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(54) Title: METHOD FOR FORMING RESISTIVE SWITCHING MEMORY ELEMENTS WITH IMPROVED SWITCHING BEHAVIOR

(57) Abstract: Methods for producing RRAM resistive switching elements having optimal switching behavior include crystalline phase structural changes. Structural changes indicative of optimal switching behavior include hafnium oxide phases in an interfacial region between a resistive switching layer and an electrode.



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METHOD FOR FORMING RESISTIVE SWITCHING MEMORY ELEMENTS
WITH IMPROVED SWITCHING BEHAVIOR

5 **FIELD OF THE INVENTION**

The present invention relates generally to semiconductor memories and more particularly to a method for forming a resistive switching memory element with improved switching behavior.

BACKGROUND OF THE INVENTION

10 All but the simplest of electronic devices utilize nonvolatile memories. When an electronic device must retain information during and after being placed in an unpowered state, nonvolatile memories must be provided. Several types of nonvolatile memories are known in the art. Nonvolatile memories may be portable, auxiliary, or integrated in a circuit, or as a component, in both general and embedded computer systems. Most generally, nonvolatile
15 memories are found in digital cameras, cellular telephones, music players, and as the key component in portable memory devices (e.g. USB based flash drives).

Nonvolatile memory is often formed using electrically-erasable programmable read only memory (EEPROM) technology. EEPROM, also known as flash memory, uses an architecture that is inadequate in its access, erase and write times, for the increasing operational speed
20 requirements and decreasing size requirements of electronic devices. A memory architecture with faster access, erase and write times scalable to smaller devices is needed. Volatile memories (such as Random Access Memory (RAM)) are fast and inexpensive. Nonvolatile memories must improve before they can become a successful replacement in applications currently using volatile flash memories. Resistive switching memories are a type of nonvolatile memory which may
25 provide an alternative to flash memories.

Resistive switching nonvolatile memories are formed of arrays of resistive switching memory with resistive switching elements where each element has two or more stable resistive states. Bi-stable resistive switching elements have two stable states. The application of an electric field having a particular voltage or current results in a desired element resistance. Voltage
30 pulses are typically used to switch the memory element from one resistance state to the other.

Resistive switching elements use a "forming process" to prepare a memory device for use. The forming process is typically applied at the factory, at assembly, or at initial system configuration. A resistive switching material is normally insulating, but a sufficient voltage (known as a forming voltage) applied to the resistive switching material will form one or more
35 conductive pathways in the resistive switching material. Through the appropriate application of various voltages (e.g. a set voltage and reset voltage), the conductive pathways may be modified to form a high resistance state or a low resistance state. For example, a resistive switching

material may change from a first resistivity to a second resistivity upon the application of a set voltage, and from the second resistivity back to the first resistivity upon the application of a reset voltage.

To function properly, a resistive switching element must have two well defined resistive states. Therefore, it would be advantageous if a method existed for determining predictable switching behavior in a resistive switching element.

BRIEF DESCRIPTION OF THE DRAWINGS

The numerous objects and advantages of the present invention may be better understood by those skilled in the art by reference to the accompanying figures in which:

FIG. 1 shows a flowchart depicting one method for producing a resistive switching element with improved switching behavior by modifying the structure of a metal oxide;

FIG. 2 shows a tables of bandgap energies in a HfO_2 film for different crystal phases;

FIG. 3 shows a flowchart depicting another method for producing a resistive switching element with improved switching behavior by doping a metal oxide;

FIG. 4 shows a flowchart depicting another method for producing a resistive switching element with improved switching behavior by monitoring the structure of a metal oxide;

FIG. 5 shows a cross-section of a resistive switching element taken with a transmission electron microscope;

FIG. 6 shows a flowchart depicting another method for producing a resistive switching element with improved switching behavior by doping and monitoring the structure of a metal oxide; and

FIG. 7 shows a flowchart depicting a method for operating a resistive switching element having a metal oxide configured to undergo structural changes when a switching voltage is applied.

DETAILED DESCRIPTION

The present invention relates to methods for producing and operating Resistive Random Access Memory (RRAM) resistive switching elements having predictable switching behavior. Embodiments of the present invention may determine predictable switching behavior in a resistive switching element by monitoring an interfacial region between the dielectric and an electrode for structural changes associated predictable switching behavior. Other embodiments of the present invention may include operating a RRAM with a resistive switching element configured to undergo structural changes when a switching voltage is applied.

Metal silicates indicate that the interfacial structure between the dielectric and the electrode has been converted from one crystal phase to another, including an amorphous phase. An amorphous interfacial layer between the dielectric and the electrode generally improves the switching behavior in resistive switching elements.

5

RRAM Cell Formation

A RRAM cell includes two electrodes with a resistive switching element, generally comprising a dielectric metal oxide, placed between the two electrodes. In RRAM, forming is a process by which the resistive switching element in the RRAM cell is put into its low resistance state for the first time. The process is performed by applying a voltage, called the forming voltage, across two electrodes of a resistive switching element to form one or more conductive pathways in the resistive switching element. Conductive pathways formed during the forming process reduce the resistance of the resistive switching element. Once the forming process is complete, a certain voltage, called the reset voltage, applied across the two electrodes will reset the conductive pathways, thereby increasing the resistance of the resistive switching element. Another voltage, called the set voltage, applied across the two electrodes will reform the conductive pathways, thereby reducing the resistance of the resistive switching element. A typical forming voltage for a RRAM resistive switching element is about seven volts while the set voltage and reset voltage are typically lower than the forming voltage.

A RRAM cell may be regarded as storing a logical bit; where the resistive switching element has increased resistance, the RRAM cell may be regarded as storing a “0” bit; where the resistive switching element has reduced resistance, the RRAM cell may be regarded as storing a “1” bit. Other circuitry, known in the art, reads the resistive state of the resistive switching element by applying a read voltage to the two electrodes and measuring the corresponding current through the resistive switching element. Where the current through the resistive switching element is greater than some predetermined baseline current, the resistive switching element must be in a reduced resistance state, and therefore the RRAM cell is storing a logical “1;” where the current through the resistive switching element is less than some predetermined baseline current, the resistive switching element must be in an increased resistance state, and therefore the RRAM cell is storing a logical “0.” The read voltage is typically some predetermined voltage, less than the set voltage, the reset voltage and the forming voltage. The read voltage must be sufficient to determine the resistive state of the resistive switching element, but must not alter the conductive pathways of the resistive switching element.

Forming voltage, set voltage, reset voltage and read voltage, and the increased resistive state and reduced resistive state, are all functions of the electrodes used in the resistive switching element, a type of resistive switching material used in the resistive switching element, and the processes performed on those electrodes and resistive switching material such as doping and

annealing. Manufacturers desire RRAM with discrete, well defined increased and reduced resistive states, and reduced forming voltage.

Modifying the Metal Oxide to Produce Structural Changes as in FIG. 1

5 Referring to FIG. 1, a method for producing a RRAM cell with improved switching behavior is shown. A first electrode may be deposited 100 onto a substrate. The first electrode is a material suitable for use in a RRAM cell, such as polycrystalline silicon (poly-Si). A metal oxide resistive switching element may then be deposited 102 onto the first electrode by atomic layer deposition (ALD), chemical vapor deposition (CVD), physical vapor deposition (PVD) or
10 some equivalent process to form a stack. The metal oxide may be a dielectric suitable for use in a resistive switching element such as hafnium oxide or HfO_x . The metal oxide may then be modified 104 by the application of thermal treatment and or an electrical field. The physical structure of the metal oxide is modified to form regions in the metal oxide, near the first electrode, indicative of optimal resistive switching behavior. Regions indicative of optimal resistive
15 switching behavior include an interfacial layer between the metal oxide and the electrode containing different phases of hafnium oxide (HfO_2). A second electrode may then be deposited 106 onto the stack. The second electrode is a material suitable for use in a RRAM cell such as titanium nitride or TiN.

Different phases of HfO_2 may be formed in a local region upon thermal treatment or when
20 an electrical field is applied to the structure, causing the hafnium oxide structural transformation and transitions from a first phase to another crystal phase. The different phases may include an amorphous or a crystalline phase. Different crystal phases may have different bandgaps and barrier heights; for example, referring to FIG. 2, a tetragonal crystal phase of HfO_2 may have a bandgap of 5.45 eV, an orthorhombic crystal phase may have a bandgap of 5.60 eV, a monoclinic
25 crystal phase may have a bandgap of 5.65 eV, a cotunnite crystal phase may have a bandgap of 6.10 eV, a cubic crystal phase may have a bandgap of 6.30 eV and an amorphous crystal phase may have a bandgap of 5.70 eV. Varying crystal phases in a metal oxide indicate bistable states, useful in RRAM. When the metal oxide is in an amorphous phase near the first electrode, the resistive switching element is in a low resistance state.

30 Alternatively, the metal oxide may be modified by converting Hf_4O_8 to Other oxides of hafnium such as Hf_4O_7 . Such compositional change may result in oxygen vacancies. Oxygen vacancies in a metal oxide may modulate current and thereby enhance the switching behavior of the metal oxide in a RRAM cell. Converting Hf_4O_8 to Other oxides of hafnium such as Hf_4O_7 may be accomplished by annealing the metal oxide or by doping the metal oxide.

35

Doping and Annealing the Metal Oxide as in FIG. 3

Referring to FIG. 3, another method for producing a RRAM cell with improved switching

behavior is shown. A first electrode may be deposited 300 onto a substrate. The first electrode is a material suitable for use in a RRAM cell, such as poly-Si. A metal oxide resistive switching element may then be deposited 302 onto the first electrode by ALD, CVD, PVD or some equivalent process. The metal oxide may be a dielectric suitable for use as an insulator in a resistive switching element such as hafnium oxide or HfO_x . The metal oxide may then be doped 304 with a dopant to add oxygen vacancies to the metal oxide. Oxygen vacancies are a specific type of anomaly in the structure of a dielectric material that enhances the ability of the dielectric material to form conductive pathways. The dopant may be a material such as aluminum (Al), titanium (Ti) or zirconium (Zr). The metal oxide may be annealed 306 to encourage the formation of oxygen vacancies. The metal oxide may then be modified 308 by the application of an electrical field. The physical structure of the metal oxide is modified to form regions in the metal oxide, near the first electrode, indicative of optimal resistive switching behavior. Regions indicative of optimal resistive switching behavior include a local region of transitioning crystalline phases such as from tetragonal to orthorhombic. Transitioning crystallinity may also include transitioning from a crystalline phase to an amorphous phase. Alternatively, the metal oxide may be modified by converting Hf_4O_8 to Other oxides of hafnium such as Hf_4O_7 . Conversion of Hf_4O_8 to Other oxides of hafnium such as Hf_4O_7 adds oxygen vacancies to the resulting metal oxide that promote the formation of conductive pathways. A second electrode may then be deposited 310 onto the stack. The second electrode is a material suitable for use in a RRAM cell such as titanium nitride or TiN.

The structural changes described can be local or homogenous in the metal oxide with respect to the first or second electrode, or both, or with respect to other metal oxide layers in the RRAM cell. FIG. 5 shows a cross-section of a RRAM cell using transmission electron microscopy. A RRAM cell produced according to the present invention may have a first electrode 500, a resistive switching element 502 comprising one or more layers of a metal oxide, and a second electrode 504. The resistive switching element 502 may be configured to undergo structural changes in response to the application of a switching voltage. For example, a resistive switching element 502 comprised of one or more layers of metal oxide film may undergo a crystalline conversion whereby the crystalline structure of at least one of the metal oxide films is converted from an amorphous film to a crystalline film, or from a crystalline film to an amorphous film. Alternatively, at least one of the metal oxide films comprising hafnium may undergo conversion from Hf_4O_8 to different oxides of hafnium. Configuring the resistive switching element 502 to undergo structural changes may be accomplished by doping one of the one or more metal oxide films with a dopant such as aluminum, titanium or zirconium. Configuring the resistive switching element 502 to undergo structural changes may also be accomplished by annealing the resistive switching element 502. Such structural changes may occur in a region near either the first electrode or the second electrode, and may enhance the

formation of conductive pathways in the metal oxide. Optimal switching behavior may depend on the manufacture's desired forming, set or reset voltages.

Monitoring the Metal Oxide as in FIG. 4

5 Referring to FIG. 4, another method for producing a RRAM cell with improved switching behavior is shown. A first electrode may be deposited 400 onto a substrate. The first electrode is a material suitable for use in a RRAM cell, such as poly-Si. A metal oxide resistive switching element may then be deposited 402 onto the first electrode by ALD, CVD, PVD or some equivalent process. The metal oxide may be a dielectric suitable for use as an insulator in a
10 resistive switching element such as hafnium oxide or HfO_x . The metal oxide may then be modified 404 by the application of an electrical field. The metal oxide may be modified to form regions in the metal oxide, near the first electrode, indicative of optimal resistive switching behavior. Alternatively, the resistive switching element may include several metal oxide layers; in which case a first metal oxide layer may be modified to form regions in the first metal oxide,
15 near a second metal oxide, indicative of optimal resistive switching behavior. Regions indicative of optimal resistive switching behavior include an interfacial layer between the metal oxide and the electrode a local region of transitioning crystalline phases such as from tetragonal to orthorhombic. Transitioning crystallinity may also include transitioning from a crystalline phase to an amorphous phase. Alternatively, the metal oxide may be modified by converting Hf_4O_8 to
20 Other oxides of hafnium such as Hf_4O_7 . Regions of the metal oxide near the first electrode, or near a second metal oxide, may be monitored 406 for structures indicative of optimal resistive switching behavior. Monitoring the metal oxide may be accomplished by x-ray spectrography, transmission electron microscopy or some other equivalent process. A second electrode may then be deposited 408 onto the stack. The second electrode is a material suitable for use in a RRAM
25 cell such as titanium nitride or TiN.

Monitoring the Doped Metal Oxide as in FIG. 6

Referring to FIG. 6, another method for producing a resistive switching element with improved switching behavior is shown. A first electrode may be deposited 600 onto a substrate.
30 The first electrode is a material suitable for use in a resistive switching element, such as poly-Si. A metal oxide may then be deposited 602 onto the first electrode by ALD, CVD, PVD or some equivalent process to form a stack. The metal oxide may be a dielectric suitable for use as an insulator in a resistive switching element such as hafnium oxide or HfO_x . The metal oxide may then be doped 604 with a dopant to add oxygen vacancies to the metal oxide. Oxygen vacancies
35 are a specific type of anomaly in the structure of a dielectric material that enhances the ability of the dielectric material to form conductive pathways. The dopant may be a material such as Al, Ti or Zr. The metal oxide may then be modified 606 by the application of an electrical field. The

metal oxide may be modified to form regions in the metal oxide, near the first electrode, indicative of optimal resistive switching behavior. Alternatively, the resistive switching element may include several metal oxide layers; in which case a first metal oxide layer may be modified to form regions in the first metal oxide, near a second metal oxide, indicative of optimal resistive switching behavior. Regions indicative of optimal resistive switching behavior include an interfacial layer between the metal oxide and the electrode a local region of transitioning crystalline phases such as from tetragonal to orthorhombic. Transitioning crystallinity may also include transitioning from a crystalline phase to an amorphous phase. Alternatively, the metal oxide may be modified by converting Hf_4O_8 to Other oxides of hafnium such as Hf_4O_7 . Regions of the metal oxide near the first electrode, or near a second metal oxide, may be monitored for structures indicative of optimal resistive switching behavior. A second electrode may then be deposited onto the stack. The second electrode is a material suitable for use in RRAM cell such as titanium nitride or TiN.

Operating a RRAM as in FIG. 7

Referring to FIG. 7, one embodiment of a method for operating a RRAM cell is shown. In a RRAM cell, such as in FIG. 5, having a first electrode 500, a metal oxide resistive switching element 502 and a second electrode 504, the RRAM cell may be operated by applying a switching voltage to one of either the first electrode 500 or the second electrode 504, and then detecting a structural change in the metal oxide resistive switching element 502, in at least one of a region near the first electrode 500 and a region near the second electrode 504, in response to the switching voltage pulse. Such structural change may be a change in the crystalline structure of the metal oxide from a first crystal phase to a second crystal phase. A change in the crystalline structure may include a change to or from an amorphous crystalline phase.

Where the metal oxide is comprised of hafnium, the structural change may be the formation of hafnium silicide masses. Alternatively, a metal oxide comprised of Hf_4O_8 may undergo conversion to different metal oxides such as Hf_4O_7 .

The resistive switching element may be configured to undergo such structural changes by doping the metal oxide with a dopant such as aluminum, titanium or zirconium. The resistive switching element may also be configured to undergo such structural changes by annealing.

It is believed that the present invention and many of its attendant advantages will be understood by the forgoing description, and it will be apparent that various changes may be made in the form, construction and arrangement of the components thereof without departing from the scope and spirit of the invention or without sacrificing all of its material advantages. The form herein before described being merely an explanatory embodiment thereof, it is the intention of the following Claims to encompass and include such changes.

CLAIMS

1. A method for operating a RRAM cell, the RRAM cell including a first electrode, a metal oxide resistive switching element on the first electrode, and a second electrode on the metal oxide resistive switching element, comprising:
 - 5 applying a switching voltage pulse to one of said first electrode and second electrode; and
 detecting a structural change in the metal oxide at a region near at least one of the first
 electrode and the second electrode.
2. The method of 1, wherein the structural change of the metal oxide is a crystalline change from
10 a first crystal phase to a second crystal phase.
3. The method of 2, wherein the metal oxide is comprised of hafnium.
4. The method of 3, wherein the structural change is presence of hafnium silicide.
15
5. The method of 3, wherein the structural change is presence of different hafnium oxides.
6. The method of 3, wherein the structural change of the metal oxide is conversion of Hf_4O_8 to
 different oxides of hafnium.
20
7. The method of 1, wherein a dopant is added to the metal oxide so that the metal oxide will
 undergo a structural change when a switching voltage pulse is applied.
8. The method of 7, wherein the dopant is at least one of aluminum, titanium and zirconium.
25
9. The method of 8, wherein the structural change of the metal oxide is conversion of Hf_4O_8 to
 different oxides of hafnium.
10. The method of 1, wherein the metal oxide is annealed so that the metal oxide will undergo a
30 structural change when a switching voltage pulse is applied.
11. A method for determining an optimal doping concentration of a resistive switching element in
 a RRAM cell, comprising:
 - 35 monitoring an interfacial region between a first metal oxide and a second metal oxide in
 the resistive switching element for a structural change; and
 doping the first metal oxide with a dopant until the structural change is detected,
 wherein the structural change is configured to facilitate the formation of conductive

pathways in the resistive switching element.

12. The method of 11, wherein the dopant is configured to add oxygen vacancies in the metal oxide.

5

13. The method of 11, wherein the first metal oxide is comprised of hafnium oxide.

14. The method of 13, wherein the structural change comprises formation of hafnium silicide masses.

10

15. The method of 13, wherein the structural change comprises conversion of Hf_4O_8 to different oxides of hafnium.

16. The method of 11, wherein the second metal oxide is comprised of hafnium oxide.

15

17. The method of 16, wherein the structural change comprises conversion of Hf_4O_8 to different oxides of hafnium.

18. A method for producing RRAM cell with improved switching behavior comprising:

20

depositing a first electrode comprising polycrystalline silicon;
depositing a dielectric film onto the first electrode;
doping the dielectric film with a dopant;
depositing a second electrode.

25

19. The method of 18, wherein:

the dielectric film comprises hafnium oxide;
the dopant comprises one of aluminum, titanium and zirconium; and
the structural change is a plurality of hafnium oxide phases.

30

20. The method of 18, wherein:

the dielectric film comprises hafnium oxide; and
the structural change is conversion of Hf_4O_8 to different oxides of hafnium.

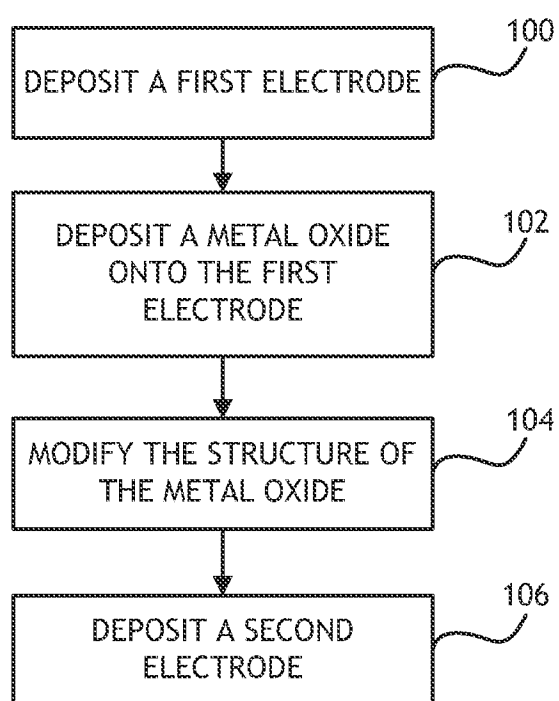


FIG. 1

Phase	E _g (eV)
Tetragonal	5.45
Orthorhombic	5.60
Monoclinic	5.65
Amorphous	5.70
Cotunnite	6.10
Cubic	6.30

FIG. 2

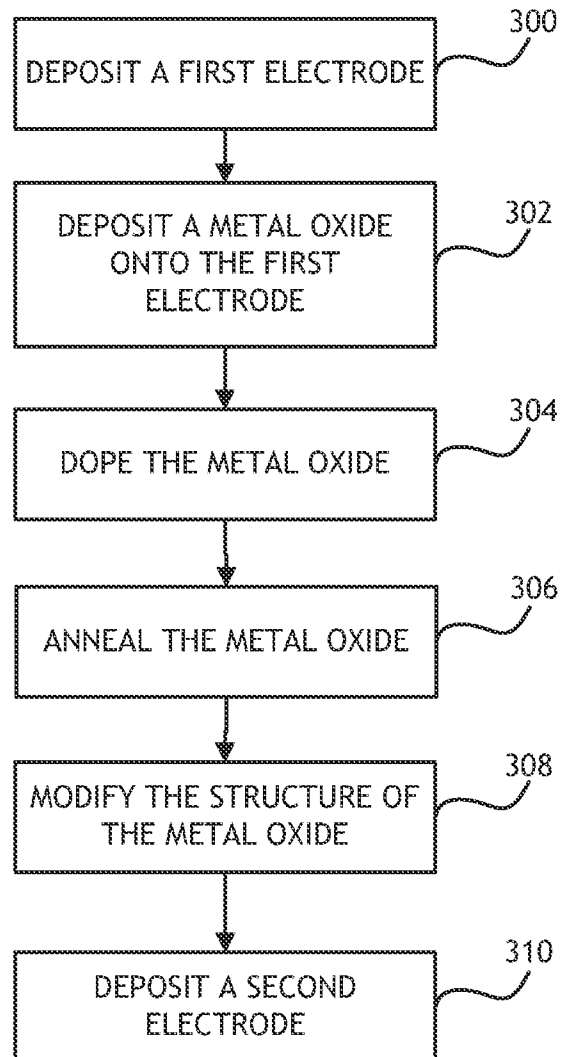


FIG. 3

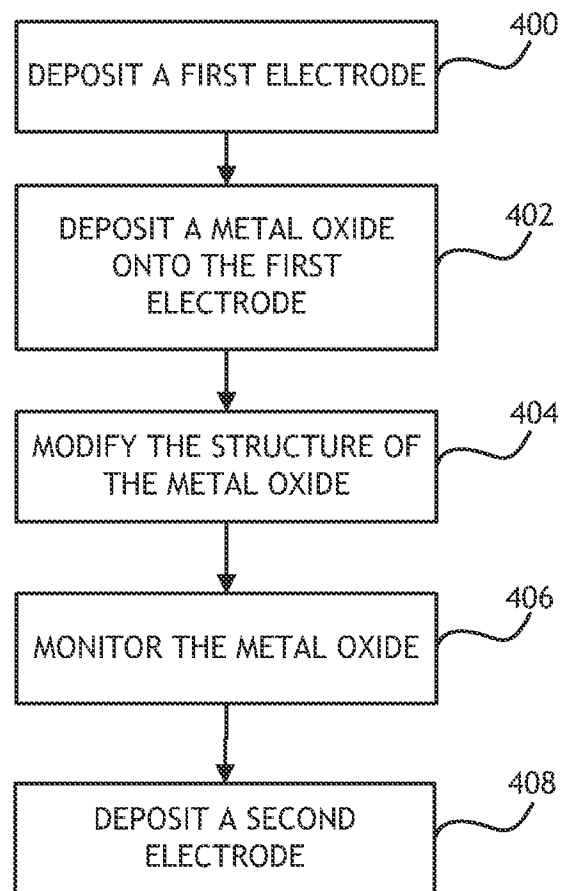


FIG. 4

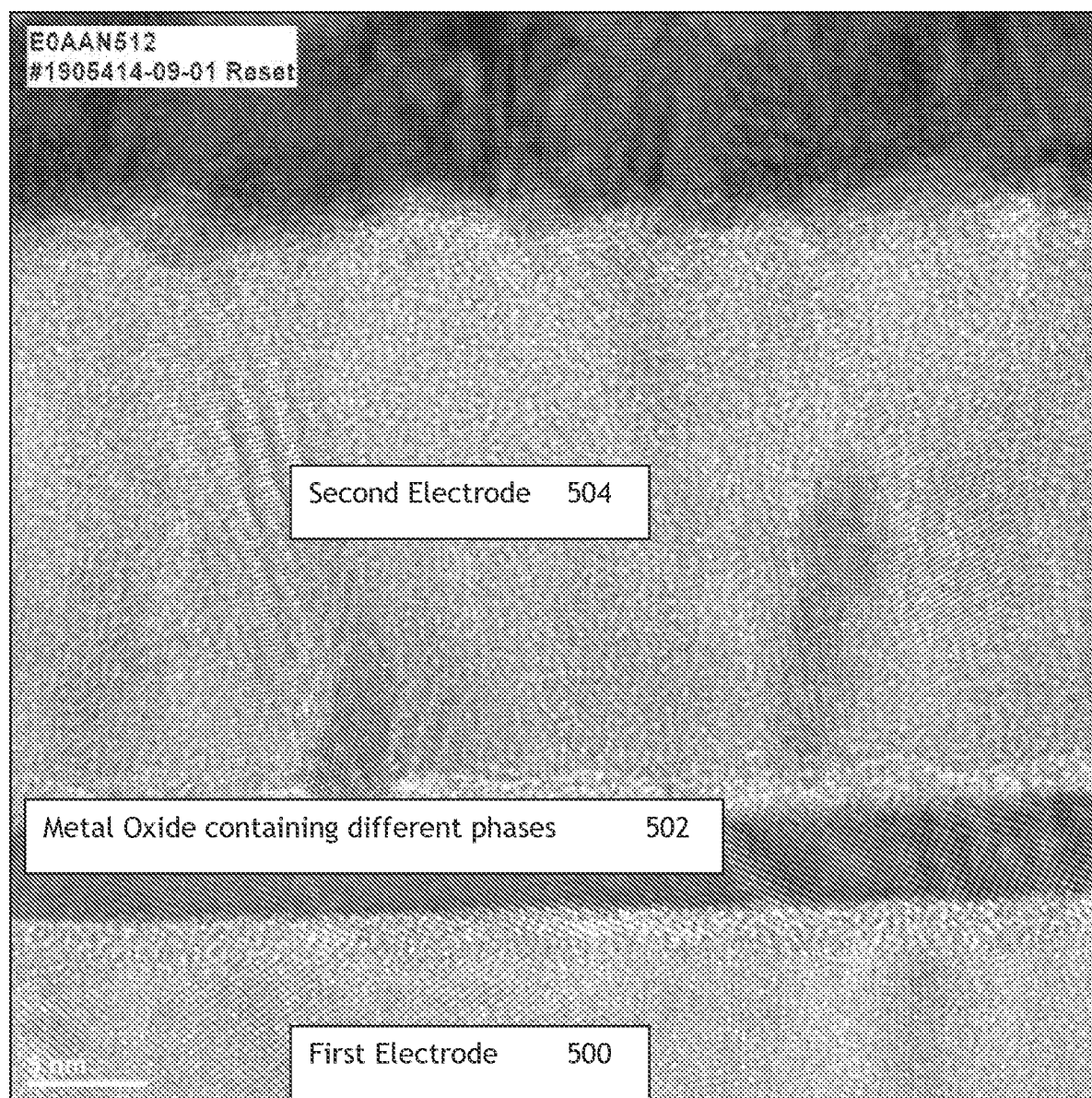


FIG. 5

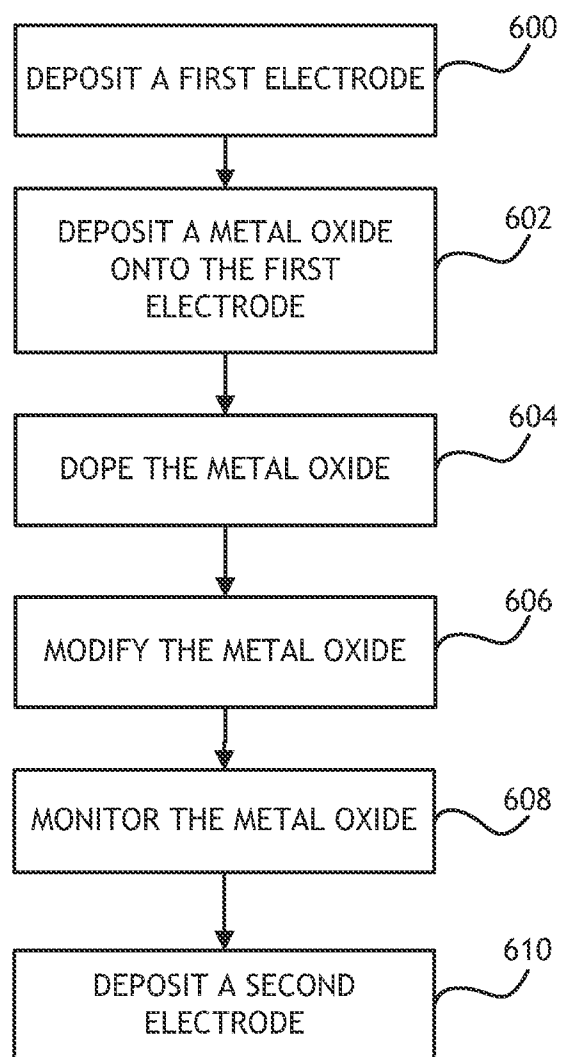


FIG. 6

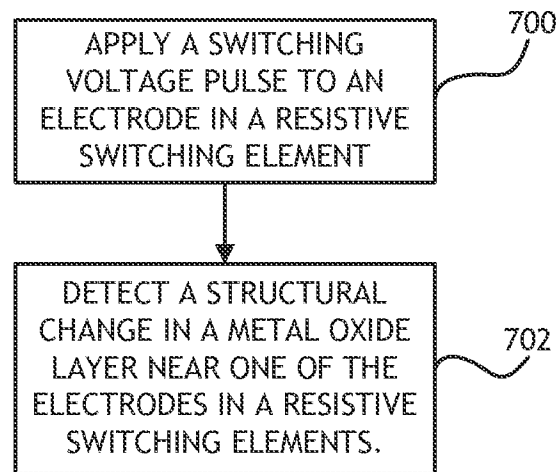


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/63221

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01L 21/469 (2013.01)

USPC - 438/785

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC -- 438/785

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC -- 438/785 or 257/E21.011 or 257/E21.018 or 257/E21.648 or 438/240

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PubWEST (USPT,PGPB,JPAB,EPAB); Google; Patbase

Search Terms: switching element/layer RRAM cell electrode switching pulse metal oxide hafnium crystalline hafnium oxide hafnium silicide nonvolatile memory oxygen deficiency/void/vacancy dopant aluminum conductive traces annealing

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US 2010/0258782 A1 (Kuse et al.) 14 October 2010 (14.10.2010), entire document especially Abstract, para [0020], [0023]-[0025], [0041], [0049], [0035]-[0036] and [0089]	1, 7, 10-13 and 15-17 ----- 2-6, 8-9 and 14
Y	US 2009/0026434 A1 (Malhotra et al.) 29 January 2009 (29.01.2009), entire document especially Abstract, para [0047] and [0044]	2-6 and 8-9
Y	US 2011/0253968 A1 (Choi et al.) 20 October 2011 (20.10.2011), entire document especially Abstract, para [0032] and [0037],	4 and 14
A	US 2011/0006275 A1 (Roelofs et al.) 13 January 2011 (13.01.2011), entire document	1-17
A	US 7,674,446 B2 (Irumata et al.) 09 March 2010 (09.03.2010), entire document	1-17
A	US 2004/0159828 A1 (Rinerson et al.) 19 August 2004 (19.08.2004), entire document	1-17
A	US 2008/0001172 A1 (Karg et al.) 03 January 2008 (03.01.2008), entire document	1-17

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

16 February 2013 (16.02.2013)

Date of mailing of the international search report

28 FEB 2013

Name and mailing address of the ISA/US

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Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/63221

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
-see extra sheet-

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-17

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US 12/63221

Continuation of Box III: Observations where unity of invention is lacking

Invention Groups:

Group I: claims 1-17
Group II: claims 18-20

Reasons for Lack of Unity of Invention:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: claims 1-17, drawn to a method for a first metal oxide and second metal oxide and detecting a structural change.

Group II: claims 18-20, drawn to a method for depositing a first electrode comprising polycrystalline silicon and depositing a dielectric film onto the first electrode.

The inventions listed as Groups I - II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

The special technical feature of the Group I invention is a method for a first metal oxide and second metal oxide and detecting a structural change. The special technical feature of the Group II invention is a method for depositing a first electrode comprising polycrystalline silicon and depositing a dielectric film onto the first electrode. None of these special technical features are common to the other groups, nor do they correspond to a special technical feature in the other groups. Therefore, unity of invention is lacking.