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, Ge$_2$Se$_3$/SnTe, and Ge$_2$Se$_3$/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.
References Cited

OTHER PUBLICATIONS


Oblea et al., "Memristor SPICE Model Simulation & Device Hardware Correlation", May 6, 2010, Publisher: IEEE; Published in: US.
FIG. 1

Distribution of Devices

ON

OFF

Resistance (Ohms)

FIG. 2

Voltage (V)

Current (mA)

WRITE '0'

WRITE '1'

V_T

Voltage (V)
FIG. 11

FIG. 12
FORCED ION MIGRATION FOR CHALCOGENIDE PHASE CHANGE MEMORY DEVICE

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional of U.S. patent application Ser. No. 11/875,805, filed Oct. 19, 2007, and entitled “Forced Ion Migration for Chalcogenide Phase Change Memory Device,” which claims priority to provisional patent application Ser. No. 60/853,068, filed on Oct. 19, 2006, the disclosure of which is hereby incorporated by reference in its entirety. This application with, and is related to, U.S. patent application Ser. No. 13/085,265, filed Apr. 12, 2011, also entitled “Forced Ion Migration for Chalcogenide Phase Change Memory Device,” and also a divisional application of U.S. patent application Ser. No. 11/875,805.

DESCRIPTION

This work was partially supported by a NASA Idaho EPS-CoR grant, NASA grant NCC5-577.

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 lifetime, high power requirements, and radiation sensitivity of Flash. At the forefront of this research is the phase-change random access memory (PRAM) [see Bez, R.; Pirovano, A. “Non-volatile memory technologies: emerging concepts and new materials” Materials Science in Semiconductor Processing 7 (2004) 349-355; and Lacaita, 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, $V_t$, is applied to the amorphous material [see Adler, D.; Henisch, 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). The device can be returned to an amorphous state by allowing more current through the device, thus heating the material above the melting temperature, and then quickly removing the current to quench the material into an amorphous, high resistance state (‘write 0’ current region, FIG. 2).


SUMMARY OF THE INVENTION

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; Lacaita, A. L. "Phase-change memories: state-of-the-art, challenges and perspectives" Solid-State Electronics 50 (2006) 24-31; and Chen, M.; Rubin, K. A.; Barton, R. W. "Compound materials for reversible, phase-change optical data storage" Appl. Phys. Lett. 49 (1986) 502-504], we know of no reports of phase-change memory operation with GeSe-based binary glasses. In this work, we have explored the possibility of inducing a phase-change response in the SnSe/Sn chalcogenide stack structures. We selected the Ge$_{50}$Se$_{50}$ glass since, like the GeTe glass, it contains homopolar 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$_{50}$S$_{50}$Te$_{5}$ at moderately elevated temperature" Jpn. J. Appl. Phys. 41 (2002) 7400-7401]. Additionally, the Ge$_{50}$Se$_{50}$ glass offers the advantage of higher glass transition temperatures (GeSe: $T_g=613$ K [see Feltz, A. Amorphous Inorganic Materials and Glasses, VCH Publishers Inc., Newyork, 1993, pg. 234]) over the Te-based glasses (GeTe: $T_g=423$ K [see Chen, M.; Rubin, K. A. "Progress of erasable phase-change materials" SPIE Vol. 1078 Optical Data Storage Topical Meeting (1989) 150-156]; GST: $T_g=473$ 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 memory 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 material 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.
using an Inficon IC 6000 with a single crystal sensor head. The base system pressure was 1×10⁻⁷ 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 Å W/800 Å Si₃N₄ and, (2) two wafers processed for device fabrication consisting of vats etched through a Si₃N₄ 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 Ge₄Se₃ films 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 Å 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 films 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’ DS5000, was used to qualitatively identify amorphous or polycrystalline films. TEM measurements were made with a Phillips Model CM300.

Electrical measurements were made using a Micromanipulator 6200 microprobe station equipped with temperature 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 umx80 um pads for electrical contact to the top and bottom electrodes.

Results and Discussion

The GeTe and Ge₄Se₃ 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 film deposition (11-7 Torr), oxygen is most likely incorporated into the SnTe, SnSe, and GeTe films during deposition. Our previous X-ray photoelectron spectroscopy measurements on evaporated films have shown that the percentage of oxygen in an evaporated film can be as high as 10%.

Table 1 provides the ICP results for the films characterized wafers that were included in the evaporation step with the device wafers in this study, as well as for a sputtered Ge₄Se₃ film wafer. Note that the only elements measured by ICP analysis were Ge, Se, Sn, and Te. The presence of oxygen is not detected with ICP and is not factored into the overall film composition. The evaporated SnTe and SnSe layers are almost stoichiometric, whereas the GeTe layer was deposited slightly Te-rich (53% compared to 50%). The sputtered Ge₄Se₃ films are stoichiometric.

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 film.

(a) GeTe/SnTe device—A TEM cross section image of a GeTe/SnTe device is shown in FIG. 5. The evaporated material has reduced step coverage over the sidewalls of the via, leading to thinner films in this region of the devices. The pre-sputter etch clean etches into the W bottom electrode by roughly 300 Å. Thus, the device structure consists of not only a via through Si₃N₄, but also an indented bottom electrode which subsequently allows the chalcogenide phase-change material to be in contact at the sides and bottom of the layer near the metal electrode.

Typical DC IV-curves for devices with the GeTe/SnTe stack structure are shown in FIG. 6. These curves were collected by forcing the current thru the devices from 10 pA to 100 µA and measuring the corresponding voltage across the devices with the positive potential on the electrode adjacent to the SnTe layer (the top electrode). The IV-curves, showing a 'snap-back', i.e. negative resistance, at the threshold voltage as well as a reduction in device resistance after sweeping the current, are characteristic of a phase-change memory device. There is slight device-to-device variation observed in IV-curves of unique devices (FIG. 6a-c). However, in each case the threshold voltage is less than 1.8 V and there are at least two ‘snap-back’ regions in the IV-curves. The additional ‘snap-back’ responses indicate that our devices may exhibit multi-state behavior. However, the stability of each resistance state is as yet unclear. Additionally, the cycling endurance and switching properties of each state have not been explored. Similar results, though not as well defined as those in FIG. 6, have been obtained on stacked Chalcogenide layers of GST/Si-doped GST [see Lai, Y. F.; Feng, J.; Qiao, B. W.; Cai, Y. F.; Lin, Y. Y.; tang, T. A.; Cai, B. C.; Chen, B. “Stacked chalcogenide layers used as multi-state storage medium for phase-change memory” Appl. Phys. A 84 (2006) 21-25] and are being explored as multi-state phase-change memories.

When the electrodes are reversed and a negative potential is placed on the device top electrode, the DC IV-curve is altered, as shown in FIG. 7, but the device still exhibits phase-change behavior. In this electrical configuration the threshold voltage has increased above 2V. In either potential polarity configuration, the threshold voltage and programming currents that we observe for the GeTe/SnTe stack structure are lower than those reported for recent single devices comprised of GST [see Lv, H.; Zhou, P.; Lin, Y.; Tang, T.; Qiao, B.; Lai, Y.; Feng, J.; Cai, B.; Chen, B. “Electronic Properties of GST for Non-Volatile Memory” Microelectronics Journal, in press].

Table 2 provides a comparison of the typical initial resistance of a device prior to switching and the programmed resistance after switching, as well as the measured threshold voltage for both the positive and negative current sweep cases. The resistances were measured at +20 mV in each case, a potential too low to perturb the state of the bit. Included in Table 2 are the typical programmed resistances when the current is swept to 1 mA (for both the positive and negative potential cases). Of note is the programmed resistance when
the current is swept to a -1 mA (top electrode at a negative potential) compared to the case when the current is swept to +1 mA. There is almost an order of magnitude decrease in the programmed resistance when +1 mA is forced at the top electrode compared to the bottom electrode. However, our results indicate that it is not necessary to use a current as high as 1 mA in order to program the bits (see the 100 uA results in Table 2).

(b) Ge2Se3/SnTe device—When the GeTe glass is replaced with a Ge2Se3 glass, the resultant Ge2Se3/SnTe devices exhibit resistance variable memory switching, FIG. 8. However, there are two distinct differences in the DC IV-curve compared to the GeTe/SnTe case. First, the threshold voltage, when the top electrode is at a positive potential, is higher in the Ge2Se3 case (greater than 3.5 V compared to less than 1.8 V for the GeTe/SnTe case). Second, the threshold voltage occurs at a current which is an order of magnitude lower than in the GeTe devices. Additionally, the Ge2Se3/SnTe devices exhibit better device-to-device consistency in their IV-curves compared to the evaporated GeTe/SnTe devices, most likely due to the better via sidewall film step-coverage inherent in the sputtered Ge2Se3 film, as well as a reduction in film impurities (such as oxygen).

FIG. 9 shows the corresponding current sweep IV-curves for the Ge2Se3/SnTe structure with a negative potential on the top electrode. The IV-curves for this negative sweep current show a much more well-defined threshold voltage than the positive current sweep case. In addition, the current at the threshold voltage is much higher than the positive current sweep case (FIG. 8). However, the negative potential Ge2Se3/SnTe IV curve (FIG. 9) shows similar threshold voltages and currents to the negative potential Ge2Te3/SnTe IV-curve (FIG. 7).

(c) Ge2Se3/SnSe device—When the SnTe layer is replaced with a SnSe layer in the Ge2Se3 stack, resistance switching is observed (FIG. 10) when a positive voltage is applied to the top electrode. The DC IV-curves for the Ge2Se3/SnSe device (FIG. 10) and the Ge2Se3/SnTe device (FIG. 8) show no differences due to the SnSe layer. However, when a negative potential is applied to a device that has not previously seen a positive potential, no threshold voltage is observed in the IV-curve (FIG. 11). This is in contrast to the case of the negative potential applied to a Ge2Se3/SnTe device (FIG. 9) where phase-change switching is observed with a threshold voltage less than 3 V.

The absence of a threshold voltage in the negative current sweep IV-curve (FIG. 11), but its presence in the positive current sweep IV-curve (FIG. 10) of the Ge2Se3/SnSe device implies that during the application of a positive potential there may be Sn-ion migration from the SnSe layer into the Ge2Se3 layer which chemically alters the Ge2Se3 layer to a (Ge2Se3),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 Ge2Se3/SnTe device when a positive potential is applied to the top electrode. However, unlike the Ge2Se3/SnSe device, switching is observed in the Ge2Se3/SnTe device when a negative potential is applied to the top electrode. A possible explanation for the observed negative potential switching in the Ge2Se3/SnTe device (FIG. 9) is that

<table>
<thead>
<tr>
<th>Device Stack</th>
<th>Initial Resistance (Ohms)</th>
<th>Programmed Resistance (Ohms)</th>
<th>Programmed Resistance (Ohms)</th>
<th>Threshold Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge2Se3/SnTe</td>
<td>&gt;5 x 10^6</td>
<td>1 x 10^6</td>
<td>5 x 10^3</td>
<td>1.6 V/2.5 V</td>
</tr>
<tr>
<td>Ge2Se3/SnTe</td>
<td>&gt;6 x 10^6</td>
<td>2 x 10^3</td>
<td>7 x 10^2</td>
<td>3.7 V/3.7 V</td>
</tr>
<tr>
<td>Ge2Se3/SnTe</td>
<td>&gt;6 x 10^6</td>
<td>1 x 10^3</td>
<td>5 x 10^2</td>
<td>3.7 V/3.7 V</td>
</tr>
<tr>
<td>Ge2Se3/SnTe</td>
<td>&gt;6 x 10^6</td>
<td>2 x 10^3</td>
<td>No data</td>
<td>~2.5 V</td>
</tr>
</tbody>
</table>

A '—' indicates no measurable response. Resistance was measured at 20 mV.

(a) Ge2Se3/SnTe device—When the SnTe layer is replaced with a SnTe layer in the Ge2Se3 stack, resistance switching is observed (FIG. 10) when a positive voltage is applied to the top electrode. However, unlike the Ge2Se3/SnSe device, switching is observed in the Ge2Se3/SnTe device when a negative potential is applied to the top electrode. A possible explanation for the observed negative potential switching in the Ge2Se3/SnTe device (FIG. 9) is that...
tive potential is applied to the top electrode, and no phase-change behavior is observed in the IV-curve. If it were possible for Se anions to be forced into the Ge$_2$Se$_3$ glass from the SnSe layer (analogous to the Te anions from the SnTe layer), they would succeed only in making the Ge$_2$Se$_3$ glass Se-rich and thus still incapable of phase-change switching. Alternatively, if a positive potential is initially applied across the Ge$_2$Se$_3$/SnSe 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 Ge$_2$Se$_3$ layer, creating a (Ge$_2$Se$_3$)$_x$Sn$_y$ 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$_x$Se$_y$ chalcogenide glass and adding small concentrations of various metals, and measuring the thermal properties of these materials. Metals we have tested include, Sn, Zn, In, and Sb. The Sn and In addition showed the presence of two crystallization regions whereas the Zn showed three crystallizations regions. Thus the Ge$_x$Se$_y$Zn$_z$ 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$_x$Se$_y$/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$_2$Se$_3$/SnTe 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.; Montegazza, D.; Lacaita, A. L. “Parasitic reset in the programming transient of PCM” 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 stacked 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 Namyanan, 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$_x$Sey.

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.

I claim:

1. A device suitable for phase-changing memory operation, comprising:
   - a plurality of stacked chalcogenide layers, wherein an electric field is applied to move an ion from one chalcogenide layer to another.
   - the device of claim 1 wherein one chalcogenide layer is a Ge-chalcogenide layer, and another chalcogenide layer is a Sn-chalcogenide layer.
   - the device of claim 2 wherein the Ge-chalcogenide layer comprises GeTe.
   - the device of claim 2 wherein the Ge-chalcogenide layer comprises Ge$_2$Se$_3$.
   - the device of claim 2 wherein the Sn-chalcogenide layer comprises SnTe.
   - the device of claim 2 wherein the Sn-chalcogindie layer comprises SnSe.

* * * *