FORCED ION MIGRATION FOR CHALCOGENIDE PHASE CHANGE MEMORY DEVICE

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See application file for complete search history.

References Cited
U.S. PATENT DOCUMENTS
6,784,018 B2 8/2004 Campbell et al.

ABSTRACT
Non-volatile memory devices with two stacked layers of chalcogenide materials comprising the active memory device have been investigated for their potential as phase-change memories. The devices tested included GeTe/SnTe, Ge2Se3/SnTe, and Ge2Se3/SnSe stacks. All devices exhibited resistance switching behavior. The polarity of the applied voltage with respect to the SnTe or SnSe layer was critical to the memory switching properties, due to the electric field induced movement of either Sn or Te into the Ge-chalcogenide layer.

One embodiment of the invention is a device comprising a stack of chalcogenide-containing layers which exhibit phase-change switching only after a reverse polarity voltage potential is applied across the stack causing ion movement into an adjacent layer and thus “activating” the device to act as a phase-change random access memory device or a reconfigurable electronics device when the applied voltage potential is returned to the normal polarity. Another embodiment of the invention is a device that is capable of exhibiting more than two data states.


Campbell et al, “Parallel Polarization EPR Characterization of the Mn(II) Center of Oxidized Manganese Superoxide Dismutase”, “Journal of the American Chemical Society”, May 1, 1999, pp. 4714-4715, vol. 121, No. 19, Published in: US.


Oblea et al, “Memristor SPICE Model Simulation & Device Hardware Correlation”, May 6, 2010, Publisher: IEEE. Published in: US.


* cited by examiner
**FIG. 1**

Distribution of Devices

- ON
- OFF

Resistance (Ohms)

**FIG. 2**

Current (mA)

- WRITE '0'
- WRITE '1'

Voltage (V)

$V_T$
FIG. 7

FIG. 8
FIG. 9

FIG. 10
FORCED ION MIGRATION FOR CHALCOGENIDE PHASE CHANGE MEMORY DEVICE

DESCRIPTION

This application is a divisional application claiming priority to U.S. Non-provisional application Ser. No. 11/875,805, filed Oct. 19, 2007, now U.S. Pat. No. 7,924,608 which is hereby incorporated by reference in its entirety.

This application claims priority of my prior, co-pending provisional patent application, Ser. 60/853,068, filed on Oct. 19, 2006, entitled “Forced Ion Migration for Chalcogenide Phase Change Memory Device,” which is incorporated herein by reference.

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BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to electronic memory devices, and more particularly to a method of inducing a non-phase-change stack structure into a phase-change stack memory structure.

2. Related Art

Research into new random access electronic memory technologies has grown significantly in the past 10 years due to the near realization of the scaling limits of DRAM and the low cycle lifetime, high power requirements, and radiation sensitivity of Flash. At the forefront of this research is the phase-change random access memory (PCRAM) [see Bez, R.; Pirovano, A. “Non-volatile memory technologies: emerging concepts and new materials” Materials Science in Semiconductor Processing 7 (2004) 349-355; and Lacaia, A. L. “Phase-change memories: state-of-the-art, challenges and perspectives” Solid-State Electronics 50 (2006) 24-31].

Phase-change memory is a non-volatile, resistance variable memory technology whereby the state of the memory bit is defined by the memory material’s resistance. Typically, in a two state device, a high resistance defines a logic ‘0’ (or ‘OFF’ state) and corresponds to an amorphous phase of the material. The logic ‘1’ (‘ON’ state) corresponds to the low resistance of a crystalline phase of the material. The ‘high’ and ‘low’ resistances actually correspond to non-overlapping resistance distributions, rather than single, well-defined resistance values (FIG. 1).

The phase-change material is switched from high resistance to a low resistance state when a voltage higher than a ‘threshold’ voltage, Vt, is applied to the amorphous material [see Adler, D.; Hensch, H. K.; Mott, N. “The Mechanism of Threshold Switching in Amorphous Alloys” Reviews of Modern Physics 50 (1978) 209-220; and Adler, D. “Switching Phenomena in Thin Films” J. Vac. Sci. Technol. 10 (1973) 728-738] causing the resistance to significantly decrease (FIG. 2). The resultant increased current flow causes Joule heating of the material to a temperature above the material glass transition temperature. When a temperature above the glass transition temperature, but below the melting temperature, has been reached, the current is removed slowly enough to allow the material to cool and crystallize into a low resistance state (write 1 current region, FIG. 2).


SUMMARY OF THE INVENTION


Devices with three types of material stacks were fabricated for this study: GeTe/SnTe; Ge2Se2/SnTe; and Ge2Se3/SnSe. While Te-based chalcogenides are well studied for use in phase-change memory applications [see Bez, R.; Pirovano, A. “Non-volatile memory technologies: emerging concepts and new materials” Materials Science in Semiconductor Processing 7 (2004) 349-355; Lacaia, A. L. “Phase-change memories: state-of-the-art, challenges and perspectives” Solid-
respectively, of a resistance variable memory. In this work, we have explored the possibility of inducing a phase-change response in the Ge$_2$Se$_3$/Sn chalcogenide stack structures. We selected the Ge$_2$Se$_3$ glass since, like the GeTe glass, it contains homopolyer Ge—Ge bonds which we believe may provide nucleation sites for crystallization during the phase-change operation, thus improving the phase-change memory response [see An, S.-H.; Kim, D.; Kim, S. Y. “New crystallization kinetics of phase-change of Ge$_2$S$_2$Te, at moderately elevated temperature” Jpn. J. Appl. Phys. 41(2002) 7400-7401]. Additionally, the Ge$_2$Se$_3$ glass offers the advantage of higher glass transition temperatures (Ge$_2$Se$_3$: Tg=613 K [see Feltz, G. J. J.; Remeika, B. M.; Feltz, G. J. J.; Mat. Res. Soc. Symp. Proc. 556 (2000) 169-174]; SnTe: Tg=625 K [seeands, M.; Rubin, K. A. “Progress of eraseable phase-change materials” SPIE Vol. 1078 Optical Data Storage Topical Meeting (1989) 150-156]; GST: Tg=473 K [see Hamann, H. F.; O’Boyle, M.; Martin, Y. C.; Rooks, M.; Wickramasinghe, H. K. “Ultra-high-density phase-change storage and memory” Nature Materials 5 (2006) 383-387]), thus providing more temperature tolerance during manufacturing.

One possible benefit of the metal-chalcogenide layer is the potential for formation of an Ohmic contact between the electrode and the memory layer due to the presence of a low bandgap material like SnTe (Eg=0.18 eV at 300K [see Esaki, L.; Stiles, P. J., “New Type of Negative Resistance in Barrier Tunneling” Phys. Rev. Lett. 16 (1966) 1108-1111]) between the electrode and the chalcogenide switching layer. An Ohmic contact will allow a lower voltage to be applied to the memory cell since a Schottky barrier does not need to be overcome in order to achieve the current necessary for phase-change switching. Another potential benefit of the Sn-chalcogenide layer is better adhesion of the layer to the electrode. The better adhesion provided by the SnTe layer may help prevent delamination of the electrode from the chalcogenide memory layer, as can occur after repeated thermal cycles [see Hudgens, S.; Johnson, B. “Overview of Phase-Change Chalcogenide Nonvolatile memory Technology” MRS Bulletin, November 2004, 829-832]. In addition to these potential benefits, the Sn-chalcogenide may provide a region with ‘graded’ chalcogenide concentration between the Sn-chalcogenide and the Ge-chalcogenide memory switching layer due to the ability of the chalcogenide to form bridging bonds between the Sn and Ge atoms in the Sn-chalcogenide and Ge-chalcogenide layers, respectively. Lastly, as we show in this work, the Sn-chalcogenide may assist in phase-change memory switching by donating Sn-ions to the Ge-chalcogenide layer during operation, thus allowing chalcogenide materials which normally do not exhibit phase-change memory switching to be chemically altered post processing into an alloy capable of phase-change response.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph depicting an example distribution of low and high resistance values defining a logic ‘1’ and ‘0’ state, respectively, of a resistance variable memory.

FIG. 2 is a graph depicting the relationship between current through the memory cell material and the formation of a low (write ‘1’) or high (write ‘0’) resistance state.

FIG. 3 is a top perspective schematic view of the device structures according to the present invention as tested. The notation Ge—Ch/Sn—Ch indicates a device with this structure with the films listed in the order nearest the bottom electrode to nearest the top electrode.

FIG. 4 is a graph depicting XRD spectra of SnTe and SnSe evaporated films.

FIG. 5 is a TEM image of a GeTe/SnTe device according to the present invention.

FIG. 6 is a set of IV-curves for three unique GeTe/SnTe devices according to the present invention, showing the device-to-device variation typically observed in these devices. A positive potential was applied to the top electrode in each case.

FIG. 7 is a representative IV-curve for a GeTe/SnTe device according to the present invention, with a negative potential applied to the top electrode. A positive potential has never been applied to the device top electrode prior to this measurement.

FIG. 8 is a representative IV-curve for a Ge$_2$Se$_3$/SnTe device according to the present invention, with a positive potential applied to the top electrode.

FIG. 9 is a representative IV-curve for a Ge$_2$Se$_3$/SnTe device according to the present invention, with a negative potential applied to the top electrode. A positive potential has never been applied to the device top electrode prior to this measurement.

FIG. 10 is a representative IV-curve for a Ge$_2$Se$_3$/SnSe device according to the present invention, with a positive potential applied to the top electrode.

FIG. 11 is an IV-curve of a Ge$_2$Se$_3$/SnSe device according to the present invention, with the top electrode at a negative potential. A positive potential has never been applied to the device top electrode prior to this measurement.

FIG. 12 is an IV-curve of a Ge$_2$Se$_3$/SnSe device according to the present invention, obtained with a negative potential applied to the top electrode after the application of a positive potential ‘conditioning’ signal consisting of a DC current sweep limited to 30 nA.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to the Figures, there are shown some, but not the only, embodiments of the invention.

FIG. 3 shows a top perspective view of a device structure according to the present invention, used in this study. The device structure consists of a via through a nitride layer to a W bottom electrode deposited on 200 mm p-type Si wafers. The chalcogenide material layers were deposited with the Ge-chalcogenide layer first, followed by the Sn-chalcogenide layer. Prior to deposition of the first chalcogenide layer, the wafers received an Ar+ sputter etch to remove residual material and any oxide layer that may have formed on the W electrode. The Ge, Se, layer was deposited by sputtering with an Ulvac ZX-1000 from a target composed of press Ge-Se powder. The Ge, Sn, and SnSe layers were prepared by thermal evaporation of GeTe, SnTe, and SnSe (all from Alfa Aesar, 99.999% purity) using a CHA Industries SE-600-RAP thermal evaporator equipped with three 200 mm wafer planetary rotation. The rate of material deposition was monitored using an Inficon IC 6000 with a single crystal sensor head. The base system pressure was 1x10$^{-7}$ Torr prior to evaporation.

Using the planetary rotator, evaporated films were deposited on two types of wafers simultaneously in each experiment: (1) a film characterization wafer consisting of a p-type Si wafer substrate with the layers 350 A W/800 A Si$_3$N$_4$ and, (2) two wafers processed for device fabrication consisting of wires etched through a Si$_3$N$_4$ layer to a W electrode for bottom electrode contact (FIG. 3). The film characterization wafer present in each evaporation step was used to characterize the actual thin-film material stoichiometry post evaporation since...
thermally evaporated films often have a stoichiometry different than the starting material. The evaporation chamber was opened to the ambient atmosphere between the GeTe, SnTe, and SnSe film depositions in order to expose the GeTe films to similar ambient atmospheric conditions as the sputtered GeSe layers, which had to get exposed to the atmosphere during transfer from the sputtering tool to the evaporator for the Sn-chalcogenide film deposition. After the evaporation step(s) were complete, the device fabrication wafers continued processing through top electrode deposition (350 A sputtered W), photo steps, and dry etch to form fully functional devices consisting of a bottom electrode, chalcogenide material layers, and top electrode. Dry etch was performed by ion-milling with a Veeco ion-mill containing a quadrupole mass spectrometer for end-point detection.

The elements were characterized with ICP to determine the variation in composition of the film compared to the starting material. ICP data provided film stoichiometry with an accuracy of +/-0.8% using a Varian Vista-PRO radial ICP. The chalcogenide films were removed from the wafer prior to ICP analysis with an etching solution of 1:1 HCl:HNO3. XRD, performed with a Siemens’ D5000, was used to qualitatively identify amorphous or polycrystalline films. TEM measurements were made with a Philips Model CM300.

Electrical measurements were made using a Micromanipulator 6200 microprobe station equipped with a temperature and pressure controllable wafer chuck, a Hewlett-Packard 4145B Parameter Analyzer, and Micromanipulator probes with W tips (Micromanipulator size 7A). The tested devices were 0.25 um in diameter with 80 um x 80 um pads for electrical contact to the top and bottom electrodes.

Results and Discussion

The GeTe and Ge2Se3 films were amorphous as deposited with no observable XRD peaks. The SnTe and SnSe films were polycrystalline, as indicated by their XRD spectra (FIG. 4). Due to the nature of the evaporation process, and the relatively high pressure of the evaporation chamber prior to performed with Siemens’ DS500, was used to qualitatively indicate only relative concentrations of Ge, Se, Sn, or Te in the films.

Note that ICP analysis does not measure oxygen in the film, therefore the concentrations of the elements indicate only relative concentrations of Ge, Se, Sn, or Te in the films.

TABLE 1

<table>
<thead>
<tr>
<th>Device Stack</th>
<th>Layer 1 Composition</th>
<th>Layer 2 Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeTe/SnTe</td>
<td>Ge2Te3</td>
<td>Sn0.4Ge0.6Te3</td>
</tr>
<tr>
<td>Ge2Se/SnTe</td>
<td>Ge2Se2</td>
<td>Sn0.4Ge0.6Se2</td>
</tr>
<tr>
<td>Ge2Se/3SnSe</td>
<td>Ge2Se2</td>
<td>Sn0.4Ge0.6Se2</td>
</tr>
</tbody>
</table>

Note that ICP analysis does not measure oxygen in the film, therefore the concentrations of the elements indicate only relative concentrations of Ge, Se, Sn, or Te in the films.
positive potential, no threshold voltage is observed in the potential is applied to a device that has not previously seen a positive current sweep case. In addition, the current at the application of the positive potential is much higher than the positive current DC IV-curves. This is in contrast to the case of the SnTe IV curve (Fig. 9), which exhibits better device-to-device consistency in their IV-curves. The absence of a threshold voltage in the negative current sweep IV-curve (Fig. 10) of the GeSe/Se device implies that during the application of a positive potential there may be Sn-ion migration from the Se layer into the GeSe layer which chemically alters the GeSe layer to a (GeSe),Sn alloy capable of phase-change operation. The migration of Sn ions into the lower glass layer may also explain the switching observed in the GeSe/Se device when a positive potential is applied to the top electrode. However, unlike the GeSe/Se device, switching is observed in the GeSe/Se device when a negative potential is applied to the top electrode. A possible explanation for the observed negative potential switching in the GeSe/Se device (Fig. 9) is that Te- ions from the SnTe layer may be electrically driven by the negative potential into the underlying GeSe glass layer, thus creating (GeSe),Te regions capable of phase-change switching.

**Conclusions**

Phase-change memory switching was observed in devices consisting of two stacked layers of chalcogenide material: a Ge-based layer (GeTe or GeSe), and a tin chalcogenide layer (SnTe or SnSe). The observed switching is dependent upon the polarity of potential applied to the electrode adjacent to the SnTe or SnSe layer. When a positive potential is applied to this electrode, the formation of Sn-ions and their migration into the adjacent GeTe or GeSe layer most likely contributes to the phase-change response of the material. We attribute the switching of the GeSe/Se device under negative applied potential, with no previously applied positive ‘conditioning’ voltage, to the migration of Te ions into the GeSe layer during application of the negative potential. The positive Te ion migration may alter the GeSe glass layer into a (GeSe),Te alloy capable of phase-change memory operation.

In the case of the GeSe/Se device, no Te ions are available to migrate into the GeSe glass layer when a negative potential is applied to the top electrode, and no phase-change behavior is observed in the IV-curve. If it were possible for Se ions to be forced into the GeSe glass from the SnTe layer (analogous to the Te ions from the SnTe layer), they would succeed only in making the GeSe glass Se-rich and thus still incapable of phase-change switching. Alternatively, if a positive potential is initially applied across the GeSeSnTe device and the current is limited to a low enough value to prohibit Joule heating, but still allow a high enough potential across the device for Sn-ion migration, Sn-ions may migrate into the GeSe layer, creating a (GeSe),TeSn alloy which is capable of phase-change switching when a negative potential is applied to the top electrode. The addition of metal ions, forced into the chalcogenide switching layer during the first ‘forming’ electrical pulse, not only facilitates electrical switching, but it also may allow for
more than one ON resistance state. This phase-change memory alloy, formed in-situ, may exhibit more than one crystallization temperature. Each crystallization temperature corresponds to a unique phase of the material, and thus a unique resistance. This means that by proper selection of the metal that is allowed to migrate into the chalcogenide glass, the alloy can be tuned to have more than one crystalline phase.

We further investigated this concept by synthesizing materials using the Ge-Se chalcogenide glass and adding small concentrations (1 and 3%) of various metals, and measuring the thermal properties of these materials. We have tested Sn, Sn, In, and Sb. The Sn and In addition showed the presence of two crystallization regions whereas the Zn showed three crystallization regions. Thus the Ge-Se-Zn alloy has the potential to have four logic states. This alloy can be formed in-situ, for example, by using a device comprising the layers of Ge-Se/ZnSe.

GeTeSn materials have been well studied for their application as optical phase-change materials [see Chen, M.; Rubin, K. A. “Progress of erasable phase-change materials” SPIE Vol. 1078 Optical Data Storage Topical Meeting (1989) 150-156]. GeTe exhibits fast crystallization under optically induced phase-change operation (<30 ns) and it crystallizes in a single phase (no phase separation) making it attractive for phase-change operation. However, the number of optically induced write/erase cycles that could be achieved was quite low (<500) [see Chen, M.; Rubin, K. A. “Progress of erasable phase-change materials” SPIE Vol. 1078 Optical Data Storage Topical Meeting (1989) 150-156]. Our initial electrical cycling endurance tests on the GeTe/SnTe and Ge-Se/SeTe devices and have shown endurance greater than 2 million cycles. Due to the potential for parasitic capacitances during the endurance cycling measurements, care must be taken in the measurement experimental setup [see Ielmini, D.; Mantegazza, D.; Lacaita, A. L. “Parasitic reset in the programming transient of PCMs” IEEE Electron Device Letters 26 (2005) 799-801]; with this in mind, better cycling measurements are currently in progress [see Campbell, K. A.; Anderson, C. M., Microelectronics Journal 38 (2007) 52-59].

Future studies will investigate the temperature dependence, AC switching and lifetime cycling endurance of each of these device types. Additionally, we will investigate the phase-change switching response of stack structure devices that use a metal-chalcogenide layer with a metal different than tin, such as zinc, which is expected to have much different mobility in an applied field as well as a much different chemical incorporation into the Ge-chalcogenide glass layer. It is possible that the presence of Ge—Ge bonds in the Ge-based layer assist in the incorporation of the metal ions or of the Te anions into the glass by providing an energetically feasible pathway (that of the Ge—Ge bonds) for Te- or metal-ion incorporation [see Narayanan, R. A.; Asokan, S.; Kumar, A. “Influence of Chemical Disorder on Electrical Switching in Chalcogenide Glasses” Phys. Rev. B 63 (2001) 092203-1-092203-4; and Asokan, S. “Electrical switching in chalcogenide glasses—some newer insights” J. Optoelectronics and Advanced Materials 3 (2001) 753-756]. Ge—Ge bonds are known to be thermodynamically unstable [see Feltz, A. Amorphous Inorganic Materials and Glasses, VCH Publishers Inc., New York, 1993, pg. 234], and in the presence of other ions, will easily break and allow formation of a new bond (e.g. GeTe or GeSn). Future work will investigate the role of the Ge—Ge bond by testing the electrical performance of devices made with Ge-chalcogenide stoichiometries that provide no Ge—Ge bonds, such as Ge-Se.

Although this invention has been described above with reference to particular means, materials, and embodiments, it is to be understood that the invention is not limited to these disclosed particulars, but extends instead to all equivalents within the scope of the following claims.

What is claimed is:

1. A device suitable for phase-change memory operation, comprising:
   a plurality of stacked chalcogenide layers, wherein one chalcogenide layer contains an ion which has moved from another chalcogenide layer.
   2. The device of claim 1 wherein one chalcogenide layer is a Ge-chalcogenide layer, and another chalcogenide layer is a Sn-chalcogenide layer.
   3. The device of claim 1 wherein the Ge-chalcogenide layer comprises GeTe.
   4. The device of claim 2 wherein the Ge-chalcogenide layer comprises GeSe.
   5. The device of claim 2 wherein the Sn-chalcogenide layer comprises SnTe.
   6. The device of claim 2 wherein the Sn-chalcogenide layer comprises SnSe.
   7. The device of claim 1 wherein an electric field is applied to the device to move the ion from one chalcogenide layer to another.
   8. The device of claim wherein the device has at least three logic states.
   9. The device of claim wherein the ion is a metal ion.
   10. The device of claim wherein the one chalcogenide layer that incorporates the metal ion forms a new chalcogenide alloy with a plurality of crystalline phases.
   11. A device suitable for phase-change memory operation, comprising:
      a plurality of stacked chalcogenide layers, wherein one chalcogenide layer contains an ion which has moved from another chalcogenide layer, and wherein at least one of the stacked layers is a Ge-chalcogenide layer deposited on a passivation layer.
   12. The device of claim wherein the passivation layer comprises SiNx.
   13. The device of claim wherein the plurality of stacked layers comprises a top-most surface and a bottom-most surface, and a top electrode is attached to the top-most surface and a bottom electrode is attached to the bottom-most surface.
   14. The device of claim wherein at least one of the top and bottom electrodes comprises W.
   15. The device of claim wherein the passivation layer includes a via, and the Ge-chalcogenide layer is attached to a bottom electrode through the via.
   16. The device of claim wherein the electrode comprises an indentation.
   17. A device suitable for phase-change memory operation, comprising:
      a plurality of stacked chalcogenide layers, wherein one chalcogenide layer contains an ion which has moved from another chalcogenide layer.
   18. The device of claim wherein the Ge-Se-based binary glass layer comprises Ge-Se/Sn-chalcogenide stacked layer structure.
   19. The device of claim wherein the Ge-Se binary glass contains an ion from the Sn-chalcogenide layer.
   20. The device of claim wherein the Ge-Se binary glass also contains Zn, In, or Sb.