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Horak et al.

(54) **METHOD OF MAKING INTEGRATED CIRCUIT (IC) INCLUDING AT LEAST ONE STORAGE CELL**

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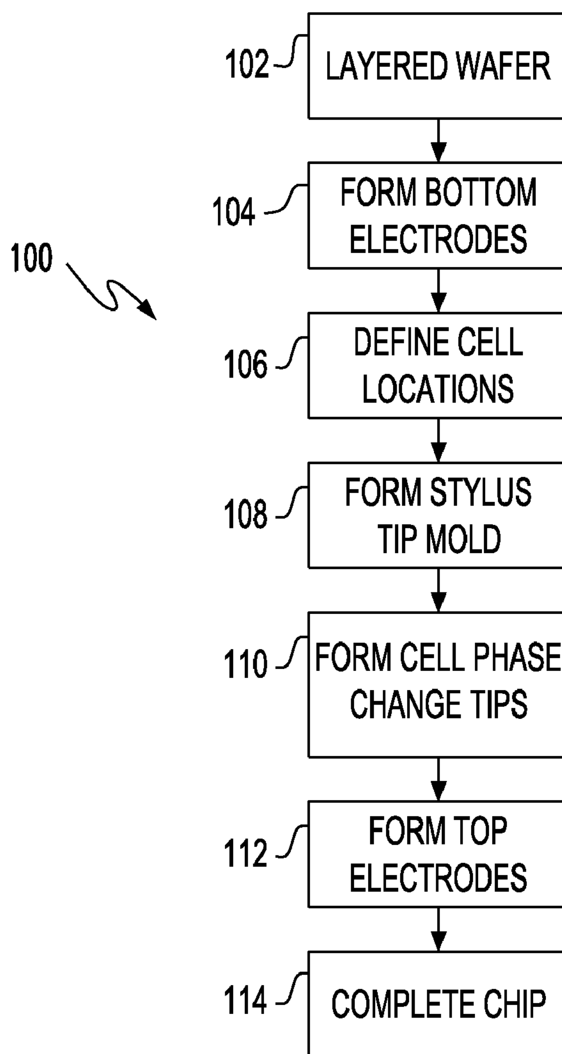
(57) **ABSTRACT**

A storage cell, integrated circuit (IC) chip with one or more storage cells that may be in an array of the storage cells and a method of forming the storage cell and IC. Each storage cell includes a stylus, the tip of which is phase change material. The phase change tip may be sandwiched between an electrode and conductive material, e.g., titanium nitride (TiN), tantalum nitride (TaN) or n-type semiconductor. The phase change layer may be a chalcogenide and in particular a germanium (Ge), antimony (Sb), tellurium (Te) (GST) layer.



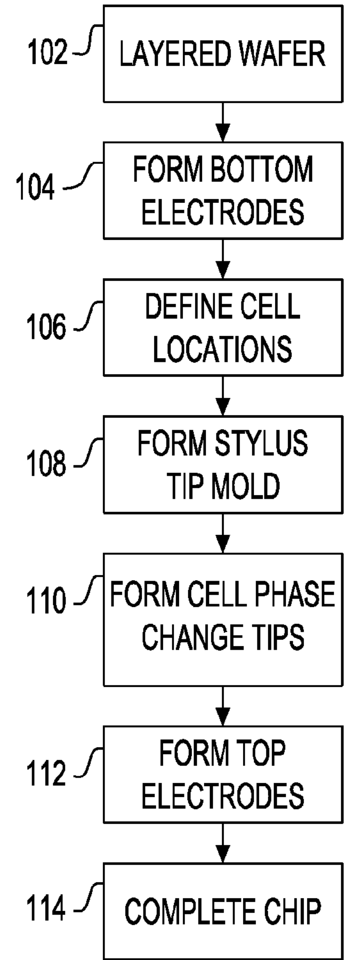


FIG. 1

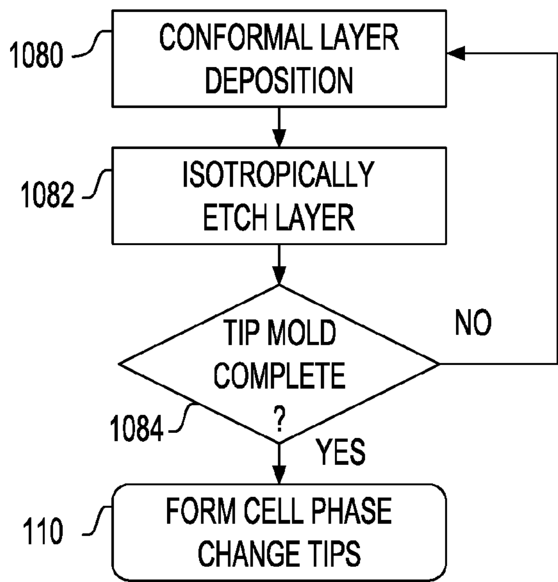
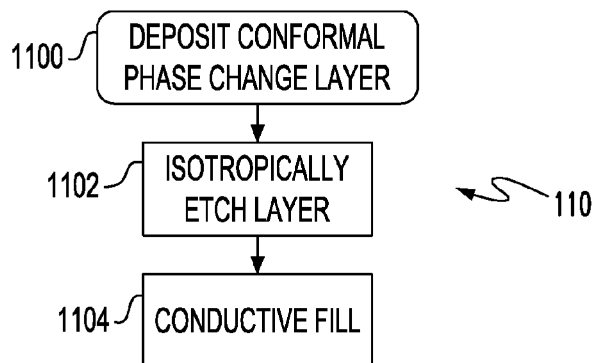


FIG. 2A

FIG. 2B



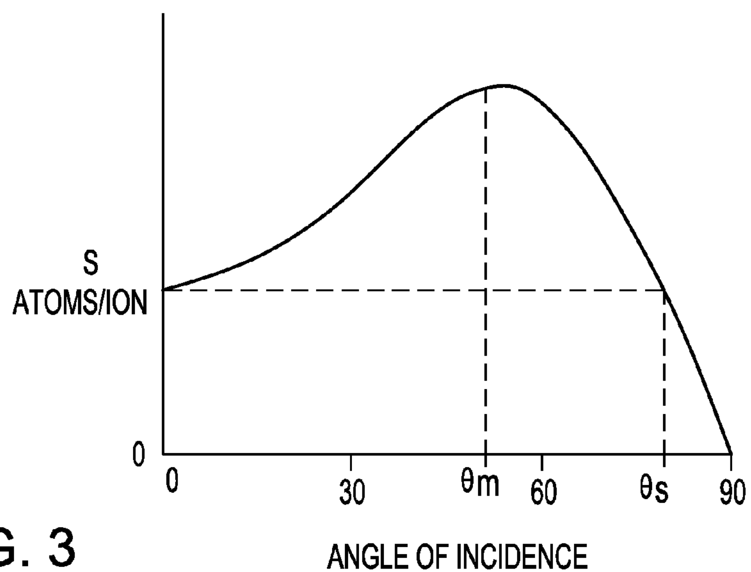


FIG. 3

FIG. 4A

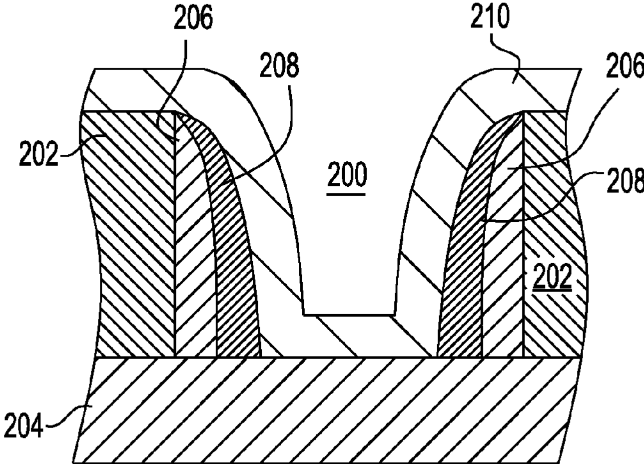


FIG. 4B

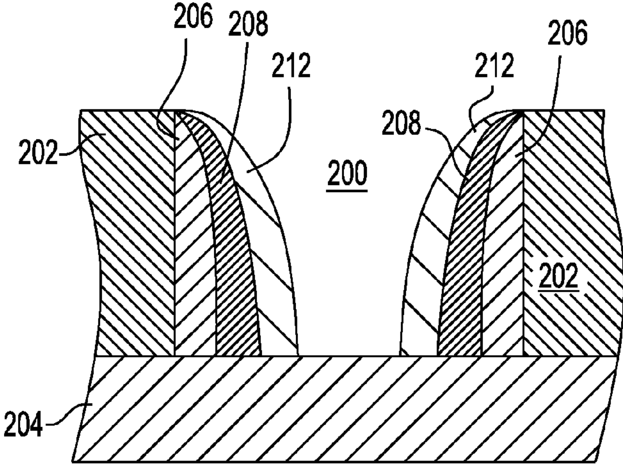


FIG. 4C

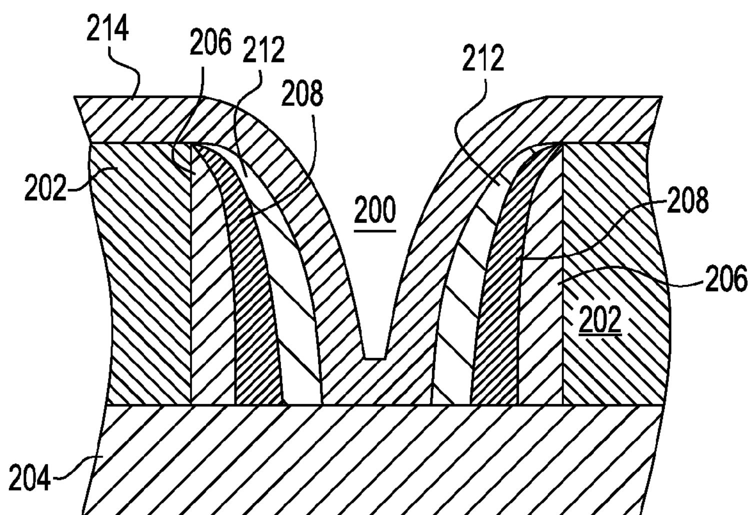
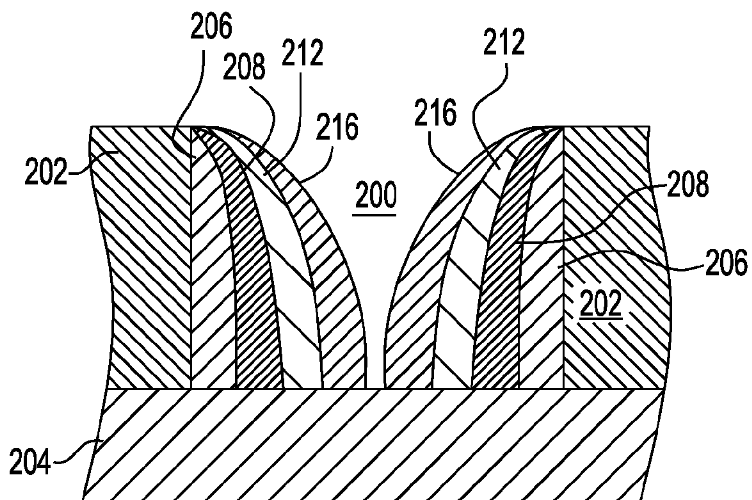


FIG. 4D



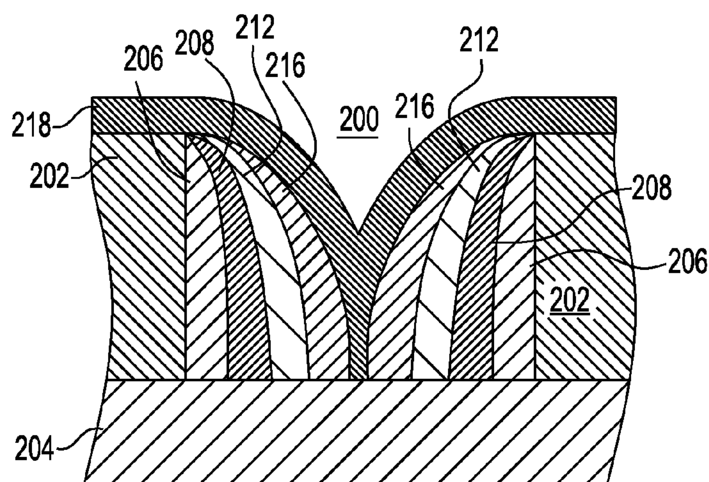


FIG. 4E

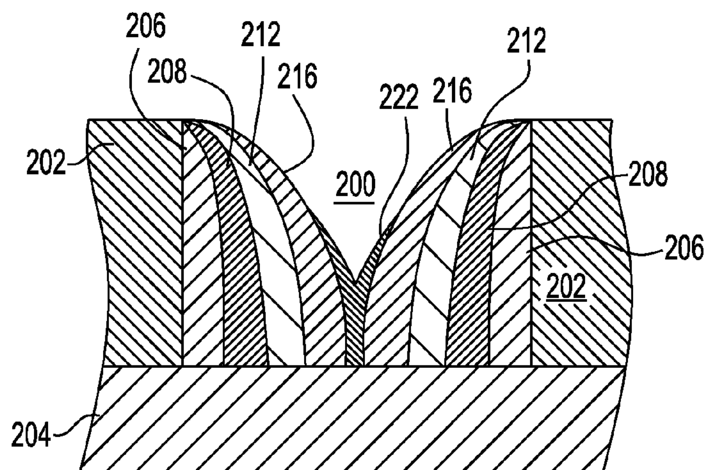


FIG. 4F

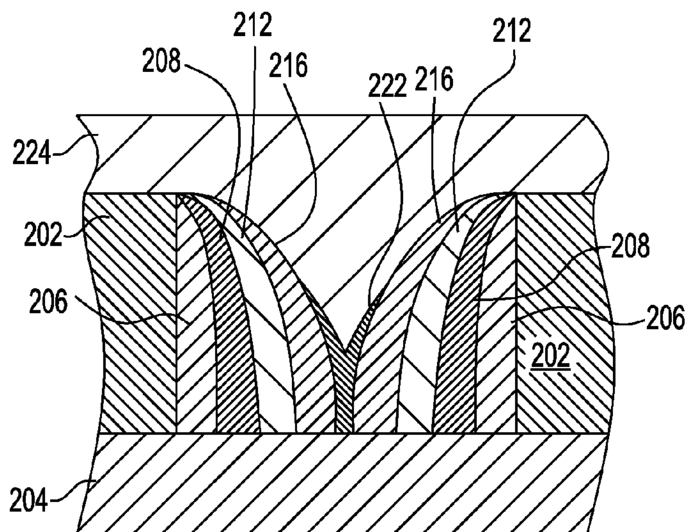


FIG. 4G

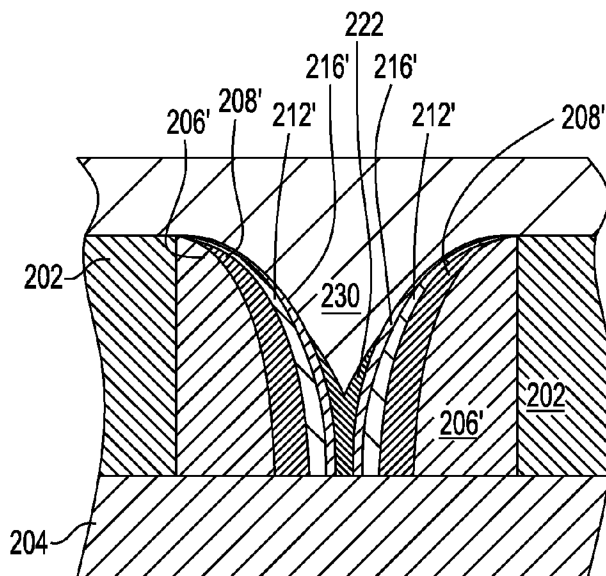


FIG. 6

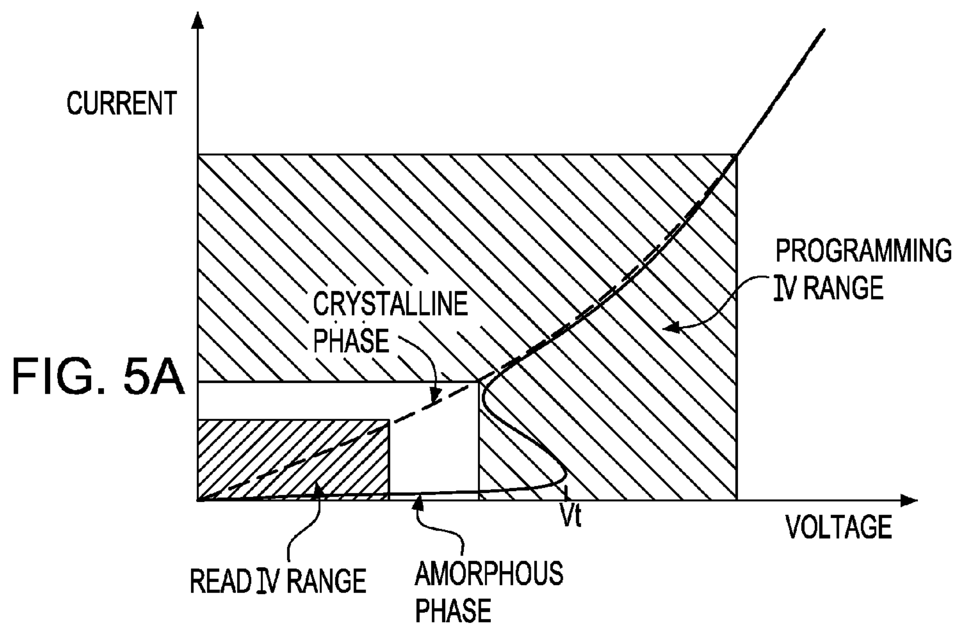


FIG. 5A

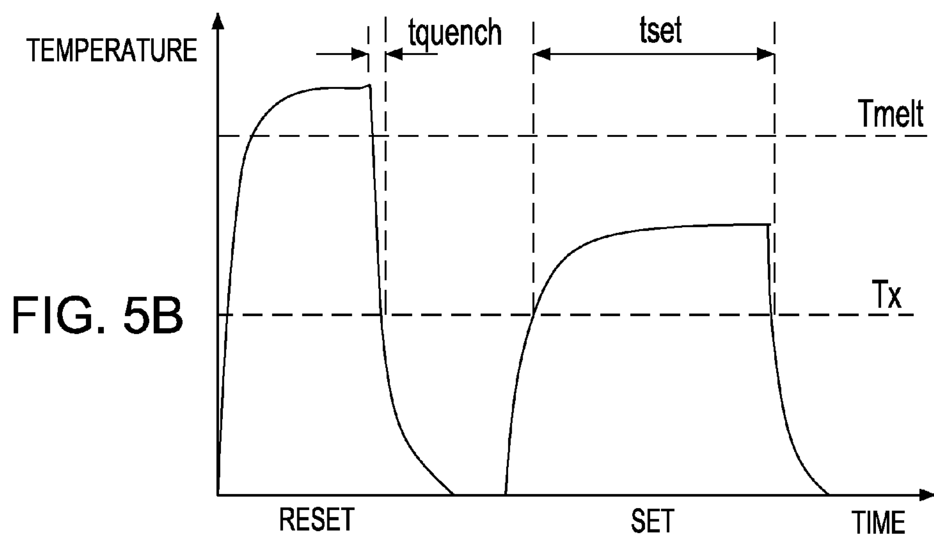


FIG. 5B

METHOD OF MAKING INTEGRATED CIRCUIT (IC) INCLUDING AT LEAST ONE STORAGE CELL

CROSS REFERENCE TO RELATED APPLICATION

[0001] The present invention is a divisional application of copending U.S. application Ser. No. 10/732,580 (Attorney Docket No. YOR9200300501US1) "PHASE CHANGE TIP STORAGE CELL" to David V. Horak et al., and related to U.S. application Ser. No. 10/732,582 (Attorney Docket No. YOR920030482US1) "FIELD EMISSION PHASE CHANGE DIODE STORAGE ELEMENT AND MEMORY" to Stephen S. Furkay et al., now issued as U.S. Pat. No. 7,052,923 B2, and U.S. application Ser. No. 10/732,579 (Attorney Docket No. YOR920030483US1) "INTEGRATED CIRCUIT WITH UPSTANDING STYLUS" to David V. Horak et al., all filed Dec. 10, 2003, and assigned to the assignee of the present invention.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention is related to solid state storage and particularly to solid state storage cells with a phase change material memory element.

[0004] 2. Background Description

[0005] Solid state, phase change materials that are chalcogen (Group VI elements such as sulfur (S), selenium (Se) and tellurium (Te)) alloys with at least one of germanium (Ge), arsenic (As), silicon (Si) and antimony (Sb) are known as chalcogenides and are well known. Chalcogenides exist in at least two different classifiable solid states or phases. The most extreme two states can be classified simply as amorphous and crystalline states with other less easily discernable states ranging between those two states. The amorphous state has a disordered atomic structure and the crystalline state generally is polycrystalline. Each phase has very different electrical properties. In its amorphous state, the material behaves as an insulator, i.e., an open circuit; in its crystalline state, the same material behaves resistively, as a p-type semiconductor. The resistivity of these materials varies in between amorphous and crystalline states.

[0006] In particular, when heat is applied to some phase change chalcogenides, the material switches phases from one (e.g., amorphous phase) state to a second (e.g., crystalline phase) state. The transitions between these states is selectively reversible with heat, i.e., the phase change material may be set/reset. As with anything that has two or more discernable and selectable states, each of the 2 stable states can be designated as a logic one and the other a logic zero. Thus, phase change material has found use in storage devices and particularly, for non-volatile storage, e.g., as a memory cell storage media. In addition, multiple bit memory elements have been made using the intermediate states inherent in the variation in resistivity between amorphous and crystalline.

[0007] Typically, controlled heat must be precisely provided to the phase change storage media to effect reversible transitions between amorphous and crystalline states and back. Normally, such heat is provided using resistive heating. Unfortunately, a relatively of large current is needed for each memory element to heat the phase change material. In particular, resetting the phase change material may require heating the crystalline material to its melting point, generally above 600° C. Thus, it maybe difficult on one hand to provide sufficient localized heat to raise the crystalline phase change material to its melting point and, on the other hand, to avoid accidentally heating other adjacent cells to the phase change set point and inadvertently setting adjacent cells.

[0008] One prior approach to localize heating in phase change switching is to minimize the phase change material contact area. Unfortunately, reducing the contact area normally increases cost, which is inversely proportional to the size of the contact. In particular, attaining a contact size below the minimum photolithographic image size for a particular technology complicates the process significantly and, correspondingly, increases cost. Further, normally, reducing contact size, reduces the heat delivery capability and increases resistance/reduces current delivered to the phase change material; all of which interferes with setting/resetting the material rather than enhancing it.

[0009] Thus, there is a need for improved and very localized or focused heat delivery to phase change material in memory cells.

SUMMARY OF THE INVENTION

[0010] It is a purpose of the invention to improve heat delivery to phase change material in memory cells;

[0011] It is another purpose of the invention to focus heat delivered to phase change material in individual memory cells;

[0012] It is yet another purpose of the invention to reduce the power required to deliver sufficient heat to set and reset phase change material in individual memory cells.

[0013] The present invention relates to a storage cell, integrated circuit (IC) chip with one or more storage cells that may be in an array of the storage cells and a method of forming the storage cell and IC. Each storage cell includes a stylus, the tip of which is phase change material. The phase change tip may be sandwiched between an electrode and conductive material, e.g., n-type semiconductor. The phase change layer may be a chalcogenide and in particular a germanium (Ge), antimony (Sb), tellurium (Te) or GST alloy.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The foregoing and other objects, aspects and advantages will be better understood from the following detailed description of a preferred embodiment of the invention with reference to the drawings, in which:

[0015] FIG. **1** shows a flow diagram for an example of a method of forming a preferred embodiment cross point array of nonvolatile storage devices;

[0016] FIGS. **2**A-B show an example of a preferred method of forming tip molds for cells and styli with phase change tips;

[0017] FIG. **3** shows that a plasma etch with enhanced sputtering enhances preferential erosion of horizontal layers;

[0018] FIGS. **4**A-G show a cross sectional example of a preferred stylus tip cell;

[0019] FIG. **5**A shows an example of a current verses voltage (I-V) characteristic for a typical chalcogenide suitable as a phase change memory material for preferred embodiment cross point cells;

[0020] FIG. **5**B shows an example of typical chalcogenide memory programming temperature evolution profiles for preferred embodiment cross point cells;

[0021] FIG. **6** shows a cross-section of another example of forming a stylus by depositing sequentially thinner layers such that spacers decrease in thickness axially.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0022] Turning now to the drawings and more particularly, FIG. **1** shows a flow diagram for an example of a method **100** of forming preferred embodiment nonvolatile storage devices according to the present invention, e.g., in a cross point storage array. In particular, preferred embodiment devices have chalcogenide phase change storage media in a stylus tip with a focused heating field in the stylus for enhanced Joule heating power delivery that improves phase change alteration. Preferably, Joule heating delivery is enhanced by delivering heat through and to the phase change material in the tip or apex of the stylus. In particular during a write, the hottest stylus region is spaced away from the bulk of the stylus and at the apex and so, contained entirely within the phase change material.

[0023] Cell formation begins in step **102** with a layered wafer. In particular, the layered wafer may be a partially patterned integrated circuit with standard insulated gate field effect transistor (FET) technology circuit devices, commonly referred to as CMOS. Storage cells are formed as described hereinbelow between 2 conductor layers, referred to as top and bottom electrode layers. Further, circuit devices, both N-type FETs (NFETs) and P-type FETs (PFETs), may be connected together by wiring that may be, in part, on one or both of the 2 conductor layers. So, in step **104** bottom electrodes are formed in a conductor layer at the surface of the layered wafer. Then in step **106**, a field layer is formed on the bottom electrode layer and orifices are formed in the field layer to define cell locations. In step **108** a tip or stylus mold is formed in each of the cell locations. The tip mold is such that a preferred stylus or field tip forms pointing down into the wafer and toward the bottom electrodes, e.g., described in U.S. application Ser. No. 10/732,579 (Attorney Docket No. YOR920030483US1) entitled "INTEGRATED CIRCUIT WITH UPSTANDING STYLUS" to David V. Horak et al., filed coincident herewith, assigned to the assignee of the present invention and incorporated herein by reference. In step **110**, a stylus is formed in each cell location with phase change material contained in and forming the tip of the stylus. Then in step **112**, the array is completed when top electrodes are formed over the cells. By orienting the bottom electrodes in one direction and the top electrodes in a second, each cell is uniquely identifiable by the intersection of one bottom electrode with one top electrode. Finally in step **114**, using standard semiconductor manufacturing end of the line (EOL) steps, the memory (macro, chip, etc.) is completed.

[0024] It should be noted that heretofore, stylus shaped field tips have been formed using a hard mask and a wet etch to define tips upstanding like stalagmites, standing on and pointing upward from the wafer. By contrast, a preferred embodiment stylus shaped field tip is formed inverted from these stalagmite shaped styli, i.e., effectively standing on the stylus apex with storage material contained within the tip, itself. Further, it should be noted that a preferred embodiment stylus with a phase change tip is suitable for any storage cell or memory cell application and has use beyond memory cell applications. For example, such a stylus has application to any circuit or chip wherein non-volatile storage may be needed, e.g., programmable logic arrays (PLAs), programmable array logic (PAL), programmable chip selects or even, circuits with programmable performance tailoring.

[0025] FIGS. **2**A-B show an example of a preferred method of forming tip molds for cells step **108** and styli with phase change tips in step **110**. The tip mold is formed by depositing successive dielectric layers and isotropically etching to remove horizontal portions of each. So, beginning in step **1080** a first conformal spacer layer is deposited. In particular, the conformal spacer layers may be silicon nitride (e.g., Si_3N_4) or oxide. Silicon nitride can be deposited with a mixture of ammonia and silicon hydride using plasma enhanced chemical vapor deposition (PECVD) or in a furnace reactor at a pressure of between about 10 milliTorr (10 mTorr) and 1 Torr. Deposition thickness can be time controlled. Alternately, oxide can be deposited by flowing ozone and tetraethylorthosilicate (TEOS) into a deposition reactor. Preferably, the wafer temperature in each such deposition is between about 300° and 500° C. and under a pressure between about 10 and 400 Torr. Deposition thickness is time controlled. Next, in step **1082** each layer is anisotropically etched, preferably with a plasma etch, to remove horizontal surfaces of the conformal layer, which also slightly reduces the height of the vertical sidewall spacer that remains in the orifice. Each additional layer is deposited and etched, repeating steps **1080** and **1082**, until the tip mold is complete in step **1084**; the layered spacers form the tip mold. Stylus formation begins in step **1100** FIG. **2**B with depositing a conformal phase change layer. The conformal phase change layer is isotropically etched in step **1102**, leaving a phase change tip in the tip mold. The volume or the remaining storage material is minimal and as long as enough remains to form a crystal and exist amorphously, enough remains in the tip. The stylus is completed in step **1104** the mold is filled by depositing a conductive material, preferably, titanium nitride (TiN) or tantalum nitride (TaN) or alternately, n-type semiconductor. Typically, the conductive fill is planarized, e.g., CMP, to the upper surface of the field layer and tip mold for top electrode formation thereon.

[0026] FIG. **3** shows plasma etch sputtering yield with respect to target normal, which shows that enhancing sputtering enhances preferential erosion of horizontal layers with a maximum occurring at a sputtering angle (θ_m) of about 50° across an angular range of 0 to an upper angular limit (θ_s) of about 80°. So, if in step **1082** and **1102** the isotropic etch does not have a sputtering component, the curvature of the deposited conformal film normally would translate to the spacer that will become part of the tip mold. However, enhanced sputtering enhances preferential plasma erosion of the horizontal portions of the conformal layer for a more pronounced sidewall curvature. The more pronounced the sidewall curvature, the more pronounced the tip mold and the tip itself. So, to enhance sputtering during the plasma etch, the wafer is biased (either with a self bias or using an appropriate external DC bias) with respect to plasma. In particular, the conformal layer may be etched in step **1104** in a plasma reactor at pressures between 1 and 250 mTorr using a fluorinated plasma, e.g., using feed gasses such as CHF_3, CF_4 and/or $O_2C_2F_6$.

[0027] FIGS. **4**A-G show a cross sectional example of a preferred stylus tip cell formed according to the preferred method of FIG. **2**A-B. In this example, an orifice **200** in a surface layer **202** to an underlying (bottom) electrode layer **204**. Preferably, the orifice **200** has a circular horizontal cross section. Tip formation in step **108** of FIG. **2**A as successive

conformal layers are deposited in step **1080** and isotropically etched in step **1082** to form sidewall spacers **206**, **208**, forming a ring around the interior of the orifices **200**. Preferably, for a 125 nm diameter memory cell, successive 15 nm thick layers are deposited for each of sidewall spacers **206**, **208**. Again in step **1080**, a third 15 nm thick conformal layer **210**, is deposited completing the cross section in the example of FIG. **4**A. After isotropically etching third conformal layer **210** in step **1082**, a third spacer **212** is formed in FIG. **4**B, also forming a ring around the interior of the orifice **200**. Similarly, in FIG. **4**C, a fourth 15 nm thick conformal layer **214** is formed in step **1080** and isotropically etched in step **1082** to form fourth spacers **216** in FIG. **4**D, which completes a tapered mold in the orifice **200**. It should be noted that although spacer rings **206**, **208**, **212** and **216** are shown as individual layers, this is primarily for illustration. If such spacers **206**, **208**, **212** and **216** are the same material, once formed, each would merge with previously formed spacer rings for a uniform, rather than layered, tip mold **218**.

[0028] It should be noted that if an isotropic etch is employed that does not have a sputtering component, normally, the spacer would have the curvature of the deposited conformal film. Further, height is removed from each spacer **206**, **208**, **212** and **216** as it is slightly etched down with horizontal portion removal. Accordingly, the combined after etch thickness of the four spacers must be less than half the width of the orifice and may extend the full height of the orifice **200** to avoid plugging the orifice **200**.

[0029] Stylus tip cell formation in step **110** of FIG. **2**B begins in step **1100** as shown in FIG. **4**E as a phase change material layer **218**, preferably a conformal layer, is deposited in the orifice **200**. Optionally, a conductive barrier layer (e.g., TiN, not shown) may be formed on the bottom electrode **204** before or after mold formation and before the step **1100** of depositing the conformal phase change material layer **218**. The phase change material layer **218** contacts the bottom electrode **204**, directly or indirectly, e.g., through a conductive barrier layer (not shown). Then, in step **1102** using RIE for example, the horizontal portions of phase change layer **218** are removed, leaving a phase change tip **222** in the orifice. In this example, the phase change tip **222** volume is minimized with a cross section shaped similar to an arrowhead. Finally, in step **1104** the orifice is filled with conductive material **224**, plugging the mold and completing the stylus. As noted herein above, preferably, conductive material **224** is, preferably, TiN or TaN and, alternately, an n-type semiconductor. The phase change tip **222** is sandwiched between the conductive material **224** (which may be formed with and act as a top electrode) and the bottom electrode **204**. In particular, in its crystalline phase, the phase change tip **222** is an asymmetric resistor in the current path between the conductive material **224** and the bottom electrode **204** and favors electron conduction when the top electrode is biased negatively with respect to the bottom electrode. In its amorphous phase, the phase change tip **222** acts as an insulator, i.e., opening the current path. Thus, analogous to old diode based read only memories (ROM), a one and a zero can be represented by the absence and presence of asymmetric resistance (i.e., of crystalline phase change material) in the path or vice versa. Thereafter, processing continues in step **112** of FIG. **1** as the conductive material fill **224** is planarized, e.g., CMP, leaving a conductive plug completing each stylus and top electrodes are formed. Optionally, the conductive material fill **224** may be patterned to integrally form the top electrodes with the conductive plugs.

[0030] FIG. **5**A shows an example of a current verses voltage (I-V) characteristic for a typical chalcogenide suitable as a phase change memory material for preferred embodiment cross point cells. FIG. **5**B shows an example of typical chalcogenide memory programming temperature evolution profiles for preferred embodiment cross point cells. Joule heating is applied to the cell GST tip to switch phases: switching to its amorphous (RESET) phase by heating the GST to T_{melt} and allowing it sufficient time to cool (t_{quench}); and, alternately, crystallizing (SET) the GST by heating it to T_x and allowing it sufficient time to cool (t_{set}). Thus, by switching the GST tip between crystalline and amorphous phase and back, the stylus switches from including a diode junction and being an open between the top electrode and bottom electrode and back. So, for example, amorphous GST may be a logic zero and crystalline GST may be a logic one.

[0031] FIG. **6** shows a cross-section of another example of a preferred stylus **230** formed by depositing sequentially thinner layers such that spacers decrease in thickness axially, i.e., the initial spacer layer is much thicker than the final spacer layer. In this example the first or outer layer **206'** is substantially thicker than the inner layers **208'**, **212'** and **216'**. In particular the outer layer **206'** is from one quarter to one third the thickness of the horizontal dimension of the orifice. Subsequent spacer layers are each one quarter to one third as thick as the remaining opening at the bottom part of the spacer **208'**. So, the effective thickness of each succeeding layer decreases geometrically the with the number of layers. Finally, a stylus tip and conductive material are deposited to form the stylus **230** in the tapered mold.

[0032] Advantageously, by depositing the phase change material layer in the mold and etching the layer so that only the phase change tip remains, the phase change material is volume limited and concentrated in the stylus tip, bounded on all sides by the tip mold and on top by the conductor to the top electrode. So, the energy required to change phases is minimized because heat generated for setting/resetting the phase change material tip is, more or less, contained within the phase change material itself. Also, the memory cell has a more controlled resistance due to the limited for phase change material volume. Additionally, the tip mold material is a better heat insulator than conductor, which in combination with the conductive plug focuses the heat delivered to the cell on changing the phase, further improving device switching efficiency.

[0033] While the invention has been described in terms of preferred embodiments, those skilled in the art will recognize that the invention can be practiced with modification within the spirit and scope of the appended claims.

What is claimed is:

1. A method of forming an integrated circuit (IC) including at least one storage cell, said method comprising the steps of:

a) forming a bottom electrode;

b) defining a tip mold at each cell location;

c) forming a cell tip of a phase change material in each defined said tip mold; and

d) filling said each defined tip mold with a conductive material.

2. A method of forming an IC as in claim **1**, wherein the step (c) of forming the cell tip comprises the steps of:

i) depositing a conformal phase change material layer; and

ii) removing horizontal portions of said conformal phase change material layer.

3. A method of forming an IC as in claim **2**, wherein the step (ii) of removing horizontal portions comprises etching said conformal phase change material layer with a plasma etch having an enhanced sputtering component.

4. A method of forming an IC as in claim **3**, wherein said IC is on a layered wafer and the step (ii) of removing horizontal portions comprises biasing said layered wafer during said plasma etch, biasing said layered wafer enhancing sputtering.

5. A method of forming an IC as in claim **4**, wherein said layered wafer is self biased.

6. A method of forming an IC as in claim **3**, wherein said phase change layer is a chalcogenide layer.

7. A method of forming an IC as in claim **4**, wherein said chalcogenide is a germanium (Ge), antimony (Sb), tellurium (Te) based (GST based) material.

8. A method of forming an IC as in claim **3**, wherein said conductive material comprises a metal nitride.

9. A method of forming an IC as in claim **3**, wherein the step (b) of forming the tip mold comprises the steps of:

i) forming a conformal layer on a surface layer of said layered wafer;

ii) removing horizontal portions of said conformal layer from said surface layer; and

iii) repeating steps (i) and (ii) 3 times, whereby four concentric spacer layers form said tip mold.

10. A method of forming an IC as in claim **9**, wherein each succeeding said conformal layer is formed thinner than its immediately preceding layer.

* * * * *