An experimental investigation on the switching reliability of a phase change memory device with an oxidized TiN electrode

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Fluctuations (or drifts) in switching voltages such as programming set/reset voltages and threshold voltage pose serious obstacles to the reliable operation of electrical phase change memory devices. Using a phase change memory device having a GeSb2Te4 phase change material and TiN electrode, these fluctuations are demonstrated to result from device resistances varying with programming cycles. Fluctuating resistances appear to stem primarily from large contact resistances at the interface between the phase change material and the TiN electrode and from inhomogeneous phase distribution across the GeSb2Te4 layer due to unsuccessful heat confinement near the interface with TiN. Oxidation of a TiN electrode surface (via thermal annealing at 350 °C under an atmospheric gas mixture of 97.9 vol % N2 and 2.1 vol % O2) is very effective in the reduction of fluctuations in device resistances and switching voltages hence the resulting increase in the programming cycles by two orders of magnitude. From a high resolution transmission electron microscopy, the oxidized surface was shown to consist of a titanium oxide layer primarily with Ti2O3 crystallites which is presumed to yield enhanced stability of the device by the following two effects. Firstly, Ge, Sb, and Te atoms would have stronger bonds to oxygen atoms than to nitrogen atoms by about 0.5 eV, thereby producing more robust interface. Accordingly, the magnitude of contact resistance and its variation are reduced significantly so as to have little influence on the device resistances and their fluctuations. Secondly, thermally and electrically more resistive nature of the oxide layer would tend to yield, by enhanced generation and confinement of Joule heat, more uniform temperature distribution across the phase change material layer, rendering possibly a more homogeneous single phase material hence steadier sheet resistances with programming cycles. © 2006 American Institute of Physics. [DOI: 10.1063/1.2338130]

I. INTRODUCTION

The electrical phase change memory (originally known as the Ovonic memory) has been revitalized as one of the promising nonvolatile memory devices for next generations.1 This memory utilizes fast and reversible transitions between amorphous (reset) and crystalline (set) phases of Te-based chalcogenide semiconductors such as Ge2Sb2Te5 and GeSb2Te4, together with large concurrent changes in electrical resistivity by a factor of 104−106. Through remarkable progresses in the reduction of operating current and in the cal resistivity by a factor of 10±4 –10±6. Through remarkable progress in the reduction of operating current and in the

Concerning the device reliability, however, problems are still lingering on the way to practical use. For instance, variations in resistance4 and even malfunctions5 at successive switching operations seriously limit read operation and device cyclability as well. According to Lai,5 failures observed at successive switching operations may be categorized into three different types: stuck-set, stuck-reset, and reset migration. When a PCM device is stuck-set or stuck-reset, it cannot be switched to a reset or a set state, respectively, any more. In a device with the reset migration failure, programming reset current or reset voltage drifts with switching cycles. It has been suggested that the stuck-set and stuck-reset are closely related with physical failures such as undesirable phase segregation, detachment of phase change material layer from electrodes, etc., while the reset migration may be caused somehow by the instability of interface between phase change material and electrodes.

In this study, it is reported that migrations in threshold voltage Vth, set voltage Vset, and reset voltage Vreset are significantly reduced in pore-type phase change memory devices with an oxidized TiN electrode. These devices are shown to yield a better programming cyclability probably
because of such stabilized switching characteristics. As it turns out, these results may be attributed not only to reduced contact resistance and its variation resulting from stronger Ge-, Sb-, and Te-O bonds at the interface of GeSb$_2$Te$_4$ with an oxidized TiN but also to homogenization of an amorphous or a crystalline phase of GeSb$_2$Te$_4$ material stemming from an electrically and thermally resistive nature of titanium oxide interface layer.

II. EXPERIMENT

A. Device fabrication and electrical switching tests

Pore-type phase change memory devices were fabricated to have a GeSb$_2$Te$_4$ phase change material and an oxidized TiN electrode with either 50 or 70 nm contact hole, as shown in Fig. 1. It was previously reported$^6$ that a surface oxidation of TiN electrode is quite effective to reduce set and reset voltages, lowering power consumption in phase change memories. The surface oxidation was made via thermal annealing of a half-formed device with a bare contact hole at 350 °C under an atmospheric gas mixture of 97.9 vol % N$_2$ and 2.1 vol % O$_2$ prior to GeSb$_2$Te$_4$ deposition. From cross-sectional transmission electron microscopy, it was found that the oxidized layer on the TiN surface has a thickness ranging from 5 to 10 nm with varying the annealing time from 10 to 60 min. For comparison, a reference device without oxidation was also prepared.

In as-fabricated devices, the GeSb$_2$Te$_4$ material has an amorphous phase. In order to prepare the devices for subsequent switching operations,$^7$ they were all first fired by sweeping a current up to 5 mA. The threshold voltages at first firings were scattered in the range of 1.0–1.6 V for all devices and unaffected by oxidation treatments. A first-fired device was then reversibly switched between set and reset states. Between set and reset operations, resistances of the device were measured at the read voltage of 0.2 V. Transient on/off tests were also carried out by cyclic repetition of an essentially identical sequence of write pulses that would affect, in each cycle, switchings from a reset state to a set state and lastly to another reset state. Each cycle led to a resistance-voltage ($R$-$V$) plot from which representative values of $V_{\text{set}}$ and $V_{\text{reset}}$ are readily determined.

B. Measurement of contact resistance at the GeSb$_2$Te$_4$/TiN interface

In order to examine the electrical characteristics of the interfaces between the memory material and the electrodes, contact resistances were measured using a transmission line model (TLM) method.$^8$ The method is well known as a very simple and reliable technique to measure both the contact resistance at a metal/semiconductor Ohmic interface and the sheet resistance of semiconductor. Shown in Figs. 2(a) and 2(b) are a schematic layout and an optical image of our TLM pattern with GeSb$_2$Te$_4$ material on a patterned electrode of either TiN or oxidized TiN for 30 min (hereafter “oxidized” refers to “oxidized for 30 min” unless specified otherwise). According to the model, a total resistance $R_T$ between combinations of two Al pads is given by Eq. (1) when parasitic resistances due to metallic layers (Al and TiN) are assumed to be negligible,

$$R_T = 2R_c + R_{\text{sh}} \frac{d}{W},$$

where $R_c$ is the contact resistance at GeSb$_2$Te$_4$/TiN interface, $R_{\text{sh}}$ is the sheet resistance of GeSb$_2$Te$_4$ material, $d$ is the distance of two TiN pads, and $W$ is the width of GeSb$_2$Te$_4$ transmission line (200 μm), respectively. By a linear fitting of measured $R_T$ data with respect to $d$ in the manner of Eq. (1), $R_c$ and $R_{\text{sh}}$ can be readily determined from the intercept with $R_T$ axis (i.e., $2R_c$ for $d=0$) and the slope ($R_{\text{sh}}/W$) respectively.

C. Compositional and structural analyses of the GeSb$_2$Te$_4$/TiN interface

The oxidation treatment of TiN electrode may produce changes not only in the chemical composition and the bonding character of the surface layer of TiN electrode itself but also the bonding environment of Ge, Sb, and/or Te atoms facing TiN electrode. To obtain information in this regard, x-ray photoelectron spectroscopy (XPS) was performed with the layered structures of GeSb$_2$Te$_4$ on either nonoxidized TiN or oxidized one. In addition, a high resolution transmis-
III. RESULTS AND DISCUSSION

A. Improvement of memory switching performance in the device with an oxidized TiN electrode

Shown in Fig. 3(a) are changes in resistance with switching counts for the devices having a nonoxidized and an oxidized TiN electrode, respectively. With the test scheme stated above, over 60 switchings were made between high-resistive amorphous (reset) and low-resistive crystalline (set) states of both devices and some elementary stability characteristics were compared between the two. In the case of a nonoxidized TiN electrode, the resistance values of the two limiting states ($R_{\text{set}}$ and $R_{\text{reset}}$) are significantly fluctuating with switching counts, along with a drift in the resistance ratio in the range of $10^1 - 10^2$. Correspondingly, $I$-$V$ curves were found to vary with switching counts, as illustrated in Fig. 3(b), by the curves of a few selected reset states. It should be noticed that the $I$-$V$ slope (device resistance) as well as the snapback voltage for a threshold switching varies among different curves.

By contrast, a device with oxidized TiN electrode tends to yield much steadier values of $R_{\text{set}}$, $R_{\text{reset}}$, and $V_{\text{th}}$ with cycles, as shown in the lower half of Fig. 3(a), and in the $I$-$V$ curves of Fig. 3(c). Erratic variations in $R_{\text{set}}$ and $R_{\text{reset}}$ are found much reduced and correspondingly, the $I$-$V$ switching curves appear more robust. The effects of oxidized TiN electrode are more clearly seen from Figs. 4(a) and 4(b) summarizing the results for various oxidation times. Along with reduced scatters, mean values of $R_{\text{set}}$, $R_{\text{reset}}$, and $V_{\text{th}}$ are characteristically much smaller for all devices with oxidized TiN electrode. In addition, it is noticeable from Fig. 4(b) that $V_{\text{th}}$'s at the first threshold switching are considerably higher than those of successive switchings (so called as first-firing effect) in all devices, indicating that they are independent of TiN oxidation process.

As for set and reset voltages, TiN oxidation treatment also yields a noticeable stabilizing effect, as shown in Fig. 5, representing $R$-$V$ plots from transient on/off tests with the device having an oxidized TiN electrode and the reference one, respectively. For the device with an oxidized TiN, $R$-$V$ plots appear more reproducible with the switching voltages.
V_{\text{set}} and V_{\text{reset}}, which tend to have less variations in the ranges of 0.4–0.6 V and 2.0–3.0 V, respectively. Complying with these results, a device with oxidized TiN electrode was also found to have a pronouncedly improved endurance against extended programming cycles relative to the one with a nonoxidized TiN. Shown in Fig. 6 are the low-field resistance values of the devices varying with cycles. Compared with a poor cyclability (less than 10^2 cycles) of the device with a nonoxidized TiN, the device with an oxidized TiN continues working properly until it gets stuck at \( 3 \times 10^2 \) \( \Omega \) after 10^6 cycles, failing to reproduce a reset state any further (stuck-set fail). The detailed mechanism of this failure is not understood yet but it may be related with an undesirable phase formation at the interface between GeSb_2Te_4 and oxidized TiN materials.

From the experimental findings described above, the following two questions apparently arise. Firstly, “what are the possible causes of the fluctuations in reset and set resistances and correspondingly in reset, threshold, and set voltages?” And secondly, “how these fluctuations may be suppressed by the oxidation of TiN electrode?” We attempt to answer these questions in the following sections.

### B. Reductions in contact resistance and its variation in the device with an oxidized TiN electrode

For the TLM analysis to be valid, a GeSb_2Te_4 material must have an Ohmic contact with a TiN electrode. Shown in Figs. 7(a) and 7(b) are typical I-V curves taken from four different material combinations at \( d=70 \mu m \): an amorphous (a-) and a crystalline (c-) GeSb_2Te_4 materials in contact with a patterned TiN electrode either nonoxidized or oxidized, respectively. Notice that all the contacts are Ohmic. [c] and [d] Resistances due to TLM measurements as a function of interpad distance for an amorphous and a crystalline GeSb_2Te_4 phase change material, respectively. [e] and [f] Contact and sheet resistances determined from the intercepts with \( R_T \) axis and the slopes \( (R_s/W) \) for (c) and (d), respectively.

From Figs. 7(c) and 7(d), the combinations having a-GeSb_2Te_4 materials are found to yield fairly linear \( R_T \)-d relations with pronouncedly positive slopes while linearities and finite slopes are not so obvious for those having c-GeSb_2Te_4. From the measurement geometry of a TLM pattern, \( R_T \) is supposed to vary in proportion to \( d \) when \( R_c < R_{sh} \), whereas such a proportionality may not be present when \( R_c > R_{sh} \). Thus, it follows that the combinations having a-GeSb_2Te_4 fall into the former category while those having c-GeSb_2Te_4 into the latter one. Indeed, it is clearly demonstrated in Figs. 7(e) and 7(f) that \( R_c \)'s of the interfaces with a-GeSb_2Te_4 are smaller by an order of 10^4–10^5 than \( R_{sh} \)'s, whereas \( R_c \)'s of the interfaces with c-GeSb_2Te_4 are compa-
From comparison between the two cases, however, it is evident that remarkable changes were made in O enrichment as well as N depletion. These changes are presumed to attend the formation of a thin titanium oxide surface layer, which is known to occur frequently during reactive sputtering deposition of TiN. In both cases, significant amounts of O and C are detected in the interior and at the surface of TiN. Presumably, they were incorporated from a low-vacuum environment or a contaminated chamber wall during reactive sputtering deposition of TiN.

From comparison between the two cases, however, it is evident that remarkable changes were made in O and N profiles at the surface of TiN by oxidation treatment: prominent O enrichment as well as N depletion. These changes are presumed to attend the formation of a thin titanium oxide surface layer, which is known to occur frequently during oxidation of TiN especially with porous columnar grains. In fact, Ti 2p XPS spectra of Fig. 8(d) display strong Ti–O peaks near the interface of the oxidized TiN with GeSb2Te4, as compared with the nonoxidized case of Fig. 8(c).

C. Presence of titanium oxide layer on the oxidized TiN interface and its possible effect on contact resistance

XPS is an effective tool to obtain information on the compositional profile (qualitative) and atomic bonding character of constituent elements with a depth resolution of below 10 nm. Shown in Figs. 8(a) and 8(b) are the depth profiles of some elements in the layered structures of SiO2 (capping layer) 50 nm/GeSb2Te4 50 nm/TiN 50 nm (a) without and (b) with oxidation. In both cases, significant amounts of O and C are detected in the interior and at the surface of TiN. Presumably, they were incorporated from a low-vacuum environment or a contaminated chamber wall during reactive sputtering deposition of TiN.
an oxidized TiN. Shown in Fig. 9 are (a) a high-
magnification bright-field image and (b) an atomic-resolution
image of an oxidized TiN. The surface oxide layer is found
to be 7–8 nm thick and appears to consist mostly of crystal-
lites in an amorphous matrix otherwise. From an electron
diffraction pattern reconstructed by a fast Fourier transform
[see Fig. 9(c) or 9(d)] of the atomic-resolution image of the
selected area in Fig. 9(b), d spacings were determined to
show a good agreement with some of the known d spacings
of titanium sesquioxide (Ti$_2$O$_3$), as summarized in Table I.

Ti$_2$O$_3$ is thermodynamically favored to form over TiO$_2$
but not over Ti$_n$O$_{2n-1}$ (4 ≤ n ≤ 9, Magnéli phases) during
oxidation of TiN (or Ti) under an atmospheric environ-
ment in the temperature range of 273–1273 K. Nevertheless,
Ti$_2$O$_3$, a phase with less oxygen content than Magnéli
phases, comes to presence, which may be accountable by an
oxygen-deficient environment of the present oxidation pro-
cess (a gas mixture of 97.9 vol % N$_2$ and 2.1 vol % O$_2$).
Ti$_2$O$_3$ is known as a semiconductor or a semimetal with the
electrical resistivity of 3 × 10$^{-4}$–5 × 10$^{-2}$ Ω cm in the tem-
perature range of 250–1000 K. Since the oxide layer is not
only very thin but is largely made up of electrically conduct-
ing Ti$_2$O$_3$ crystallites, its sheet resistance would make little
increment to the device resistance: the resistance of a
7-nm-thick oxide layer with 10$^{-3}$ cm in the contact area of
50×50 nm$^2$ is no more than 28 Ω, which is too small to
affect the device resistance.

With regard to changes in atomic bonding character at
the GeSb$_2$Te$_4$/TiN interface due to the formation of the ox-
ide layer, XPS spectra of Fig. 10 taken from SiO$_2$/amorphous
GeSb$_2$Te$_4$/TiN layered structures are very suggestive. It is
noticed that all the peaks due to Ge, Sb, and Te atoms are
shifted to higher bonding energies by about 0.5 eV in the
interface by oxidation treatment. These shifts can be taken as
signatures of higher bond strengths of Ge, Sb, or Te element
with O rather than with N in view of the respective bond
strengths in diatomic gas phases, as listed in Table II. It is
mostly likely that the formation of stronger bonds of Ge, Sb,
and Te atoms with O in the oxidized TiN would render an interface that could possibly have less defects due to increased barrier for defect formation hence a reduced contact resistance.

D. Evolution of temperature profiles in the devices with nonoxidized and oxidized TiN electrodes

The aforementioned oxide layer is presumed to be electrically and thermally more resistive than TiN (see Table III) and, therefore, most likely to enhance generation and retention of Joule heat for a given electrical input power. In order to examine the possible consequences of such changes on the stabilization of resistances and switching voltages, spatial and temporal temperature profiles were calculated by use of a MATLAB®-based finite element method (FEM) toolkit. For calculations, the device was assumed to have a cylindrical symmetry with the radial cross section schematically shown in Fig. 11(a) and the material constants listed in Table III were utilized. Illustrated in Figs. 11(b) and 11(c) are the serial snapshots of the temperature profiles in the course of heating by a 1 mA reset pulse of 20 ns duration at the central axis of symmetry of the respective devices without and with an interface oxide layer of 10 nm thick. For this calculation, the electrical resistivity of the interface oxide was taken to be an interface oxide layer of 10 nm thick. For this calculation, the electrical resistivity of the interface oxide was taken to be 3×10−2 Ω cm and the thermal conductivity of 5 W/m K. With a different choice of constants, calculated temperatures in the GeSb2Te4 layer of the device with an oxidized TiN were found to vary significantly in magnitude but to remain always higher than in the nonoxidized case inasmuch as the electrical and the thermal resistivities of the oxide are higher than TiN. These relatively higher temperatures can account for lower switching voltages of the oxide-formed devices in Figs. 4(b) and 5 of the present study and in Fig. 3 of our previous study6 as well.

More importantly, a drastic difference in the temperature profile can be noticed within the GeSb2Te4 layer by comparison between Figs. 11(b) and 11(c). In the case of a device without the interface oxide layer, the temperature distribution across the GeSb2Te4 layer is very inhomogeneous. Near the TiN bottom electrode, in particular, heat confinement is exceedingly difficult, leaving a vicinal layer of phase change material in a melting-free solid state all the time. Accordingly, a reset operation would always yield a tandem structure of a crystalline and an amorphous phase across the GeSb2Te4 layer. In a device with the interface oxide layer,

![FIG. 10. Ge 3d, Sb 4d, and Te 4d XPS spectra across the interfaces of amorphous GeSb2Te4 material with nonoxidized or 30 min oxidized TiN electrode.](image)

TABLE III. Some physical constants of amorphous and crystalline GeSb2Te4, SiO2, Al, TiN, and Ti2O3 at room temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mass density ρ (×10^6 g/m³)</th>
<th>Specific heat c (J/g K)</th>
<th>Thermal conductivity κ (W/m K)</th>
<th>Electrical resistivity ρ_{elec} (μΩ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline GeSb2Te4</td>
<td>6.47</td>
<td>0.202</td>
<td>0.5</td>
<td>10^12 – 10^14</td>
</tr>
<tr>
<td>Amorphous GeSb2Te4</td>
<td>&lt;6.47</td>
<td>0.202</td>
<td>0.17</td>
<td>10^7 – 10^9</td>
</tr>
<tr>
<td>SiO2 (fused silica)</td>
<td>2.27</td>
<td>1.05</td>
<td>1.4</td>
<td>10^15</td>
</tr>
<tr>
<td>Al</td>
<td>2.71</td>
<td>0.897</td>
<td>237</td>
<td>3</td>
</tr>
<tr>
<td>TiN</td>
<td>5.24</td>
<td>0.784</td>
<td>22</td>
<td>100</td>
</tr>
<tr>
<td>Ti2O3</td>
<td>4.375</td>
<td>0.697</td>
<td>1–10^4</td>
<td>3 × 10^4–5 × 10^2</td>
</tr>
</tbody>
</table>


*Reference 14.

*Measured values using a four-point probe in this study.

*Assumed to be medium values of TiO2 and Ti.

*Reference 11.
temperature near the interface can be raised remarkably to reduce and furthermore to reverse temperature gradients across the phase change layer by way of enhanced generation and confinement of Joule heat by the oxide layer. As a result, a reset operation would produce a melt-quenched amorphous phase possibly across the entire GeSb2Te4 layer.

Simple as it may be, another explanation is advanced, based on the observed differences, as to why reset resistances and accordingly switching voltages of a device with a TiN are more fluctuating than those of a device with an oxidized TiN. In view of the markedly steep temperature distribution within the phase change layer facing with a TiN electrode, a tandem structure of a crystalline and an amorphous phase appears very unstable to change its composition with respect to fluctuations in input reset voltage, for instance. Considering a large difference in electrical resistivity of the two phases, the tandem structure of a varying composition may give rise to a serial resistance of large fluctuating magnitudes accordingly. As for a set operation, these arguments may apply similarly.

The oxidation process employed in the present work has a good compatibility with standard complementary metal-oxide semiconductor (CMOS) processes. Due to its relatively low thermal budget (350 °C for tens of minutes), the process is supposed to have little adverse effect on the device structure formed in the previous steps and its resulting characteristics. In fact, similar processes have been widely used to improve the performance of TiN diffusion barriers.9 We believe that the present oxidation process can be also adopted to fabricate T-plug-type memory cells constituting some of the latest prototypes of phase change random access memories.1–3

IV. CONCLUSION

Large fluctuations in set and reset resistances and the corresponding set, threshold, and reset voltages are observed commonly in pore-type phase change memory devices with a GeSb2Te4/TiN cell structure and they deteriorate the cycling performance of the device. It is suggested that these fluctuations have much to do with fluctuations in contact resistance of a large magnitude at the GeSb2Te4 material/TiN interface and additionally with the phase inhomogeneity such as a two-phase reset state resulting from an inferior heat confinement in the GeSb2Te4 layer near the TiN electrode.

The oxidation of TiN electrode at 350 °C under an atmospheric gas mixture of 97.9 vol % N2 and 2.1 vol % O2 was found to reduce the values of set and reset resistances and their fluctuations, resulting in the stabilization of switching voltages. Consequently, the devices with an oxidized TiN electrode were made to endure beyond 10⁴ programming cycles, which are higher by two orders of magnitude than the devices without oxidation. These results may be attributed to a thin titanium oxide layer of several nanometers thick between GeSb2Te4 material and TiN electrode. It was shown that this oxide layer consist primarily of Ti2O3 crystallites in an otherwise amorphous matrix and provides Ge, Sb, or Te atoms at the interface with chances of forming O bonds having increased binding energies by about 0.5 eV relative to the respective N bonds. This may lead to a more robust, defectless interface with significantly decreased contact resistance and its variation, consequently resulting in the reduced fluctuations of set/reset resistances and switching voltages. In addition, thermally and electrically more resistive nature of the interface oxide layer than TiN could play an important role in stabilizing these switching parameters by producing more uniform temperature profiles to have steadier sheet resistances of GeSb2Te4 material.

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