Nanoscale Switching and Degradation of Resistive Random Access Memory Studied by In Situ Electron Microscopy

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Abstract

The metal-filament-type resistive random access memories (ReRAMs) with copper were investigated from the point of view of dynamical microstructure evolution in the repetitive switching operations using in situ transmission electron microscopy (in situ TEM). Through a series of experiments for uncovered solid electrolyte films, stacked devices, and nanofabricated cells, formation and erasure of the copper filaments and deposits were confirmed. The behavior of the filament and deposit depended on the switching condition and history. Based on these in situ TEM results, the switching schematics and the degradation process were discussed.

Keywords: in situ transmission electron microscopy, resistive random access memory, ReRAM, conductive bridge random access memory, CBRAM, memristor, conductive filament

1. Introduction

The resistive random access memory (ReRAM) has great potential as a candidate of the next-generation nonvolatile memory because of the high-speed operation, the wide memory window, and the high-density storage per cost [1]. In addition, its capability of the multilevel or analogue memory control and its hysteretic nonlinear current-to-voltage (I–V) characteristics are suitable for the operation of the artificial neural network hardware using memristors, and this research field is very active especially in these years [2–5]. Because of these advantageous properties, vast numbers of works on ReRAMs have been reported as described in numerous review
articles [6–14]. In these years, highly integrated memory chips have been reported [15–17], and a 16 Gbits chip with 180 MB/s write and 900 MB/s read performance fabricated at the 27 nm node has already been demonstrated using the Cu-based ReRAM [18]. Commercialized or nearly commercialized ReRAM chips have also been reported [19–21]. However, there are still ambiguous issues of the switching and device degradation mechanisms, while basic principles of the ReRAM operations have been discussed using the electrochemistry of solid materials.

The ReRAM operation is performed by simply applying voltage to the device having a capacitor structure with a switching layer between the top and bottom electrodes (TE and BE) as shown in Figure 1(a). The initial state of the device is typically the high-resistance state (HRS). It converts into the low-resistance state (LRS) by applying voltage (SET or “Forming” for the first SET). Subsequent voltage returns the resistance to HRS (RESET) as shown in Figure 1(b). The $I$–$V$ curves are hysteretic with the resistance ratio HRS/LRS typically $10^2$ or larger (Figure 1(c)). The operation is called “bipolar” when the voltage polarity for SET and RESET should be reversed, while it is “unipolar” without polarity change. The ReRAM families energetically investigated have been the valence change memory (VCM) composed of a thin oxide layer between two noble electrodes, and the conductive bridging RAM (CBRAM; there are also other naming) composed of a solid electrolyte with an electrochemically active electrode (Cu or Ag) and an inactive electrode (Pt or TiN). In this report, we study some CBRAMs showing the bipolar switching as shown in Figure 1(b).

The CBRAM operation has been explained based on electrical measurements and electronic and electrochemical discussions [8, 10, 14, 22]. Assuming that the TE is Cu, positive voltage to the TE generates Cu cations through oxidation of the electrode at the interface with the solid electrolyte. These cations move along the electric field and are metallized after receiving electrons at the BE interface. A Cu filament is formed there and grows toward the TE. When this filament connects two electrodes, SET switching is completed. Voltage reversal induces the opposite reaction, and the filament is ruptured (RESET). This simple model based on the results of the electrical measurements is plausible, which is an analogical model of electroplating. However, the switching details like filament evolution at SET/RESET and the behavior of the filament during device degradation are hard to be accomplished only with electrical measurements, which are important for usage of ReRAM with guaranteed reliability as the actual electronic device in the circuit.

Figure 1. (a) Schematic structure of ReRAM, and typical experimental data of (b) an $I$–$V$ switching curve and (c) a cyclic endurance graph of Cu/WO$_x$/TiN CBRAM cells.
To overcome this problem, *in situ* transmission electron microscopy (*in situ* TEM) has been applied on a variety of ReRAMs [12, 14, 23, 24] including CBRAMs [25–29] and other families [30–37], which enable real space observations during ReRAM switching. In some examples, formation and erasure of a Cu or Ag filament were confirmed at quick switching of CBRAM [25, 27]. In another report, the filament growth scheme was categorized in terms of its dependence on the cation mobility and the reduction rate [38]. Comprehension of the filament formation has been much advanced with the sake of *in situ* TEM. On the other hand, *in situ* TEM works on RESET and the multiple operations are still rare, although they are quite important for development of reliable ReRAM devices.

For filling the lack of this knowledge, we have performed *in situ* TEM of SET/RESET and/or multiple switching cycles for an uncovered solid electrolyte, stacked CBRAMs, and nanofabricated CBRAM cells. In this contribution, we will review our work in these years [25, 29, 39–44] and discuss the role of the filament at SET/RESET, the filament growth/erasure mode influenced by the switching history, the CBRAM degradation, and the localization of the filament to achieve stable switching.

2. Experimental procedure of *in situ* TEM

A schematic diagram of the *in situ* TEM system is shown in Figure 2(a). The TEM (10⁻⁵ Pa) was equipped with a home-made TEM piezoholder, a piezocontrol system, a current measurement unit, and a CCD camera system (30 frames/s) [45]. The Pt-Ir electrode set in the TEM holder is movable to select the location of the fixed ReRAM sample to be measured (Figure 2(b)). The TEM experiments were performed with the beam current density much less than the 170 fA/nm² (typical current density for our high-resolution TEM observations).

The *I–V* measurements were carried out using a source measure unit (SMU). The sweeping rate was typically between 0.3 and 1.6 V/s. The pulse switching operation (pulse width of

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Figure 2. Schematics of (a) the *in situ* TEM system and (b) the geometry of the sample and the probe.
100–500 μs) was occasionally performed. The measurements were done with current compliance of SMU to prevent sample destruction. However, this current compliance was occasionally insufficient because of the parasitic capacitance of the system. In some cases, a MOSFET was installed in the piezoholder to control the compliance current \(I_{\text{comp}}\) strictly. To investigate the microstructural change, the TEM images were recorded simultaneously with the current measurements by using a charge coupled device (CCD) video camera. The video contrast was occasionally enhanced nonlinearly to enable a clear identification of the faint contrast. Frame averaging was also used to reduce the noise.

3. Filament formation and erasure in chalcogenide containing Cu

Filament formation and erasure will be demonstrated using GeS containing copper (Cu:GeS) [25, 39]. Though the switching speed and the retention property were not good enough for actual devices, this material is good for easy investigation of the filament evolution. The Cu:GeS thin film was sputter deposited at room temperature (RT) on a wedge-shaped Pt-Ir substrate that acted as the electrode. The film was 8–60 nm thick and was amorphous including Ge nanocrystals. A sharp Pt-Ir probe (the counterelectrode) contacted the Cu:GeS layer, and the \(I–V\) measurements were performed. The probe was grounded, and the substrate was biased. In this sample, the Cu ion source was Cu:GeS itself. The atomic composition estimated using EDX was Cu:Ge:S = 4:4:2. Though the PtIr/Cu:GeS/PtIr structure was electrochemically symmetric, it showed the asymmetric ReRAM switching (i.e., bipolar switching) because of the shape difference between the substrate and the probe.

3.1. In situ SET and RESET operation

The \(I–V\) curve is plotted in the left panel of Figure 3, where the current compliance was \(I_{\text{comp}} = 500\ nA\). Clear hysteretic curve was seen as investigated in other studies of solid electrolytes [6, 10, 46, 47]. TEM video images are presented in the right panel of Figure 3 where each image corresponds to the states (a)–(i) marked in the \(I–V\) graph. There was no special contrast just before the voltage sweep started (Figure 3(a)). The current gradually increased until about 2.5 V, and a deposit-like dark contrast grew from the probe (cathode with this voltage polarity) (Figure 3(b)–(c)). Afterward, the current quickly reached \(I_{\text{comp}}\). This is SET giving LRS. Correspondingly, the deposit was enlarged (Figure 3(d)–(e)) and contacted the substrate. In RESET with negative biasing of the substrate, there were sudden jumps at −0.5 and −2 V, which are abnormal with the usual bipolar switching. This is special for the sample without the Cu electrode (thus, amount of Cu is limited) and was neither conventional SET nor RESET [8, 10, 14, 22]. In Figure 3(f)–(g), the deposit was contracted with negative voltage from the substrate (cathode) to the probe (anode). The deposit detached from the substrate in Figure 3(h), and the resistance returned to HRS. This was the RESET switching. At the end of this cycle, the image reverted almost to that of the original (Figure 3(i)).

The deposit size and the current corresponded; therefore, this deposit is expected to act as the conductive filament. The polarity dependence may be attributed not to the electrochemical...
3.2. SAD and EDX of the conductive filament

Selected area diffractometry (SAD) and energy dispersive X-ray spectroscopy (EDX) were performed in real time during the operation (but other area than Figure 3). In this subsection, the results are briefly summarized. Detailed experimental data are seen in Refs. [25, 39].

The crystal structure of the filament was studied using in situ SAD. When a deposit was formed, sharp spots appeared in the patterns. They twinkled like stars. This indicates that nanocrystals were formed, and their orientation frequently changed during the voltage scan. The 1152 frames of the SAD video (35 s) were summed, and Debye rings were identified. The estimated $d$-values were those of Cu reflections. For the elemental analysis, the EDX of the filament was performed with voltage application (+1 V). The Cu peak was greatly enhanced relative to the initial state. The composition estimated using the thin foil approximation was Cu:Ge:S = 7:2:1, while the region containing no filaments showed 4:4:2. The filament was an agglomeration of nanocrystals with a relatively large amount of Cu; probably metallic Cu or its alloy with either Ge and/or S.
3.3. Decrease of the SET voltage and the residue of the filament

The SET voltage usually goes down after forming. This was considered to be caused by the wreckage of the filament [8, 10, 14, 22]. To understand this phenomenon, we performed three continuous SET cycles from the initial state. Because of a short retention of this sample, the deposit disappeared automatically without negative voltage. Thus, only the positive cycles were investigated. The SET voltage in the 1st, 2nd, and 3rd cycles decreased from 2.25 to 1.83 V (2nd) and 1.50 V (3rd). In this experiment, the probe position was changed as seen in Figure 4, where the arrows indicate the point where the probe hit in the 1st cycle. A filament appeared and disappeared at the probe in the 1st cycle (Figure 4(a1, a2)). Afterward, the probe was shifted as seen in Figure 4(b1). When positive voltage was applied, a filament appeared elongating into the region where the 1st filament was formed. In the 3rd cycle, measurement was conducted without changing the probe position from the 2nd cycle (Figure 4(c1)). A filament was formed at the same place (Figure 4 (c2)). The region where the filament has been formed has priority in subsequent switching. Residuals of the filament should remain as extremely small metallic nanocrystals, which cannot easily be detected by SAD or conventional TEM. They are thought to act as nuclei of the filaments and to reduce the SET voltage.

3.4. Summary

The fundamental behavior of the conductive filament in Cu:GeS was demonstrated by using in situ TEM, in situ SAD, and in situ EDX. The switching scheme is understood as follows.

When the substrate is positively biased, Cu ions in GeS move to the cathode (probe) and a metallic deposit appears there. It consists of Cu-based nanocrystals. The deposit expanded and finally touched the anode (substrate), and the resistance state is LRS. Even in this stage, the microstructure changes with voltage application. The deposit dissolves by polarity reversal, and it shrinks from the cathode (substrate) to the anode (probe). This process gives HRS. The formation/erasure of the deposit clearly corresponded to SET/RESET. Therefore, the conductive filament must be formed in the deposit. This behavior of the filament follows the electrochemical model [8, 10, 14, 22]. With the continuation of the switching cycle, the SET voltage decreased. This is caused by the residuals (probably Cu nanocrystals) that remain even in HRS. These residues are thought to act as nuclei of the filaments.

![Figure 4. In situ TEM images of the (a) 1st, (b) 2nd, and (c) 3rd switching cycle of a Cu:GeS film. Images (a1), (b1), and (c1) are before the SET cycle, and those of (a2), (b2), and (c2) are after SET. The probe position was shifted between (a) and (b), while it was unchanged between (b) and (c). The arrow marks the portion where the probe was contacted in the 1st cycle.](image-url)
4. CBRAM having the stacked structure with the Cu electrode

The special constitution of CBRAM was used in Section 3 for easy performance of experiments, such as a tip-shaped electrode and nonuse of Cu electrode. Operation was slow, and the current was much less than μA. This is satisfactory for a characterization of conductive filaments. However, to understand realistic operation, the multiple switching cycles should be achieved for multilayered CBRAMs. In Sections 5 and 6, MoO₅ and WOₓ sandwiched between electrochemically active Cu and inactive TiN electrodes are demonstrated. The dynamics of filament growth/shrinkage (Section 5) and device degradation (Section 6) are discussed through repetitive ReRAM operations with increase of the switching current.

The CBRAMs studied are Pt(100)/Cu(30)/MoOₓ(50) and Pt(100)/Cu(30)/WOₓ(20) on TiN/Si substrates, where the numbers denote the thicknesses in nm. Here, the TiN surface was oxidized due to the O₂ plasma treatment for cleaning. The oxide switching layers were prepared using reactive RF sputtering (Ar-20% O₂) of metal targets, while the others were by Ar RF sputtering. All depositions were done at RT without any heat treatment, and both oxides were amorphous. Typical TEM image and EDX map are shown in Figure 5(a) and (b). The layer structure is clearly identified, and the overall switching area is observable. Samples for in situ TEM were processed using the ion-shadow method [48], where many cone-shaped small devices were formed. The device diameter was less than 500 nm as shown in Figure 5(a). The current for switching was measured between the biased Pt/Cu and grounded TiN/Si. The current in the LRS was limited by the serially connected resistance of TiN/Si.

Figure 5. (a) TEM image and (b) EDX mapping of a Pt/Cu/WOₓ/TiN sample where clear layer stacking was seen. The I–V switching curve of (c) a TEM sample (size: 350 nm) and (d) a microdevice (size: 16 μm) of Pt/Cu/MoOₓ/TiN. They corresponded well to each other. (e) EDX spectra from the MoOₓ layer without the filament (Reg-1 and Reg-2) and the filament (Reg-3). Enhancement of the Cu signal was clearly seen in Reg-3. Inset is the TEM image showing the analyzed areas.
Multiple switching was realized during the TEM observation. An example of the $I-V$ curve measured in TEM is Figure 5(c). The current gradually increased with positive voltage, and then the resistance was quickly converted to LRS. In the negative voltage region, the current exhibited jumps giving HRS. This is the typical bipolar switching as seen in Figure 5(d) of a conventional CBRAM device fabricated on a Si wafer using the lithography technique. The similarity of fundamental features of these graphs indicates that the vacuum environment in the TEM and electron beam irradiation had no negative effects.

Checking *in situ* TEM videos, filament-like dark contrast grew in the SET cycle and shrunk/vanished in the RESET cycle. Here, this darker contrast in the oxide layer is assumed to be the Cu-based conductive filament. This assumption was confirmed by EDX for regions with/without the filament (Figure 5(e)). The filament was made up largely of Cu.

5. Switching operation of stacked CBRAM

In this section, the filament dynamics and its mechanism are demonstrated. The CBRAM discussed here is mainly the device having the MoO$_x$ [29, 41, 43, 44].

5.1. Filament formation in the SET process

An example of the SET cycle is shown in Figure 6, where the $I-V$ graph (Figure 6(a)) and the TEM video images (Figure 6(b)–(g)) are compared. The initial resistance was 40 MΩ, and thus the Cu inclusion level in MoO$_x$ was small. For initialization, 15 positive/negative cycles were done, and the resistance decreased to 500 kΩ. Clear SET/RESET switching started after this treatment. Here, the gray contrast on the right of the image is unrelated to the switching because it showed no change of note. Increasing the voltage from state-(b), the current increased gradually. In Figure 6(c), a slight change was seen near the central area. The current increased greatly at 3 V (state-(d)), and a dark contrast appeared abruptly in a wide area from the Cu electrode (Figure 6(d)). This gathered to be a clear contrast and connected two electrodes in Figure 6(e)–(f). Its growth direction was from the anode (Cu) to the cathode (TiN), and this is opposite to the direction expected in the conventional electrochemical CBRAM.

Figure 6. (a) The SET curve and (b)-(g) corresponding *in situ* TEM images of a Cu/MoO$_x$/TiN device with little Cu inclusion. The filament quickly grew from TE to BE.
model [8, 10, 14, 22]. This behavior has been observed in other switching materials like SiO$_2$ [28], ZrO$_2$ [27], and WO$_x$ [42] that are thought not to dilute much Cu (or Ag). During the additional voltage application (over-SET named in this report), the filament grew further and changed its contact position with the Cu electrode toward the left (Figure 6(g)). Even after bridging, the filament shape continued to change. Finally, the resistance changed from 500 to 8 kΩ. The LRS retention time was longer than 5 min.

The growth direction reversed in the subsequent SET cycle (Figure 7). The switching started at states-(c) and (d). At this moment, there was no dramatic change in the TEM image (Figure 7(b)–(d)). When the current increased rapidly at state-(e), a small dark contrast appeared near the cathode (TiN). This is thought to be the nucleus of the filament. It grew, and a 35 nm thick filament bound two electrodes (Figure 7(f)–(g)). After the nucleus appeared, the bridging was completed within 200 ms. The resistance decreased from 750 to 8 kΩ.

To discuss the filament growing direction, five images sequentially extracted from the video (30 ms intervals) are shown in Figure 8. The nucleus of the filament appeared near the BE (TiN, cathode) and grew toward the TE (Cu, anode). This fits well with the electrochemical switching model [8, 10, 14, 22]. Based on the discussion in a previous report [38], the Cu ion mobility must be high in this case. This was the SET cycle after Figure 6 (and RESET). Thus, tiny Cu residuals were expected in MoO$_x$ at the starting of this SET. It may influence the Cu ion mobility. In addition, the Joule heat also can increase the ion mobility since large compliance current of > 10$^2$ A was used here.

The growth scheme from the cathode to the anode was seen also in another sample having Cu deposits near the MoO$_x$/TiN interface in the initial state. In this case, the initial resistance was small (700 kΩ), and Cu dissolution had happened already in the initial state. This may be caused by a temperature increase during ion milling for TEM sample preparation as seen in heat-treated Cu/SiO$_2$/BE [49].

Three I–V curves from the initial state are shown in Figure 9(a). The nonhysteretic curve of the 1st cycle started to be hysteretic in the 2nd cycle. Though the resistance decreased to 400 kΩ, there was no change in the video image. In the 3rd cycle, a clear hysteresis was identified, the resistance decreased to be 30 kΩ after SET, and RESET occurred. Corresponding images (Figure 9(b)–(d))

![Figure 7](image)

Figure 7. (a) The SET curve and (b)-(g) corresponding in situ TEM images of a Cu/MoO$_x$/TiN device when the switching layer was expected to contain a certain amount of Cu dissolution after the cycle in Figure 6.
showed a slight contrast change. The Cu deposit near ox-TiN/TiN (arrows) grew during SET (Figure 9(c)), and it disappeared during RESET (Figure 9(d)). This Cu deposit must play an important role in ReRAM.

Clear and abrupt current jumps began after the 4th and 5th cycles. The SET operation in the 6th cycle is shown in Figure 10(a) compared with the in situ TEM images (Figure 10(b)–(g)). A Cu deposit that grew in the 5th cycle (round contrast) was identified when the voltage sweep started (Figure 10(b)). There is an abrupt current jump at states-(c) and (d). However, the deposit did not show a clear change (Figure 10(c)–(d)). It then grew from the cathode (TiN) to the anode (Cu) with the current flow after the SET switching (over-SET) (Figure 10(e)–(g)). The deposit did not bridge two electrodes, although the resistance was reduced much.

Summarizing shortly, there were two SET modes with filament growths from the cathode or from the anode depending on the amount of Cu in the MoO$_x$ layer.

5.2. Filament shrinkage and erasure in the RESET process

The RESET process after Figure 10 is shown in Figure 11, where the filament had not bridged. At the states-(b) to (d) in Figure 11(a), the TEM images (Figure 11(b)–(d)) maintained the contrast just after SET. A clear RESET switching occurred between states-(d) and (e), but the deposit shrank only slightly (Figure 11(e)). Continuing current flow (over-RESET named in this report),

Figure 8. Details of the SET process in Figure 7, where the subsequent TEM video frames (images-1 to 5) were shown with the interval of 30 ms. The image-2 corresponds to Figure 7(e). The Cu filament grew apparently from BE to TE.

Figure 9. (a) Three $I$–$V$ switching cycles and (b)–(d) TEM images in the 3rd cycle of a MoO$_x$ CBRAM. The images showed appearance/disappearance of a deposit as indicated using arrows in (b) before SET, (c) after SET, and (d) after RESET.
it continued to shrink (but still not large change), toward the anode (TiN), giving roundish contrast (Figure 11(f) and (g)). The shrinkage direction fits the filament model [8, 10, 14, 22].

Figure 12 is another example of RESET with nonbridging (or weakly bridging) filament. In this example, the filament vanished due to large negative current (~600 μA, Figure 12(a)). The image at starting of the voltage sweep (Figure 12(b)) was not changed by RESET switching at state-(c) (Figure 12(c)). At state-(d) during over-RESET, an unexpected negative SET with large current occurred, and the filament began to shrink (Figure 12(d)–(e)). The filament vanished from the cathode (Cu) to the anode (TiN) (Figure 12(f)–(g)). Dissolution of the Cu filament was seen not only at the apex. A small precipitate near the Cu electrode (left of the images) also vanished in Figure 12(g). The current spread widely and contributed to the erasure of the filament and the precipitate nearby. Although the negative SET was abnormal, we can conclude that the large negative current was required for a complete erasure of the filament.
Figure 13 is an example to show what happens for the bridging filament, which is the RESET process of Figure 7. With negative voltage sweep, the LRS was weakly changed by RESET before (c). The resistance further increased after another weak RESET between state-(c) and (d). However, the image of Figure 13(d) did not change from Figure 13(b)–(c). This suggests that the RESET switching occurred locally in the filament, probably at the ends of filaments touching the electrodes [50, 51]. Through over-RESET with large negative current, the filament started to shrink (Figure 13(e)) and was diminished in Figure 13(f). It was erased in Figure 13(g) although some residuals remained. A clear hysteresis was seen, and the resistance changed from 9 to 200 kΩ. The details are shown in Figure 14 with 30 ms intervals. The filament shrank from the anode (TiN) to the cathode (Cu). This behavior did not fit with the reported filament model [8, 10, 14, 22]. The TiN surface was oxidized in this experiment, which must have higher resistance than the filament. The Joule heat concentrated in this region may assist the Cu dissolution there, and the Cu ions moved along the electric field and are adsorbed by the Cu TE.

5.3. Switching power and filament size

The current flow during RESET is an important factor to control the filament. This is true also for SET to form the conductive filament. The filament size is a key factor to affect the resistance
as well as the data retention of LRS. In this subsection, the relation between the switching power at SET and the filament size will be discussed using in situ TEM results.

To investigate the filament growth, five successive SET/RESET cycles were measured (Figure 15), where the over-SET process was gradually strengthened with increasing $I_{\text{comp}}$. Here, almost no over-RESET was used to prevent shrinkage of the filament. As identified in Figure 15(a), the resistance gradually decreased. Corresponding TEM images acquired after SET operations are shown in Figure 15(b)–(f). The filament grew step-by-step from the cathode (TiN) to the anode (Cu) with the increase of the injection power at SET. Though the resistance did not show drastic change even when the filament reached the Cu TE, it was because the resistance of TiN/Si serially connected to the switching layer limited the current.

There is a set of data with large SET current in Figure 16, where enough over-RESET was done to erase the filament in each cycle. During SET/RESET cycles, $I_{\text{comp}}$ was stepwise increased to 1 mA, at which the device was destructed. Figure 16(a)–(d) shows the TEM images taken just after each SET. The filament in the 1st SET with $I_{\text{comp}} = 200 \mu$A was thin, and it became thick with $I_{\text{comp}}$ (Figure 16(e)) as expected earlier [51, 52].
5.4. Summary of the switching schematics

Based on the results described above, SET/RESET operations are classified in Figure 17. There are two SET modes and two RESET modes.

When the MoO$_x$ layer contains little Cu inclusions, a high SET voltage is required. The Cu of the anode moves quickly into MoO$_x$ and generates deposits in a wide area, and they gather to form the filament (SET-1). When enough Cu has been dissolved in the initial state or during $I$–$V$ cycles, the deposit appears on the TiN cathode and grows toward the Cu anode (SET-2). For enough resistance decrease, the filament connecting two electrodes is not necessarily required. The Cu$^{2+}$ ions, oxygen vacancies and/or electrons are thought to contribute the total current. Connection of electrodes is achieved with sufficient over-SET.

There is a report on oxide CBRAMs with Ag [38]. When the Ag mobility in the oxide is low compared with the reduction rate, Ag ions are reduced to be metal before drifting for long distances, and the filament grows from the anode (Ag) to the cathode. SET-1 is categorized as this type as reported in ZrO$_2$ [27], SiO$_2$ [28] and WO$_x$ [42]. On the other hand, when MoO$_x$ contains sufficient Cu ions, the filament formation at the MoO$_x$–cathode interface can be discussed using the conventional electrochemical model [8, 10, 14, 22]. The Cu ions near the cathode can quickly reach the cathode and easily initiate the filament formation. At the same time, Cu ions are continuously generated by oxidation of the Cu electrode and supplied into MoO$_x$. As the result, the filament grows toward the anode (Cu). This is a plausible explanation for SET-2. A similar discussion was conducted in a previous report [53].

There are two RESET modes. The nonbridging filament tends to shrink toward the cathode (TiN). This is RESET-1. In this case, the filament acts as the anode. This transition is explained using the conventional model [8, 10, 14, 22]. The Cu filament is electrochemically dissolved in MoO$_x$. 

Figure 16. (a)-(d) In situ TEM images after SET with increasing the compliance current (a: 200, b: 400, c: 400 and d: 600 μA). After each SET, strong over-RESET was done to erase the filament. (e) Filament diameter increased with the compliance current. In addition, the filament position changed very much.
and becomes thin overall due to widely spread current leakage. This tendency is thought to be enhanced with temperature increase during over-RESET with high current. In contrast, the filament bridging two electrodes ruptures in a region contacting with the anode (TiN); RESET-2. This is caused by the thin ox-TiN layer. The Joule heat is preferably generated near this area because of its high resistance, and Cu of the lower part of the filament is preferably dissolved in MoO$_x$. The dissolved ions move along the widely spread electric field. In both RESET modes, the heat generated in the filament must play an important role to the electrochemical processes.

Strictly speaking, the discussion here addresses filament formation/shrinkage during over-SET/over-RESET. Sharp resistance switching in stable $I$–$V$ cycles can occur without such large changes. Even when the filament showed a remarkable change, this change did not occur at the moment of sharp SET/RESET switching. Stable switching occurs very locally.

5.5. Role of the interface region

As described above, large geometrical change of the filament (or deposit) was not identified at the switching moment. To check this phenomenon, the lower part of MoO$_x$ layer was observed (Figure 18), where nonbridging deposit (area marked with “p” in Figure 18(b7)) had been segregated at the MoO$_x$–ox-TiN/TiN interface. In the $I$–$V$ measurement of Figure 18(a), the switching current was less than 50 μA to prevent over-SET and over-RESET. While there was no change until Figure 18(b2), the bottom edge of the Cu deposit swelled out downward into ox-TiN in state-3 after the SET switching (arrow in Figure 18(b3)). This faint contrast of the filament appeared to bridge the deposit and TiN as seen in Figure 18(b4)–(b5). After the

![Figure 17. Switching schematics. There were two SET modes and two RESET modes.](image-url)
RESET switching around \(-1.5\) V, this faint contrast disappeared (Figure 18(b6) and (b7)). This filament appearance/disappearance was observed at the same position also in another switching cycle. Its width was roughly 3–5 nm. Such a small filament contributes to ReRAM switching without over-SET and over-RESET. The filament in ox-TiN appeared from Cu to TiN and disappeared from TiN to Cu. The inconsistency of this phenomenon with the conventional model \([8, 10, 14, 22]\) can be discussed with the reduction/oxidation of the Cu ions within the oxide layer \([27, 28, 54]\) or the doping/dedoping effect \([55]\).

This device structure is classified as a CBRAM with double switching layers like CuTe or Cu:MoO\(_x\) with GdO\(_x\) \([56, 57]\) showing stable operation. The thick filament in the solid electrolyte may act as a narrow electrode limiting the switching region. Power control not to erase the thick filament in the solid electrolyte layer is important for stable switching repetition.

6. Device degradation

Majority of in situ TEM works has been done to study the switching mechanism (especially SET). They were low power switching because the slow operation makes easy observations. Considering realistic devices, studies of device reliability like data retention, endurance \([58–60]\), and switching stability are required. For this purpose, multiple switching cycles with various currents should be performed. In this section, two device degradation tests will be demonstrated using Cu/MoO\(_x\)/TiN and Cu/WO\(_x\)/TiN. In both the examples, the operation was gradually strengthened in repetitive cycles to execute the accelerated aging tests \([29, 42, 44]\).

6.1. Position instability of the filament after over-RESET

For an actual operation, a large resistance ratio HRS/LRS is needed. The high HRS resistance satisfies this demand. This can be achieved using over-RESET. However, the switching cycle was fatally damaged, while the stable cycle continued without it.
The reason can be discussed using Figure 16 in Section 5.3. Five SET/RESET cycles were repeated using a Cu/MoO\textsubscript{x}/TiN CBRAM until device destruction for \( I_{\text{comp}} = 1 \) mA. The filament formed in each SET was well erased using over-RESET. A filament appeared in the 1st SET of Figure 16(a), and it was erased. In the 2nd cycle with larger \( I_{\text{comp}} \) a thicker filament appeared at the position shifted along the left (Figure 16(b)). Its position changed again to the right in the 3rd SET (Figure 16(c)). In the 4th SET, it moved to the left (Figure 16(d)). In the example of Section 3.3 (without over-RESET), the filament kept the position, and the tiny filament nuclei were expected as residues. On the other hand, the nuclei must be removed after the strong over-RESET in Figure 16. Complete erasure of the filament can give a higher resistance value in HRS, and a large memory window can be achieved. However, at the same time, it possibly induces a position change of the filament and switching instability. Power control of RESET to maintain filament residuals is thought to be important for the stable switching operation.

6.2. HRS endurance failure

Strong over-RESET induces switching instability. Therefore, the SET/RESET switching cycles were investigated on Cu/WO\textsubscript{x}/TiN without performing over-RESET for 10 times, where the voltage was back to 0 V after the RESET switching occurred. The \( I_{\text{comp}} \) was increased stepwise from 20 to 300 \( \mu \)A. A large current may increase temperature and induce widely spread leakage current. Therefore, these experiments are “accelerated aging tests” under severe conditions, which is usually done before practical use of electronic devices.

Typical \( I-V \) curves measured in TEM are shown in Figure 19(a)–(d). The characteristics of these curves are quite similar to that of a conventional device (Figure 1(b), 4 \( \mu \)m in diameter), both of which showed the sharp bipolar switching. The difference of the switching voltage from the conventional device is caused by the small device size of the TEM sample (~210 nm). The maximum SET current (\( I_{\text{comp}} \)) and the RESET currents (\( |I_{\text{max}}| \)) are summarized in Figure 19(e). The current \( |I_{\text{max}}| \) tended to increase with \( I_{\text{comp}} \) as pointed out in earlier reports.
The cyclic endurance is summarized in Figure 19(f). The HRS/LRS resistance ratio was around $10^2$. All of these properties satisfy switching fundamentals of the CBRAM devices. Thus, the in situ TEM results below can reflect the general ReRAM degradation property.

The resistance in the HRS gradually decreased in this graph, although the resistance ratio was still large. Here, the behavior of LRS could not be discussed because it was limited by the resistance of the serially connected substrate. Continuing the switching cycles, the device would reach HRS endurance failure as in conventional devices [58–60]. Corresponding TEM images in the initial state and after SET/RESET operations are listed in Figure 20(a) and (b)–(h), respectively. After switching from the initial state, a filament was formed at the position marked with a triangle in Figure 20(b). In the subsequent operations in Figure 20(c)–(d), clear change of the filament was not identified. Afterward, small deposits grew on TiN as seen in Figure 20(e)–(g) with the increase of the SET current. When $I_{\text{comp}}$ was 300 μA, a thick filament appeared at another position (Figure 20(h)). With the advancement of the cycles with increasing $I_{\text{comp}}$, the WOx layer became thin. This indicates that current widely spread in WOx when $I_{\text{comp}}$ was high. The Cu moved along this current leakage and was deposited widely at the interface. Even after the filament formation, the switching layer other than the filament changes. This must be the origin of the HRS endurance failure. This failure that occurred in the operation with weak RESET was proposed to be caused by the ruptured filament tip [58, 60]. However, based on the result here, Cu tends to accumulate at the interface not only around the conductive filament.

6.3. Summary

The switching characteristics are influenced by the electric power injected into the device. High SET current enhances the filament growth and lowering of the LRS resistance as seen in Figure 15. Although the resistance decrease in this figure was hindered behind the substrate resistance, it will be clearly seen in Figure 24(a) in the next section. High HRS/LRS resistance ratio is expected in this condition. However, strong SET (or over-SET) induces unexpected Cu deposition around the filament due to Cu dissolution and movement along the widely spread current leakage. This makes the switching layer thin and the HRS endurance failure may occur. The strong RESET (or over-RESET) can recover this failure [58], which erases the filament (and deposits) and moves Cu inclusion back to the Cu electrode. However, the filament position tends to change in the next switching cycle.

Figure 20. TEM images during device degradation of Cu/WOx/TiN. The $I$–$V$ switching cycles were performed with no over-RESET. (a) Initial, after SET/RESET of the (b) 1st ($I_{\text{comp}} = 20$ μA), (c) 2nd (50 μA), (d) 4th (100 μA), (e) 6th (150 μA), (f) 8th (200 μA), (g) 9th (250 μA), and (h) 10th (300 μA) cycles. The first filament was formed at the triangle in (b). The bright region corresponding to the WOx became thin.
This may induce switching instability. The power balance of SET and RESET is important to avoid this degradation.

7. *In situ* TEM of nanofabricated CBRAM devices

Localization of the switching area may be effective to satisfy this requirement because the low power switching can be achieved without large change and easy power control of SET and RESET is expected. The nanofabricated multistacked device has a possibility to satisfy this requirement as used in the VCM [14, 63]. In this section, there is an example of *in situ* TEM of such devices [40, 41]. The evolution of the filament and Cu condensation are discussed in the nanometer range. Data retention and pulse endurance are also discussed.

Figure 21(a) is a schematic of the TEM sample. Nine devices were fabricated on a Si chip. Each CBRAM cell is composed of a Cu–Te-based solid electrolyte layer between the TE and the bottom insulator in the contact hole (30 or 70 nm). For *in situ* TEM, the device was processed by the focused ion beam technique (FIB). The current was measured between the biased TE and the grounded Si. Repetitive *I–V* cycles during *in situ* TEM are shown in Figure 21(b), where 60 cycles were confirmed without degradation. The most important point is that the TEM sample reproduced the same characteristics as actual devices on memory chips.

7.1. *I–V* switching current and filament size

The *I–V* switching curves and TEM images of the 30-nm cell are tabulated in Figure 22 where the data before and after SET and after RESET are compared for different *I_*\_\_\_comp. In all cases, the clear and sharp ReRAM switching was realized. In the main part of this table, the contact hole area was magnified with contrast enhancement. When *I_*\_\_\_comp was larger than 125 μA, contrast change due to filament formation/rupture is seen inside the insulator layer (triangle) while it could not be identified without the contrast enhancement. Other dark contrasts visible in the insulator, which did not show any change, are not related to the resistive switching and

![Figure 21](http://dx.doi.org/10.5772/intechopen.69024)
thought to be wreckages of the solid electrolyte and/or electrodes appeared during the FIB process. The filament appeared and vanished at the same position near the edge of the contact hole. Electric field enhancement at the edge played an important role. On the other hand, no remarkable change was seen with low $I_{\text{comp}}$, while the SET/RESET switching was clearly seen. Very fine filaments must be formed in these cases.

7.2. Accumulation of Cu

To perform the elementary analyses, the EDX mapping was done. The results are shown in Figure 23, where the data in the initial state and after the SET with $I_{\text{comp}} = 60 \, \mu\text{A}$ of the 70-nm cell, and after SET with $I_{\text{comp}} = 450 \, \mu\text{A}$ of the 30-nm cell are compared.

In the initial state, both Cu and Te maps showed uniform distribution in the solid electrolyte layer. Little change in the distribution was observed for either Cu or Te after SET (60 $\mu\text{A}$) where a clear filament could not be seen in the TEM image. However, gathering of Cu was observed at the left end of the contact hole at SET with $I_{\text{comp}} = 450 \, \mu\text{A}$. In addition, the Cu moved and accumulated in the insulator layer. This was not seen in the Te map, where the insulator layer with a white contrast is still visible. This suggests that only Cu ions moved into...
the insulator by the electric field at SET. This is consistent with the filament formation shown in Figure 22 and the model predicted in a previous report of the similar double-layer CBRAM device [56]. These results prove that resistive switching here was a result of a formation process of the Cu filament as discussed in the previous section.

7.3. Data retention and pulse endurance

Resistance variation after SET for various $I_{\text{comp}}$ is shown in Figure 24(a). The LRS formed with $I_{\text{comp}} \geq 40 \mu A$ showed a good retention (more than $3 \times 10^6$ s = 3 months). Even with a small SET current generating very thin filament that was hard to be observed, a good retention could be achieved when the filament was localized in the thin insulator. The HRS retention capability was also confirmed to be more than 3 months because it is more stable than LRS. An additional issue can be discussed using Figure 24(a). The resistance just after SET decreased with $I_{\text{comp}}$. This was caused by the thickened filament with large $I_{\text{comp}}$ as shown in Figure 22.

Repeatable pulse-voltage operation is another issue to be investigated. A pulse endurance graph during in situ TEM is shown in Figure 24(b). About $10^5$ pulse switching cycles were achieved inside the TEM without any damage. These results clearly show that CBRAMs worked normally even during TEM experiments.

7.4. Summary

Considering the practical application, the switching operations of nanofabricated Cu-Te cells were explained in this section. Adopting the structure with double switching layers, the Cu
nanofilament can be localized in the thin insulator, and a sharp switching can be achieved with a low current. The accumulation of Cu in the Cu-Te layer forms a thicker filament than the one in the insulator, and it acts as a miniaturized Cu electrode that limits the switching area. Increasing the switching current, the filament becomes thick for easy TEM observations, and the retention property improves. Selecting optimum operation condition, the $10^5$ pulse switching and long retention over 3 months are possible during in situ TEM. The double-layer CBRAM can limit the switching area with short amount of Cu movement. This must be the key factor to realize stable and sharp switching properties.

8. Concluding remarks

In this contribution, we reviewed our recent in situ TEM works of various CBRAMs; uncovered Cu:GeS contacted with a needle-shaped electrode, stacked Cu/MoO$_x$/TiN or Cu/WO$_x$/TiN, and the nanofabricated Cu–Te-based ReRAM cell.

In all cases, the Cu conductive filament appeared in the SET process and shrank/vanished in the RESET process. There were two SET modes and two RESET modes. The growth/erasure direction of the filament depended on the switching history especially the amount of Cu dissolved in the switching layer. However, in the $I$–$V$ switching cycles, the filament did not necessarily show remarkable change in geometry at the SET/RESET switching moment. The local area near the electrode is thought to contribute this switching. In situ TEM in nanometer or subnanometer scale is necessary for a detailed understanding of the filament evolution.

The Cu filament grew/shrank much during over-SET/over-RESET. For such a large change, the operation current (and accompanied temperature increase) seems to play an important role. With a current increase at SET, the filament became thick and the LRS resistance decreased. However, when strong RESET was not operated, influence of widely spread leakage current...
became conspicuous, and unexpected Cu deposits were formed widely at the interface. This reduced the effective thickness of the switching layer and lead to the HRS endurance failure. While strong RESET may prevent this degradation, the filament position changed under this condition, and the switching became unstable. The switching powers at SET and RESET should be balanced for clear and stable ReRAM switching.

This was realized by adopting miniaturized CBRAM cells with double switching layers. The thin filament in nm range was localized in a thin insulator layer, while thicker Cu condensation occurred in the solid electrolyte, which could act as a protrusion of the electrode. Sharp and stable switching was performed with low current, and less degree of Cu movement was expected. This sharp switching property is applicable for conventional binary memories. On the other hand, the sharp switching is not ideal for application of the artificial neural networks that require multilevel or analogue control of the resistance. Further device designing is needed to perform stable operation for this type of devices.

The operation failure is the critical issue to ensure the practical application of ReRAMs. It is indispensable to clarify main origins of the malfunction and to guarantee device reliability. We demonstrated many in situ TEM functions that are available for reliability tests: $I$–$V$ characteristics, pulse switching, endurance, and data retention. While the time resolution is limited by the video frame rate (30 ms/frame in usual cases), other functions like TEM or scanning TEM (STEM) imaging as well as the elemental or chemical analyses using EDX or electron energy loss spectroscopy (EELS) are possible. In situ TEM is applicable to characterize nanometer-scale ReRAM cells expected for gigabit scale integration.

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