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<td>Author(s)</td>
<td>Arita, Masashi; Ohno, Yuuki; Takahashi, Yasuo</td>
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<tr>
<td>Citation</td>
<td>Physica Status Solidi A applications and materials science, 213(2): 306-310</td>
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<tr>
<td>Issue Date</td>
<td>2016-02</td>
</tr>
<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/64496">http://hdl.handle.net/2115/64496</a></td>
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Switching of Cu/MoO$_x$/TiN CBRAM occurred at MoO$_x$-TiN interface

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Received ZZZ, revised ZZZ, accepted ZZZ
Published online ZZZ

Keywords ReRAM, CBRAM, conductive filament, in-situ transmission electron microscopy

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**1 Introduction** The resistive random access memory (ReRAM) has been intensively investigated to develop next-generation nonvolatile memories as well as artificial neurons [1–4]. Solid electrolyte sandwiched between an active (e.g. Cu or Ag) top electrode (TE) and an inactive (e.g. Pt and TiN) bottom electrode (BE) is one of the candidates used for ReRAMs, which are called as the conductive bridging RAM (CBRAM), the programmable metallization cell (PMC), the atom switch or the solid electrolyte ReRAM [5-10]. The switching mode of this system is bipolar requiring both voltage polarities. Its resistance changes from the high resistance state (HRS) to the low resistance states (LRS) by applying positive voltage to the TE (Set procedure). The redox reaction is thought to generate a Cu conductive filament (CF) in the solid electrolyte switching layer, and LRS is achieved when this filament connects the TE and the BE. On the other hand, with negative voltage, the CF raptures and HRS is recovered (Reset procedure). While this operation model based on the electrochemical discussion is quite plausible, details of CBRAM switching is still ambiguous, such as microstructure evolution during the operation.

Considering practical usage of ReRAM devices in electric circuits, elucidation of the switching mechanism is inevitable to guarantee the reliability of the ReRAM operation. To overcome this problem, in-situ transmission electron microscopy (TEM) has been applied on CBRAMs [11–17] as well as other ReRAM families [18-21], and CF formation during the Set operation was experimentally confirmed. Recently, Kudo et al. [16] succeeded to achieve multiple current-voltage (I-V) switching cycles of Cu/MoO$_x$/TiN CBRAM in TEM, and CF erasure was observed during the Reset operation in addition to CF appearance at Set. However, no remarkable change in microstructure was seen at the switching moment of the I-V curve. Additional voltage application was required after Set and Reset to clearly observe the CF growth and erasure, respectively. These will be called as over-Set and over-Reset in this report, respectively. Therefore, it can be expected that the ReRAM switching occurs locally in the CF. Considering the interfaces between the Cu CF and two electrodes, Cu(CF)-Cu(TE) is more or less a homogeneous junction, because both side of the junction are Cu. On the other hand, the junction of Cu(CF)-TiN(BE) is heterogeneous. Thus, observation of the local area around the CF and the BE must be important to investigate the switching operation.

In this work, a Cu/MoO$_x$/TiN CBRAM was investigated by in-situ TEM paying attention not to perform strong over-Set and over-Reset. The microstructure change near the lower end of the MoO$_x$ layer was preferentially observed. A thin CF having a diameter of 3-5 nm appeared and disappeared in the oxidized layer of the TiN(BE). Resistive switching in a local region was experimentally confirmed.
2 Experimental procedure The Pt/Cu(TE)/MoOₓ film was RF-sputter deposited at room temperature (RT) on TiN(BE)/Si whose surface had been treated by oxygen plasma for cleaning. The solid electrolyte MoOₓ layer (50-nm-thick) was prepared by reactive RF sputtering (Ar-20% O₂). It was cut in small pieces (2.5 mm (length) × 100 μm (width) × 525 μm (thickness)), and TEM samples were fabricated by the ion shadow method for about one hour, which is an Ar ion milling method (5 kV, 1 mA, beam diameter ~ 2 mm) using carbon particles as the mask material [22]. A TEM image of the sample investigated in this work is presented in Fig. 1, which shows a clear layer stacking. The CBRAM sample had a cone shape with some irregularity. Dark contrast around A came from thicker region caused by this irregularity. The slightly bright linear contrast between MoOₓ and TiN/Ti corresponds to oxidized TiN (abbreviated as ox-TiN in this report) by oxygen plasma pre-treatment described above, which was confirmed by the XPS measurement. This is analogous structure of the double layer CBRAM which shows sharp I-V switching curves [6, 7].

In-situ TEM was performed by using a JEM-2010 microscope (200 kV, 10⁻⁵ Pa, Cₚ = 0.5 mm) attached with a home-made piezo holder [19, 21]. The CBRAM sample was fixed in this holder, and a movable Pt-Ir probe was contacted to the Pt/Cu (TE) as shown in Fig. 1. The I-V measurements were done with voltage to the TE by using a Yokogawa GS820 source-measure-unit (SMU), where the voltage sweep rate was typically 0.79 V/s. Image dynamics was recorded with a CCD camera (30 frames s⁻¹). The image contrast was enhanced non-linearly to clearly identify faint contrast of the fine CF. Contrast change during switching cycles was seen mainly in region B of Fig. 1. Processed videos are presented as supporting information; S1.3gp, S2.3gp, S3.3gp and S4.3gp.

3 Results and discussion The I-V switching curves from the pristine state (the first to the fourth cycle) are shown in Fig. 2, which were measured in TEM with a compliance current of Iₜₘₐₓ = 50 μA. The curve was reproducible in these switching cycles. While the switching was not so abrupt, Set switching started at Vₜₑₛₜ = 1.2 - 1.3 V, and Reset switching occurred at Vₜᵣₑₛₜ = -1.2 to -1.8 V. The first Set cycle is usually the initialization process to form a template of CF and is called as Forming. While the voltage to achieve Forming (V₉ₛ₉₉₉) is usually higher than Vₜₑₛₜ in subsequent switching cycles, it was nearly the same as Vₜᵣₑₛₜ in Fig. 2. The reason of this reduction in V₉₄₉₉₉ (or forming-free switching) can be inferred from the in-situ TEM result.
of the first cycle (Fig. 3). In state 1 of Fig. 3(a), the CBRAM was in the HRS. However, there was already a region with dark contrast (marked by "p" in Fig. 3(b)-1) just above the TiN BE, which may correspond to a Cu deposit as analysed in our previous works [11, 16]. Theremadarm et al. investigated heat treatment of Cu/SiO2/BE (TiN or W) [23]. They reported Cu diffusion into SiO2 and its segregation at the SiO2/BE interface, and reduction of $V_{Form}$ was discussed. Though no special heat treatment was performed in the present work, the ion shadow process (a kind of Ar ion milling) to prepare the TEM sample may cause temperature increase, a similar thing to Ref. 23 is expected to occur. This is a possible reason of Cu deposit in MoOx near the bottom interface with TiN. The increase in temperature may differ for every sample, because sample positioning relative to the Ar beam was not so accurate. Thus the amount of Cu deposit may differ for every sample.

While there was no change in the TEM image until state 2 of Fig. 3(b), the bottom edge of the Cu deposit marked with "p" swelled out downwards into ox-TiN (~5-nm-thick) in state 3 after the Set switching (arrowed position in Fig. 3(b)-3). At the same time, a faint contrast indicating a filament appeared to bridge the deposit and TiN. The swelling of the deposit and the filament were kept in states 4 and 5 (arrows). After Reset switching around $V_{Reset} \approx -1.5$ V, this faint contrast disappeared, and the swelled part shrunk upwards (states 6 and 7). This sequence can be seen dynamically in a video S1.3gp. To confirm this local switching position, the video of the second cycle was analysed in the same way. The result is shown in Fig. 4, whose contrast was coordinated with different parameters from those of Fig. 3, and a video S2.3gp. At almost the same place as that in Fig. 3, swelling occurred and the filament appeared. The filament width estimated from Figs. 3(b) and 4(b) was roughly 3-5 nm while its visual size depends on degree of contrast enhancement. Such a small filament contributes to ReRAM switching when over-Set and over-Reset does not happen. Even without a thick CF contacting to the Cu TE, the ReRAM switching was achieved. As mentioned above, Cu is thought to be dissolved in regions of MoOx other than the CF. Assuming the dissolved Cu are cations, they should move along the electric field generating ionic current and contribute to the current flow through the CBRAM. To check this clearly, the sweep rate was lowered to be 0.32 V/s (half of those in cycles 1-3) in the fourth Set cycle. In a video S3.3gp as supporting information, growth of the deposit is clearly seen. In addition, the lower edge of the Cu TE slightly contracted. Cu was surely transferred from the TE to the lower part of the MoOx layer.

The schematic $I-V$ curve and corresponding microstructure expected from experimental results are shown in Fig. 5. As described above, the surface of the BE was oxidized. The XPS measurement gave a spectrum quite similar to TiO2. Therefore, this can be classified as a CBRAM with a thin oxide layer as in [6, 7]. There was a deposit in the initial state. There was no clear contrast to confirm this deposit connected to the Cu TE (Fig. 5(b)). Set switching occurs when the voltage reaches to "c" in Fig. 5(a), and the lower part of the deposit swells into the oxidized TiN (ox-TiN) layer (Fig. 5(c)). And a filament appears in ox-TiN to connect the deposit and the BE (Fig. 5(d)). Even in this stage, no clear contrast was identified between the de-
that TiO₂ can act as the switching layer of CBRAM and al-
though to occur in the ox-TiN layer. It was pointed out
though the details are ambiguous, a similar thing is
25 or the doping/de-doping effect [26] were proposed.
vention/oxidation of the Cu ions within the oxide layer [13, 14,
and it is inconsistent to the conventional electrochemical
mechanism contributed by both copper ions and oxygen
vacancies may be another possibility to be considered. Fur-
ther investigation is required to solve this polemic dis-
cussion.

Figure 6 Device destruction with high power injection. (a) The
I-V curve and (b)-(e) corresponding TEM images extracted from
a video (S4.3gp, supporting information) showing the progress of
device destruction. From these images, it is confirmed that Cu
ions were transported in the MoO₃ layer instead of on the surface.

At the end of this section, a process of device destruc-
tion is shown to confirm that Cu moved inside the MoO₃
layer but not on the surface. After the fourth Set process,
clear Set/Reset switching was not achieved while weak
breathing of the deposit was identified during the I-V cy-
cles. Lack of switching is thought to be caused by develop-
ment of the Cu deposit which moved much into the ox-

Tin layer as seen in the video (S3.3gp). The I-V cycles
were repeated with increasing Imax and widening the volt-
age range. Finally, the sample was destructed as shown in
Fig. 6 and in a video (S4.3gp) of the eleventh I-V cycle. At
the voltage of about 2.4 V, the current sharply reached to
"b" (Fig. 6(a)). At this moment, the TEM image did not
show any change (Fig. 6(b)). Continuing the voltage applica-
tion from "b" to "e", a precipitation clearly appeared and
pushed out of MoO₃ (Figs. 6(c)-(e)). At the same time, the
Cu TE got lean. Cu dissolved from TE into MoO₃ is
thought to break the surface. Because of lack of Cu sup-
plied from the TE, there was a crossover in the I-V curve as
discussed in a previous report on Cu-CeS [27]. These phe-
nomena seen in the eleventh Set cycle can be a proof that
the CF and the deposit seen in Figs. 3 and 4 are composed of
Cu.

4 Summary and conclusion A CBRAM film
composed of Cu/MoO₃/TiN was studied by in-situ TEM to
investigate the microstructure evolution during resistive
switching. Under the switching condition without generat-
ing over-Set or over-Reset, the local area near the
MoO₃/TiN interface contributed to resistive switching. The
Cu deposit at the bottom of the MoO₃ layer swelled into
the ox-TiN layer at the interface, and thin filament with 3-5
nm in diameter was formed there in the Set process, while
reversal change was seen in the Reset process. Increasing
the switching power (voltage, current and sweep rate), the
microstructure in the MoO₃ layer changed. This will lead to
the thick CF in solid electrolyte (MoO₃ in this case) in
addition to the thin CF in ox-TiN as described in previous
reports [15, 16].

Acknowledgements This work was supported by KA-
KENHI by Japan Society of the Promotion of Science (JSPS)
(Nos. 25420279, 26630141) and the Mitsubishi Foundation, and
partly performed under the Nanotechnology Platform Program.

References
chemistry II: Electrodes, Interfaces and Ceramic Mem-
branes, 1st ed., edited by V. V. Kharton (Wiley-VCH,
Weinheim, 2011).
Nanotechnol. 4, 331 (2005).
Oh, M. Pyun, S.-o.seo, S. Heo, M. Jo, D.-K. Hwang, H. K
Electron Devices Meet. 2015, 797–800.
Tsushima, T. Sone, K. Endo, A. Kouchiyama, S. Sasaki, A.
Maesaka, N. Yamada, and H. Narisawa, Tech. Dig. Int.
be, J.T. Hasegawa, and M. Aono, IEEE Trans. Electron De-

Klopstara, and U. Böttger, in Proceedings of the 9th Confer-
ence on Nanotechnology: (IEEE NANO 2009), Genoa, Italy,

[10] Y. Bernard, V. T. Renard, P. Gonon, and V. Jousseau,

Lett. 98, 212104 (2011).

Li, J.-H. Moon, K.-J. Lee, and K. Kim, Adv. Mater. 23,
3272 (2011).


[17] M. Kudo, M. Arita, Y. Takahashi, K. Ohba, M. Shimuta, and
I. Fujiwara, in Proceedings of IEEE 7th International
Memory Workshop, Monterey, CA, USA, 2015 (IEEE, Pisc-

[18] Ch. Jooss, J. Hoffmann, J. Fladerer, M. Ehrhardt, T. Beetz, L.

Takahashi, IOP Conf. Ser.: Mater. Sci. Eng. 8, 012033
(2010).

G. H. Kim, X.-S. Li, G.-S. Park, B. Lee, S. Han, M. Kim,

Takahashi, M. Moniwa, I. Fujiwara, T. Yamaguchi, M. Aoki,
109, 053702 (2011).


M. N. Kozicki, and M. Mitkova, Thin Solid Films 518, 3293
(2010).


Res. 27, 886 (2012).