DESCRIPTION

METHOD OF FORMING NON-VOLATILE RESISTANCE VARIABLE DEVICES AND METHOD OF FORMING A PROGRAMMABLE MEMORY CELL OF MEMORY CIRCUITRY

Technical Field

This invention relates to methods of forming non-volatile resistance variable devices and to methods of forming a programmable memory cell of memory circuitry.

Background Art

Semiconductor fabrication continues to strive to make individual electronic components smaller and smaller, resulting in ever denser integrated circuitry. One type of integrated circuitry comprises memory circuitry where information is stored in the form of binary data. The circuitry can be fabricated such that the data is volatile or non-volatile. Volatile storing memory devices result in loss of data when power is interrupted. Non-volatile memory circuitry retains the stored data even when power is interrupted.

This invention was principally motivated in making improvements to the design and operation of memory circuitry disclosed in the Kozicki et al. U.S. Patent Nos. 5,761,115; 5,896,312; 5,914,893; and 6,084,796, which ultimately resulted from U.S. Patent Application Serial No. 08/652,706, filed on May 30, 1996, disclosing what is referred to as a programmable metallization cell. Such a cell includes opposing electrodes having an insulating dielectric material received therebetween. Received within the dielectric material is a fast ion conductor material. The resistance of such material can be changed between highly insulative and highly conductive states. In its normal high resistive state, to perform a write operation, a voltage potential is applied to a certain one of the electrodes, with the other of the electrode being held at zero voltage or ground. The electrode having the voltage applied thereto functions as an anode, while the electrode held at zero or ground functions as a cathode. The nature of the fast ion conductor material is such that it undergoes a structural change at a certain applied voltage. With such voltage applied, a conductive dendrite or filament extends between the electrodes, effectively interconnecting the top and bottom electrodes to electrically short them together.

Once this occurs, dendrite growth stops, and is retained when the voltage potentials are removed. Such can effectively result in the resistance of the mass of fast ion conductor material between electrodes dropping by a factor of 1,000. Such material can be returned to its highly resistive state by reversing the voltage potential between the anode and cathode, whereby the filament disappears. Again, the highly resistive state is maintained once the reverse voltage potentials are removed. Accordingly, such a device can, for example, function as a programmable memory cell of memory circuitry.

The preferred resistance variable material received between the electrodes typically and preferably comprises a chalcogenide material having metal ions diffused therein. A specific example is germanium selenide having silver ions diffused therein. The present method of providing the silver ions within the germanium selenide material is to initially chemical vapor deposit the germanium selenide glass without any silver being received therein. A thin layer of silver is thereafter deposited upon the glass, for example by sputtering, physical vapor deposition or other technique. An exemplary thickness is 200 Angstroms or less. The layer of silver is irradiated, preferably with electromagnetic energy at a wavelength less than 500 nanometers. The thin nature of the deposited silver enables such energy to pass through the silver to the silver/glass interface effective to break a chalcogenide bond of the chalcogenide material. This may form Ag_2Se, which effectively dopes the glass with silver. The applied energy and overlying silver ultimately result in the silver migrating into the glass layer such that a typical homogenous distribution of silver throughout the layer is achieved.

Saturation of silver in germanium selenide is apparently at a maximum of about 34 atomic percent or less depending on the germanium selenide stoichiometry. Yet, preferred existing technology for cell fabrication constitutes a concentration which is less than the maximum; in the case of 34 atomic percent maximum, an example concentration would be about 27 atomic percent.

After the chalcogenide material is provided with silver to a desired concentration, the top electrode material (typically silver) is next deposited. But, as the silver doping/diffusion into the chalcogenide material approaches the maximum or saturation, some Ag_2Se was discovered to form at the surface and remain there as opposed to diffusing into the glass. Further, the surface Ag_2Se was typically in the form of semicircular nodules or bumps anywhere from 50 Angstroms to 20 microns across. Unfortunately when the typical silver electrode material is subsequently deposited, such tends to mound on top of

these previous bumps. This can create voids to the doped germanium glass through the top electrode material, whereby the silver doped germanium selenide glass is partially exposed. Unfortunately, some of the photodeveloper solutions typically used for patterning the top electrode (i.e. tetramethyl ammonium hydroxide) will etch the glass that is exposed.

It would be desirable to overcome or at least reduce this problem. While the invention was principally motivated in overcoming this problem, it is in no way so limited. The artisan will appreciate applicability of the invention in other aspects unrelated to the problem, with the invention only being limited by the accompanying claims as literally worded and as appropriately interpreted in accordance with the doctrine of equivalents.

Disclosure of the Invention

The invention includes methods of forming a programmable memory cell of memory circuitry and non-volatile resistance variable devices. In one implementation, a method of forming a non-volatile resistance variable device includes forming a first conductive electrode material on a substrate. Chalcogenide comprising material is formed over the first conductive electrode material. The chalcogenide material comprises A_xSe_y, where "A" comprises at least one element which is selected from Group 13, Group 14, Group 15, or Group 17 of the periodic table. A silver comprising layer is formed over the chalcogenide material. The silver is irradiated effective to break a chalcogenide bond of the chalcogenide material at an interface of the silver comprising layer and chalcogenide material and diffuse at least some of the silver into the chalcogenide material, and an outer surface of the chalcogenide material is formed. After the irradiating, the chalcogenide material outer surface is exposed to an iodine comprising fluid effective to reduce roughness of the chalcogenide material outer surface from what it was prior to the exposing. After the exposing, a second conductive electrode material is deposited over the chalcogenide material, and which is continuous and completely covering at least over the chalcogenide material, and the second conductive electrode material is formed into an electrode of the device.

Other implementations and aspects are contemplated and disclosed.

Brief Description of the Drawings

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a diagrammatic sectional view of a semiconductor wafer fragment in process in accordance with an aspect of the invention.

Fig. 2 is a view of the Fig. 1 wafer fragment at a processing step subsequent to that shown by Fig. 1.

Fig. 3 is a view of the Fig. 1 wafer fragment at a processing step subsequent to that shown by Fig. 2.

Fig. 4 is a view of the Fig. 1 wafer fragment at a processing step subsequent to that shown by Fig. 3.

Fig. 5 is a view of the Fig. 1 wafer fragment at a processing step subsequent to that shown by Fig. 4.

Fig. 6 is a view of the Fig. 1 wafer fragment at a processing step subsequent to that shown by Fig. 5.

Best Modes for Carrying Out the Invention and Disclosure of Invention

Referring to Fig. 1, a semiconductor wafer fragment 10 is shown in but one preferred embodiment of a method of forming a non-volatile resistance variable device. By way of example only, example such devices include programmable metallization cells and programmable optical elements of the patents referred to above, further by way of example only, including programmable capacitance elements, programmable resistance elements, programmable antifuses of integrated circuitry and programmable memory cells of memory circuitry. The above patents are herein incorporated by reference. The invention contemplates the fabrication techniques and structure of any existing non-volatile resistance variable device, as well as yet-to-be developed such devices. In the context of this document, the term "semiconductor substrate" or "semiconductive substrate" is defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above. Also in the context of this document, the term "layer" encompasses both the singular and the plural unless otherwise indicated. Further, it will be appreciated by the artisan that "resistance variable device" includes devices wherein a property or properties in addition to resistance is/are also varied. For example, and by way of example only, the

device's capacitance and/or inductance might also be changed in addition to resistance.

Semiconductor wafer fragment 10 comprises a bulk monocrystalline semiconductive material 12, for example silicon, having an insulative dielectric layer 14, for example silicon dioxide, formed thereover. A first conductive electrode material 16 is formed over dielectric layer 14. By way of example only, preferred materials include any of those described in the incorporated Kozicki et al. patents referred to above in conjunction with the preferred type of device being fabricated. A dielectric layer 18 is formed over first electrode material 16. Silicon nitride is a preferred example.

An opening 20 is formed through layer 18 to conductive electrode layer 16. Such is filled with a chalcogenide comprising material 22 to a first thickness, which in this example is essentially defined by the thickness of layer 18. By way of example only, an exemplary first thickness range is from 100 Angstroms to 1000 Angstroms. The chalcogenide comprising material comprises A_xSe_y, where "A" comprises at least one element which is selected from Group 13 (B, Al, Ga, In, Tl), Group 14 (C, Si, Ge, Sn, Pb), Group 15 (N, P, As, Sb, Bi), or Group 17 (F, Cl, Br, I, At) of the periodic table. By way of example only, preferred elements for "A" are Ge and Si. An example preferred method of forming material 22 over substrate 10 is by chemical vapor deposition to completely fill opening 20, followed by a planarization technique, for example chemical mechanical polishing. Material 22 is preferably formed to be amorphous and remains amorphous in the finished device.

A silver comprising layer 24 is formed to a second thickness over chalcogenide material 22. Silver comprising layer 24 is preferably predominately (majority) elemental silver, and can consist or consist essentially of elemental silver. In one preferred embodiment, the second thickness is at least 30% of the first thickness.

Referring to Fig. 2, silver comprising layer 24 is irradiated effective to break the chalcogenide bond of chalcogenide material 22 at an interface of silver comprising layer 24 and chalcogenide material 22, and diffuse at least some of the silver into chalcogenide material 22. In Fig. 2, material 22 is designated with numeral 23 and peppered in the drawing to indicate metal ions being received therein. A preferred irradiating includes exposure to actinic radiation having a wavelength from about 164 - 904 nanometers, with radiation exposure at between 404 - 408 nanometers being a more specific example. A more specific example is a flood UV exposure tool operating at 4.5 milliwatts/cm^2

energy for 15 minutes in an oxygen-containing ambient at room temperature and pressure. All of material 24 received directly over chalcogenide comprising material 22 might be diffused to within such material, or only some portion thereof might. The thickness of layer 24 is also chosen to be suitably thin to enable the impinging electromagnetic radiation to essentially transparently pass through material 24 to the interface of such material with chalcogenide material 22. An exemplary preferred thickness is less than or equal to 200 Angstroms. Further, the apparent linear thickness of layer 24 as a percentage of the linear thickness of chalcogenide material 22 effectively results in the same approximate metal incorporation in atomic percent within the chalcogenide material. Regardless, such results in chalcogenide material 23 having an outer surface 25.

In but one embodiment, outer surface 25 is characterized by the formation of Ag_2Se as at least part of the outer surface, with in one embodiment, the irradiating being effective to form a discontinuous layer 27 of Ag_2Se formed over chalcogenide comprising materials 22/23. Further preferably, the irradiating is effective to maintain the chalcogenide material underlying the Ag_2Se in a substantially amorphous state. Even further preferably, the irradiating is effective to dope the chalcogenide comprising material to average at least 30 atomic percent silver in a lowest of a plurality of variable resistant states. Further, the invention contemplates any other method of forming Ag_2Se over chalcogenide comprising material, and for example a discontinuous layer of Ag_2Se, by any other existing or yet-to-be-developed methods.

Referring to Fig. 3 and after the irradiating, chalcogenide material outer surface 25 is exposed to an iodine comprising fluid effective to reduce roughness of chalcogenide material outer surface 25 from what it was prior to the exposing. In one preferred embodiment, such exposing occurs to Ag_2Se to be effective to etch away at least some of the Ag_2Se, more preferably effective to etch away at least a majority of the Ag_2Se, and most preferably effective to etch away substantially all of the Ag_2Se, as shown in Fig. 3. In one exemplary embodiment, roughness reduction is contemplated independent of Ag_2Se formation and removal. Further in one exemplary embodiment, etching away of at least some Ag_2Se is contemplated independent of the effect on surface roughness.

One preferred iodine comprising fluid is a liquid, for example an iodide solution such as a potassium iodide solution. An example preferred potassium iodide solution comprises from 5 to 30 grams of I_2 per one liter of a from 20%

to 50% by volume potassium iodide solution. Exposure to a vapor, a liquid solution at for example ambient temperature and pressure conditions, or elevated or reduced from ambient temperature and/or pressure conditions is of course also contemplated. A specific example is dipping the substrate into a potassium iodide solution comprising 20 grams of I_2 per one liter of a 30% potassium iodide solution.

Referring to Fig. 4 and after the exposing, a second conductive electrode material 26 is deposited over chalcogenide material 23. In the preferred embodiment, such second conductive electrode material is continuous and completely covers at least over chalcogenide material 23. An example preferred thickness range for second electrode material 26 is from 140 Angstroms to 200 Angstroms. The first and second conductive electrode materials might be the same material(s), or different material(s). By way of example only, preferred top and bottom electrode materials include silver, tungsten, platinum, nickel, carbon, chromium, molybdenum, aluminum, magnesium, copper, cobalt, palladium, vanadium, titanium, alloys thereof and compounds including one or more of these elements. In accordance with a preferred programmable metallization cell embodiment, and where "A" is Ge, at least one of materials 16 and 26 constitutes silver. During the formation of layer 26, some of it might diffuse into layer 23.

Referring to Fig. 5, material 26 is patterned into an electrode 30. Patterning to produce electrode 30 is typically and preferably conducted utilizing photolithography. Such provides but one preferred example of forming a second electrode material operatively proximate the chalcogenide material. In a preferred embodiment, such results in the formation of a non-volatile resistance variable device which is fabricated into a programmable memory cell of memory circuitry.

Referring to Fig. 6, one or more dielectric layers 32 are ultimately formed over the device. Of course, intervening conductive and semiconductive layers might also be provided to form other lines and devices outwardly of the depicted device.

CLAIMS

1. A method of forming a chalcogenide comprising device, comprising:

forming a first conductive electrode material on a substrate;

forming chalcogenide comprising material over the first conductive electrode material, the chalcogenide material comprising A_xSe_y, where "A" at least one element which is selected from Group 13, Group 14, Group 15, or Group 17 of the periodic table;

forming a silver comprising layer over the chalcogenide material;

irradiating the silver effective to break a chalcogenide bond of the chalcogenide material at an interface of the silver comprising layer and chalcogenide material and diffuse at least some of the silver into the chalcogenide material, and forming an outer surface of the chalcogenide material;

after the irradiating, exposing the chalcogenide material outer surface to an iodine comprising fluid effective to reduce roughness of the chalcogenide material outer surface from what it was prior to the exposing; and

after the exposing, depositing a second conductive electrode material over the chalcogenide material, and which is continuous and completely covering at least over the chalcogenide material, and forming the second conductive electrode material into an electrode of the device.

2. The method of claim 1 wherein the iodine comprising fluid is a liquid.

3. The method of claim 1 wherein the iodine comprising fluid is an iodide solution.

4. The method of claim 1 wherein the iodine comprising fluid is a potassium iodide solution.

5. The method of claim 4 wherein the potassium iodide solution comprises from 5 to 30 grams I_2 per 1 liter of a from 20% to 50% potassium iodide solution.

6. The method of claim 1 wherein the silver comprising layer is predominately elemental silver.

7. The method of claim 1 wherein the irradiating is effective to form Ag_2Se as at least part of the outer surface, the etching being effective to etch away at least some of the Ag_2Se and thereby at least partially contributing to said roughness reducing.

8. The method of claim 1 wherein "A" comprises Ge.

9. The method of claim 1 comprising forming the device into a programmable memory cell of memory circuitry.

10. The method of claim 1 wherein the first and second conductive electrode materials are different.

11. A method of forming a chalcogenide comprising device, comprising:

forming a first conductive electrode material on a substrate;

forming a chalcogenide comprising material over the first conductive electrode material, the chalcogenide material comprising A_xSe_y, where "A" comprises at least one element which is selected from Group 13, Group 14, Group 15, or Group 17 of the periodic table;

after forming the chalcogenide comprising material, forming Ag_2Se over the chalcogenide comprising material;

after the irradiating, exposing the Ag_2Se to an iodine comprising fluid effective to etch away at least some of the Ag_2Se; and

after the exposing, depositing a second conductive electrode material over the chalcogenide material and forming the second conductive electrode material into an electrode of the device.

12. A method of forming a non-volatile resistance variable device, comprising:

forming a first conductive electrode material on a substrate;

forming a chalcogenide comprising material over the first conductive electrode material, the chalcogenide material comprising A_xSe_y, where "A" is selected from group consisiting of elements and radicals and mixtures thereof which are more electropositive than Se;

after forming the chalcogenide comprising material, forming Ag_2Se over the chalcogenide comprising material;

after the irradiating, exposing the Ag_2Se to an iodine comprising fluid effective to etch away at least some of the Ag_2Se; and

after the exposing, depositing a second conductive electrode material over the chalcogenide material and forming the second conductive electrode material into an electrode of the device.

13. The method of claim 11 comprising forming the device into a programmable memory cell of memory circuitry.

14. The method of claim 12 wherein "A" comprises Ge.

15. The method of claim 12 comprising forming the non-volatile resistance variable device into a programmable memory cell of memory circuitry.

16. The method of claim 12 wherein the iodine comprising fluid is a liquid.

17. The method of claim 12 wherein the iodine comprising fluid is an iodide solution.

18. The method of claim 12 wherein the iodine comprising fluid is a potassium iodide solution.

19. The method of claim 18 wherein the potassium iodide solution comprises from 5 to 30 grams I_2 per 1 liter of a from 20% to 50% potassium iodide solution.

20. A method of forming a chalcogenide comprising device, comprising:

forming a first conductive electrode material on a substrate;

forming a chalcogenide comprising material over the first conductive electrode material, the chalcogenide material comprising A_xSe_y, where "A" comprises at least one element which is selected from Group 13, Group 14, Group 15, or Group 17 of the periodic table;

after forming the chalcogenide comprising material, forming a

discontinuous layer of Ag_2Se over the chalcogenide comprising material;

after the irradiating, exposing the Ag_2Se to an iodine comprising fluid effective to etch away at least some of the Ag_2Se; and

after the exposing, depositing a second conductive electrode material over the chalcogenide material, and which is continuous and completely covering at least over the chalcogenide material, and forming the second conductive electrode material into an electrode of the device.

21. The method of claim 12 wherein the exposing is effective to etc away substantially all of the Ag_2Se.

22. A method of forming a non-volatile resistance variable device, comprising:

forming a first conductive electrode materail on a substrate;

forming a chalcogenide comprising material over the first conductive electrode material, the chalcogenide comprising A_xSe_y, where "A" is selected from the group consisting of elements and radicals and mixtures thereof which are more electropositive than Se;

after forming the chalcogenide comprising material, forming a discontinuous layer of Ag_2Se over the chalcogenide comprising material;

after the irradiating, exposing the Ag_2Se to an iodine comprising fluid effective to etch away at least some of the Ag_2Se; and

after the exposing, depositing a second conductive electrode material over the chalcogenide material, and which is continouos and completely covering at least over the chalcogenide material, and forming the second conductive electrode material into an electrode of the device.

23. The method of claim 22 wherein the iodine comprising fluid is a liquid.

24. The method of claim 22 wherein the iodine comprising fluid is an iodide solution.

25. The method of claim 22 wherein the iodine comprising fluid is a potassium iodide solution.

26. The method of claim 25 wherein the potassium iodide solution comprises from 5 to 30 grams I_2 per 1 liter of a from 20% to 50% potassium iodide solution.

27. The method of claim 22 doping the chalcogenide comprising material to at least 30 atomic percent Ag in a lowest of a plurality of variable resistance states.

28. The method of claim 22 wherein the exposing is effective to etch away substantially all of the Ag_2Se.

29. A method of forming a programmable memory cell of memory circuitry, comprising:

forming a first conductive electrode material on a substrate;

forming a substantially amorphous chalcogenide comprising material over the first conductive electrode material, the chalcogenide material comprising A_xSe_y, where "A" is selected from the group consisting of elements and radicals and mixtures thereof which are more electroposotive than Se;

forming a silver comprising layer over the chalcogenide comprising material;

irradiating the silver effective to break a chalcogenide bond of the chalcogenide material at an interface of the silver comprising layer and chalcogenide material and diffuse at least some of the silver into the chalcogenide material, the irradiating being effective to form a discontinuous layer of Ag_2Se over the chalcogenide comprising material, the irradiating being effective to maintain the chalcogenide material underlying the Ag_2Se in a substantially amorphous state~~;~~ , the irradiating being effective to dope the chalcogenide comprising material to average at least 30 atomic percent silver in a lowest of a plurality of variable resistance states;

after the irradiating, exposing the Ag_2Se to an iodine comprising fluid effective to etch away at least a majority of the Ag_2Se; and

after the exposing, depositing a second conductive electrode material over the chalcogenide material, and which is continuous and completely covering at least over the chalcogenide material, and forming the second conductive electrode material into an electrode of the device.

30. The method of claim 29 wherein the iodine comprising fluid is a liquid.

31. The method of claim 29 wherein the iodine comprising fluid is an iodide solution.

32. The method of claim 29 wherein the iodine comprising fluid is a potassium iodide solution.

33. The method of claim 32 wherein the potassium iodide solution comprises from 5 to 30 grams I_2 per 1 liter of a from 20% to 50% potassium iodide solution.

34. A method of forming a chalcogenide structure, comprising:
forming a chalcogenide glass layer;
forming a metal-containing layer over the chalcogenide glass layer;
irradiating said metal-containing layer to break a chalcogenide bond of the chalcogenide glass layer at the interface of the metal-containing layer and chalcogenide glass layer, such that at least a portion of the metal-containing layer diffuses into the chalcogenide glass layer; and,
after said step of irradiating, exposing an outer surface of the chalcogenide glass layer to an iodine comprising fluid, wherein said iodine comprising fluid removes at least a portion of said outer surface that has been irradiated.

35. The method of claim 34, wherein the iodine comprising fluid is a liquid.

36. The method of claim 34, wherein the iodine comprising fluid is an iodine comprising solution.

37. The method of claim 34, wherein the iodine comprising fluid is a potassium iodide solution.

38. The method of claim 37, wherein the potassium iodide solution comprises from 5 to about 30 grams I_2 per liter of a from 20% to about a 50% potassium iodide solution.

39. The method of claim 34, wherein the irradiating is effective to form Ag_2Se as at least part of the outer surface, the etching being effective to etch away at least some of the Ag_2Se.

40. The method of claim 34, wherein the metal-containing layer is a silver comprising layer.

41. The method of claim 40 wherein the silver comprising layer is predominately elemental silver.

42. A method of forming a chalcogenide structure, comprising:

forming a first conductive layer on a semiconductor substrate;

forming a chalcogenide glass layer over said first conductive layer;

forming a metal-containing layer over said chalcogenide glass layer;

irradiating said metal-containing layer to break a chalcogenide bond of the chalcogenide glass layer at the interface of the metal-containing layer and chalcogenide glass layer thereby creating an outside surface;

removing at least a portion of said outside surface by etching with an iodine comprising fluid; and,

after said step of removing at least a portion of said outside surface, forming a second conductive layer over at least a portion of the outside surface remaining after said act of removing.

43. The method of claim 42, wherein the iodine comprising fluid is a liquid.

44. The method of claim 42, wherein the iodine comprising fluid is an iodide comprising solution.

45. The method of claim 42, wherein the iodine comprising fluid is potassium iodide solution.

46. The method of claim 45, wherein the potassium iodide solution comprises from 5 to about 30 grams I_2 per liter of a from 20% to about a 50% potassium iodide solution.

47. The method of claim 42, wherein the irradiating is effective to form Ag_2Se as at least part of the outside surface, the etching being effective to etch away at least some of the Ag_2Se.

48. The method of claim 42, wherein the metal-containing layer is a silver comprising layer.

49. The method of claim 48, wherein the silver comprising layer is predominately elemental silver.

50. The method of claim 42, wherein said first conductive layer and second conductive layer are electrodes.

51. A method of forming a chalcogenide structure, comprising;

forming a first conductive layer on a semiconductor substrate;

forming a chalcogenide glass layer over said first conductive layer;

forming a metal-containing layer over said chalcogenide glass layer;

irradiating said metal-containing layer to break a chalcogenide bond of the chalcogenide glass layer at the interface of the metal-containing layer and chalcogenide glass layer thereby creating an outside surface, said step of irradiating is effective to form Ag_2Se as at least part of the outside surface;

removing at least a portion of said outside surface by etching with an iodine comprising fluid, said etching being effective to etch away at least some of the Ag_2Se; and

after said step of removing at least a portion of said outside surface, forming a second conductive layer over at least a portion of the outside surface remaining after said act of removing.