Threshold Switching in Te–SbO Films for the Selection Device of Crossbar Resistive Memory Applications

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Threshold switching (TS) of a Te–SbO film with high thermal stability up to 300°C and DC endurance over 200 cycles was achieved. Te atoms in both as-deposited and annealed films exist as separate nanocrystalline clusters. The SbO matrix formed in the amorphous phase with the metallic Te was the metallic phase. Amorphous Te formed between the SbO nanocrystallites during electroforming was presumed to act as a conduction path, inducing TS. Formation of amorphous Te in the conduction path can be explained by electric-field-driven drift of Te from the Te nanoclusters when a high field is applied during electroforming.

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Resistance-switching random access memory (ReRAM) is considered to be one of the most promising candidates for next-generation nonvolatile memory as the down-scaling of charge-based memory, such as dynamic random access and flash memory, approaches physical limitations. This is because of the scalability, non-volatility, fast switching speed, and low power consumption characteristics of ReRAM. Among the advantages of ReRAM, its scalability using the crossbar array is expected to be beneficial because of its small cell area (4 F2). F is the minimum feature size and the availability of three-dimensional stacking. However, there are several problems in using the crossbar array, such as the cross-talk problem between neighboring cells during the writing/reading processes because of sneak current. Thus, preventing sneak current in the crossbar array is an important issue, and there have been many reports about selection devices that suppress sneak current. Initially, conventional selection devices, such as diodes and transistors, were considered for ReRAM devices. However, unidirectional diodes cannot be used for bipolar ReRAM and transistors are not suitable in the crossbar array because of its three-terminal structure. Recently, various selection devices, such as metal–insulator transition switches and mixed ionic electronic conductors, have been proposed because of their bi-directional property and two-terminal structure. However, there is still no consensus on selection devices for ReRAM.

Threshold-switching (TS) materials, such as chalcogenides, have recently been proposed as selection devices of ReRAM because of their high current density and fast switching speed, as well as their bi-directional property and two-terminal structure. TS of chalcogenide materials occurs when a voltage higher than the threshold voltage (Vth) is applied. Then, the resistance of the film rapidly changes from a high resistive state (OFF) to a low resistive state (ON). The device remains in the ON state until the applied voltage is lower than a minimum voltage called the holding voltage (Vh). Subsequently, the device returns to the high resistive OFF state, and this phenomenon is repeatedly observed. However, common chalcogenide TS materials have serious problems in terms of thermal stability because they lose TS by thermal annealing and subsequent crystallization. Crystalization of chalcogenide materials removes some defects related to valence alternation pairs (VAPs) that cause TS. Thus, preventing crystallization during the device process is considered to be one of the most important issues in chalcogenide TS selection devices. In this letter, the electrical and chemical properties of threshold-switching Te–SbO films were investigated. The Te–SbO film showed stable TS behavior even when the majority of the Te in the film was crystallized, which means that the Te–SbO film is free from the crystallization issue. Significant differences between the Te–SbO film and general TS materials were verified in various aspects, and the TS mechanism of the Te–SbO film is proposed.

Te–SbO thin films were deposited on Pt/Ti/SiO2/Si substrates by co-sputtering Sb and Te targets using reactive sputtering. The gas flow rates of Ar and O2 were 10 sccm and 1 sccm. The chamber pressure was 6 mTorr and the growth was carried out at 25°C. The thickness of the Te–SbO films was 200 nm, which was confirmed by cross-sectional field-emission scanning electron microscopy (FE-SEM, Hitachi, S4800). The chemical bonding states of the deposited film were investigated by X-ray photoelectron spectroscopy (XPS, Sigma probe). The composition of the films was estimated by energy dispersive spectroscopy (EDS, Carl Zeiss, SUPRA 55VP). For electrical characterization, a metal–insulator–metal (MIM) structure with 60-nm-thick Pt electrodes was fabricated. The top and bottom Pt electrodes were deposited using e-beam evaporation. The bottom electrode was a continuous film on a 100-nm-thick thermal SiO2/Si substrate while the top electrodes (radius = 300 μm) were patterned by shadow masking. The current–voltage (I–V) curve was measured by a HP 4145B semiconductor parameter analyzer in current–voltage sweep mode. The annealing process was carried out for 5 min on a hot plate in air ambient with Pt/Te–SbO/Pt full devices. The annealing time was varied from 1 min to 1 hr and no clear difference was observed; therefore, 5 min was used in this study. Transmission electron microscopy (TEM, JEOL, JEM-2100F) and electron diffraction were used to verify the crystallinity of the Te–SbO film. Here, the Te–SbO film was directly deposited on a Cu grid with carbon mesh for plan-view imaging.

Figure 1a shows I–V curves of the TS behavior in the Te–SbO MIM structures. The measurement was carried out in DC sweep mode with compliance current (Ic) of 10 mA and the resistance of the film was measured at 0.5 V. The pristine samples showed insulating behavior without TS and required electroforming to allow observation of the TS. During electroforming, the current abruptly increased to Ic at 3.5 V. The resistance of the pristine MIM device without annealing decreased from 1.31 × 1012 to 7.68 × 1010 Ω after electroforming. This electroforming is considered to form conduction paths in the film. After electroforming, the Te–SbO MIM device showed TS. The current abruptly increased at Vh (~0.8 V) with increasing voltage, and decreased at Vh (~0.5 V) with decreasing voltage. This TS behavior was also observed in the negative voltage sweep, which confirms bi-directional TS of the Te–SbO film. Even after annealing of MIM device up to 300°C, almost the same TS behavior was observed with
an average $V_{th} = 0.81$ V ($\sigma = 0.07$ V) and an average resistance of 8.5 $\times$ 10$^7$ $\Omega$ ($\sigma = 2.2 \times 10^5 \Omega$). This confirms the high thermal stability of the Te–SbO thin film, which is rarely achieved in chalcogenide materials. In the case of the device annealed at over 350 °C, Ohmic-like $I$–$V$ curves were observed as shown in inset of Fig. 1a. Te evaporation during high-temperature annealing was believed to cause such behavior, as confirmed by TEM and EDS analyses (data not shown).

The endurance characteristics of the as-deposited Te–SbO film without annealing were examined, and are shown in Fig. 1b. Here, the DC sweep was performed using voltage of fixed polarity (positive bias on the top electrode, forward-scan only to minimize the damage due to excess $I_{cc}$ flow for long time during reverse-scan). Switching was achieved over 200 cycles without failure, which indicates the excellent endurance characteristics of the Te–SbO film. The degradation was observed after $\sim$260 cycles. The stable operation also suggests that the Te–SbO thin film shows no drift and accumulation/loss of charged species, which is frequently observed for oxide-based resistive switching thin films.\textsuperscript{14} The distribution range of $V_{th}$ was 0.75–1.07 V with an average of 0.88 V ($\sigma = 0.09$ V), and the resistance distribution was $7.20 \times 10^2$ to $2.47 \times 10^3$ $\Omega$ with an average resistance of 1.25 $\times$ 10$^3$ $\Omega$ ($\sigma = 3.3 \times 10^2$ $\Omega$). The small distributions of $V_{th}$ and resistance were caused by electrical stress because of the DC sweep, which is also commonly reported for ReRAM devices.\textsuperscript{15} It should be mentioned that DC sweep is a harsh test environment for chalcogenide thin films considering the excessive Joule heating and electric field stress. Under actual operating conditions using AC pulses, a narrower distribution of the endurance characteristics with improved cyclability is expected.

To identify the chemical binding status of Te and Sb, XPS measurement was conducted on the as-deposited Te–SbO film. The Sb 3d$\text{_{5/2}}$ peak was detected at 530.4 eV, as shown in Fig. 2a, which is the mid-point of Sb$_2$O$_3$ ($\sim$530.0 eV) and Sb$_2$O$_5$ ($\sim$530.8 eV).\textsuperscript{16} The metallic Sb peak ($\sim$528 eV) was not detected, which indicates that every Sb atoms was oxidized and exists as SbO$_3$ ($1.5 < \pi < 2.5$).

Te 3d$\text{_{3/2}}$ peak was fitted with two separate peaks, as shown in Fig. 2b. The main fitted peak is centered at 573.2 eV, which is consistent with the metallic Te peak. The sub-fitting peak at a binding energy 576.1 eV corresponds to Te in TeO$_2$, indicating that a small portion ($\sim$5% based on estimation) of Te atoms in the Te–SbO film are oxidized. The different binding status of Te and Sb in the oxide can be understood by the difference in the Gibb’s free energy of formation ($\Delta G_f$) at 298 K: $\Delta G_f$ per mole of molecular oxygen for Sb$_2$O$_3$, Sb$_2$O$_5$, and TeO$_2$ are $-417.555$, $-331.658$, and $-269.581$ kJ/mol, respectively.\textsuperscript{17} Consequently, Te oxidation occurs after the complete oxidation of Sb. It is believed that the low O$_2$ flow rate during deposition suppressed complete oxidation of Te while Sb was almost oxidized. No Sb–Te bonding was observed, which is reasonable considering the relatively low $\Delta G_f$ of Sb$_2$Te$_3$ ($-58.542$ kJ/mol).\textsuperscript{17}

For accurate observation of the microstructure, plan-view TEM analysis of the Te–SbO film was carried out. The images from cross-sectional TEM analysis were not included to avoid any artifacts (especially Te crystallization) which may be induced during sample preparation. Figure 3a shows the diffraction pattern of the as-deposited Te–SbO film. Eight crystalline ring patterns are observed, which is consistent with the d-spacing of crystalline Te in the JCPDS database (#36-1452), as shown in Table I. After annealing at 200 °C, more crystalline Te ring patterns (11 rings) are observed, as shown in Fig. 3b. According to the diffraction patterns, it can be concluded that crystalline Te formed during deposition and additional crystallization occurred during 200 °C annealing. Figures 3c and 3d show the bright-field plan-view TEM images of as-deposited and 200 °C annealed Te–SbO films, respectively. Crystallized Te nanoclusters

![Figure 1](image1.png)

Figure 1. (a) Initial log($I$–$V$) curves of as-deposited and annealed Te–SbO films. Inset show the $I$–$V$ curve of 350 °C annealed Te–SbO film, showing Ohmic behavior. (b) DC endurance characteristics of Te–SbO film without annealing. Over 200 times of forward-scan were conducted without degradation.

![Figure 2](image2.png)

Figure 2. XPS spectra of (a) Sb 3d$_{5/2}$ and (b) Te 3d$_{3/2}$ in as-deposited Te–SbO film.

![Figure 3](image3.png)

Figure 3. Diffraction patterns and their indexing (explained in Table I) of (a) as-deposited and (b) 200 °C annealed Te–SbO films. TEM bright-field plan-view images of (c) as-deposited and (d) 200 °C annealed Te–SbO films. HRTEM images and fast Fourier transformed micrographs of (e) as-deposited and (f) 200 °C annealed Te–SbO films.
are observed as dark spots. The average areas of the nanoclusters of the as-deposited and annealed films are 474.6 (σ = 207.6) and 496.3 nm² (σ = 271.8), respectively. The similar distributions of the nanoclusters for both films indicates that 200 °C annealing did not affect the Te nanoclusters, except for improving the crystallinity. The crystallinity of Te nanoclusters was further observed by high-resolution TEM (HRTEM), as shown in Figs. 3e and 3f. Both HRTEM images show similar distributions of crystalline Te nanoclusters. The inset figures correspond to their fast Fourier transformed (FFT) images show similar distributions of crystalline Te nanoclusters. The current reached 200 °C annealing did not significantly change during 150 °C annealing. In contrast, Ohmic-like I–V behavior was observed for the 200 °C annealed MIM structure (Fig. 4d). The current reached I₉ = 10 mA at 0.19 V and the resistance was 18.95 Ω.

Among the three candidates for the conduction path (Te, Sb, and O-deficient SbO), only drifted Te can explain this change from TS to Ohmic-like conductance after 200 °C annealing. It is expected that amorphous Te in the conduction path crystallized during annealing, which corresponds to the diffraction pattern that showed additional crystallization after 200 °C annealing. In the cases of Sb and Sb-rich SbO mentioned above, the conduction path would be more insulating because Sb and Sb-rich SbO re-oxidized during annealing. It is expected that Te incorporated in the conduction path from Te nanoclusters by field-driven drift, which is similar to the movement of active electrode metals, such as Cu and Ag, in electrochemical metallization memory cells (ECM). In the case of ECMs, active electrode metals are ionized to cations and drift to the negatively biased electrode occurs. Similarly, it is expected that Te in Te–SbO could be ionized to anions and drifted by the electric field. A recent report by Yoo et al. supports our assumption. They found that the drift of ionized Te by the electric field is the origin of bipolar switching in amorphous Ge₂Sb₂Te₅ film. Figure 5a shows a schematic diagram of the pristine state of Te–SbO. There are Te nanoclusters in the amorphous SbO matrix (the size and distribution of the Te nanocluster is exaggerated in this schematic diagram). When a positive (negative) bias is applied to the top (bottom) electrode (Fig. 5b), electrons are injected from the bottom electrode into nearby Te nanoclusters. This causes the ionization of Te. The negatively charged Te ions could drift to the positive-biased top electrode under a high electric field. When the growing conduction path reaches the top electrode, Te ions become neutral Te atoms losing electrons to the top electrode and the electroforming process is complete (Fig. 5c). It is expected that the Te atoms in the conduction path exist in the amorphous phase, including three-fold coordinated atoms with dangling bonds, rather than the ordered crystalline phase. These amorphous Te atoms in the conduction path generate VAPs and therefore TS occurs in the Te–SbO film. When the electroformed Te–SbO film is annealed above 200 °C, Te atoms in the conduction path are arranged in an ordered crystalline phase and VAPs disappear (Fig. 5d). Consequently, the I–V characteristics change to Ohmic-like I–V.

### Table 1. Measured lattice spacing (d (Å)) based on the rings in Figs. 3a and 3b and the standard atomic spacing of Te along with the respective hkl indices from the JCPDS database (#36-1452).

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<td>3.229</td>
<td>2.533</td>
<td>2.234</td>
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<td>10⁻⁶</td>
<td>10⁻⁶</td>
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Figure 4. Log(I–V) curves of the as-prepared Te–SbO MIM device for (a) electroforming and (b) TS behavior. After electroforming, the MIM devices were annealed at 150 and 200 °C and (c) and (d) correspond to their I–V curves, respectively.
Figure 5. Schematic representation of the threshold switching mechanism in Te–SbO: (a) pristine state, (b) electroforming operation, (c) TS operating state, and (d) annealed after forming state.

In summary, the TS behavior of Te–SbO films was investigated. Highly stable TS was observed over 200 cycles of DC sweep. XPS and TEM analyses verified that Te in both the as-deposited and annealed Te–SbO films formed separate nanosized crystalline clusters. TS was observed even though most of Te was crystallized, which contrary to conventional TS materials. It is proposed that electroforming creates links composed of amorphous Te between crystalline Te clusters, and these regions are responsible for repeatable and reliable TS. Delaying the formation of the TS region after electroforming resulted in high thermal stability of the as-deposited Te–SbO film, suggesting a way to improve the thermal stability of TS materials.

Acknowledgment

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References