e., whether or not a thermal anneal is also performed) or performing DPN with a thermal anneal. The results also indicate that for at least some switchable resistivity materials, increasing the power applied during DPN may facilitate an improvement in yield.

TABLE 1

Sample Data				
Sample	Ratio Hf:Si	DPN (Power Applied)	Thermal Anneal (Temperature)	Yield
1	8:1	No	No	58%
3	8:1	No	Yes (600° C.)	53%
4	8:1	Yes (800 W)	Yes (600° C.)	12%
7	8:1	Yes (800 W)	No	82%
8	8:1	Yes (1200 W)	No	74%
9	8:1	Yes (2000 W)	No	90%
10	3:1	No	No	90%
21	3:1	Yes (800 W)	No	96%

FIG. 3B provides a graph illustrating a LRS (i.e., to the right of I_{read}=10 μA) and a HRS (to the left of I_{read}=1 μA) of the sample RRAM devices summarized in Table 1. In FIG. 3B, the sample RRAM device number (e.g., 1, 3, 4, 7, 8, 9, 10, and 21) is provided adjacent "_LRS" or "_HRS" in the legend. The results depicted in FIG. 3B indicate that decoupled plasma nitridation of the $HfSi_yO_x$ material facilitated tail bits extending farther into the HRS, enabling a deeper reset (i.e., a $HfSi_yO_x$ resistivity closer to the resistivity of the $HfSi_yO_x$ prior to DPN and the formation of the Ti thereon) and, hence, a more discernable difference between OFF and ON states of the memory cells.

While the present disclosure is susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and have been described in detail herein. However, the present disclosure is not intended to be limited to the particular forms disclosed. Rather, the present disclosure is to cover all modifications, equivalents, and alternatives falling within the scope of the present disclosure as defined by the following appended claims and their legal equivalents.

What is claimed is:

1. A method of forming a resistive memory element, comprising:

forming an oxide material extending continuously over a first electrode;

exposing the oxide material to a decoupled plasma nitridation process to form a treated oxide material extending continuously over the first electrode, the treated oxide material comprising at least one of a hafnium oxy-nitride, a hafnium silicon oxy-nitride, a zirconium oxy-nitride, a zirconium silicon oxy-nitride, a titanium oxy-nitride, a titanium silicon oxy-nitride, a tantalum oxy-nitride, a tantalum silicon oxy-nitride, a niobium oxy-nitride, a niobium silicon oxy-nitride, a vanadium oxy-nitride, a vanadium silicon oxy-nitride, a tungsten oxy-nitride, a tungsten silicon oxy-nitride, a molybdenum oxy-nitride, a molybdenum silicon oxy-nitride, a chromium oxy-nitride, and a chromium silicon oxy-nitride; and

forming a second electrode on the treated oxide material.

2. The method of claim **1**, wherein a power applied during the decoupled plasma nitridation process is within a range of from about 200 watts to about 2500 watts.

3. The method of claim **1**, wherein a duration of the decoupled plasma nitridation process is within a range of from about 10 seconds to about 300 seconds.

4. The method of claim **1**, wherein exposing the oxide material to a decoupled plasma nitridation process comprises nitriding the oxide material to a depth within a range of from about 1 Angstrom to about 50 Angstroms from an exposed surface of the oxide material.

5. The method of claim **4**, wherein nitriding the oxide material to a depth within a range of from about 1 Angstrom

to about 50 Angstroms from an exposed surface of the oxide material comprises varying a concentration of nitrogen throughout the depth.

6. The method of claim **1**, wherein exposing the oxide material to a decoupled plasma nitridation process comprises exposing the oxide material to a plasma comprising nitrogen and at least one other element.

7. The method of claim **6**, wherein the at least one other element comprises at least one dopant component.

8. The method of claim **1**, wherein forming an oxide material extending continuously over a first electrode comprises forming at least one of silicon dioxide, a hafnium oxide, a hafnium silicon oxide, a zirconium oxide, a zirconium silicon oxide, a titanium oxide, a titanium silicon oxide, a tantalum oxide, a tantalum silicon oxide, a niobium oxide, a niobium silicon oxide, a vanadium oxide, a vanadium silicon oxide, a tungsten oxide, a tungsten silicon oxide, a molybdenum oxide, a molybdenum silicon oxide, a chromium oxide, and a chromium silicon oxide extending continuously on the first electrode.

9. The method of claim **1**, wherein forming a second electrode on the treated oxide material comprises:

forming a reactive material on the treated oxide material; and

forming a capping material on the reactive material.

10. The method of claim **9**, wherein forming a reactive material on the treated oxide material comprises forming titanium on the treated oxide material.

11. The method of claim **1**, wherein forming an oxide material extending continuously over a first electrode comprises forming at least one of silicon dioxide, a hafnium oxide, a zirconium oxide, a titanium oxide, a tantalum oxide, a niobium oxide, a vanadium oxide, a tungsten oxide, a molybdenum oxide, and a chromium oxide to extend continuously over the first electrode.

12. The method of claim **1**, wherein forming an oxide material extending continuously over a first electrode comprises forming at least one of a hafnium silicon oxide, a zirconium silicon oxide, a titanium silicon oxide, a tantalum silicon oxide, a niobium silicon oxide, a vanadium silicon oxide, a tungsten silicon oxide, a molybdenum silicon oxide, and a chromium silicon oxide to extend continuously over the first electrode.

13. A method of forming a resistive memory element, comprising:

forming a metal oxide material on a first electrode;

exposing the metal oxide material to a decoupled plasma nitridation process to break chemical bonds between oxygen atoms and metal atoms of the metal oxide material and form a metal oxy-nitride material; and

forming a reactive material on the metal oxy-nitride material to remove unbonded oxygen atoms from the metal oxy-nitride material and form an insulative oxygen-deficient region and an conductive oxygen-deficient region in the reactive material.

14. A method of forming a resistive memory element, comprising:

forming a metal oxide material over a first electrode, the metal oxide material comprising an oxide of at least one of chromium, cobalt, hafnium, molybdenum, tantalum, zirconium, lanthanum, manganese, calcium, praseodymium, europium, silicon, germanium, and aluminum;

exposing the metal oxide material to a decoupled plasma nitridation process to simultaneously damage and passivate the metal oxide material and form a treated metal oxide material; and

forming a second electrode over the treated metal oxide material without previously repairing at least some of the damage resulting from exposing the metal oxide material to the plasma nitridation process.

15. A method of forming a resistive memory element, comprising:

forming a hafnium silicon oxide material on a titanium nitride material;

exposing the hafnium silicon oxide material to a decoupled plasma nitridation process to form a hafnium silicon oxy-nitride material over the titanium nitride material;

forming a titanium material on the hafnium silicon oxy-nitride material without previously annealing the hafnium silicon oxy-nitride material; and

forming a tungsten nitride material on the titanium material.

16. The method of claim **15**, wherein forming a hafnium silicon oxide material on a titanium nitride material comprises forming the hafnium silicon oxide material to comprise a ratio of hafnium atoms to silicon atoms in at least a portion of the hafnium silicon oxide material is within a range of from about 3:1 to about 8:1.

17. The method of claim **15**, wherein exposing the hafnium silicon oxide material to a decoupled plasma nitridation process comprises applying a power during the decoupled plasma nitridation plasma process within a range of from about 800 watts to about 2000 watts.

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