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## Significantly Improved Performance of a Conducting-bridge Random Access Memory (CB-RAM) Device Using Copper-containing Glyme Salt

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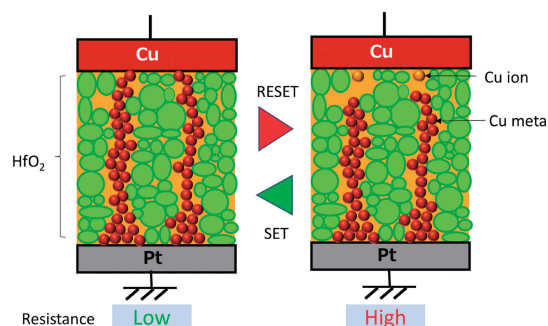
Significant improvement in cycling endurance and operating voltage dispersion has been accomplished by the addition of Cu-doped triglyme (**G3**) to the HfO<sub>2</sub> film of the Cu/HfO<sub>2</sub>/Pt-type conducting-bridge random access memory (CB-RAM); both the  $V_{\text{set}}$  distribution and the charge-transfer resistance ( $R_{\text{ct}}$ ) values were significantly reduced.

**Keywords:** Ionic liquid |  
Conducting-bridge random access memory (CB-RAM) |  
Cu-doped triglyme

Three types of memory devices are now used in a computer, viz. main memory (Dynamic Random Access Memory: DRAM), cash memory (Static Random Access Memory: SRAM), and storage memories (Flash and magnetic discs). Since both DRAM and SRAM are volatile types of memory devices, a non-volatile storage memory device is necessary during working the computer. However, the switching rates of the non-volatile memory devices currently in use are quite slow compared to volatile memory devices. A non-volatile memory device that works at a rate similar to that of DRAM might allow an innovation in computer technology. The conducting-bridge random access memory (CB-RAM) has recently gained growing interest as a next-generation high-speed non-volatile memory; the device works very fast, i.e. near the DRAM level at a low voltage and has a simple device architecture.<sup>1–4</sup> However, a serious drawback of the present CB-RAM system is that the devices have poor cycling endurance. Therefore, development of an efficient method to overcome this problem is strongly required.<sup>1–4</sup>

One of the most plausible working model of CB-RAM (Cu/HfO<sub>2</sub>/Pt) is illustrated in Figure 1: a copper filament is formed by the reduction of metal ions generated from the positively biased electrode into nanosized pore of the metal oxide (HfO<sub>2</sub>). The formation of copper filament causes a conducting bridge, and results in a low resistance state. Then, the filament ruptures upon applying negative bias to the electrode, producing a high resistance state. By repeating the process by applying negative and positive biases, the cell works as a memory device.<sup>5–9</sup>

We have been investigating the possibility of ionic liquids (ILs) as a tool to improve the performance of the CB-RAM and found that the addition of a trace amount of an IL to the Cu/HfO<sub>2</sub>/Pt cell as a CB-RAM effectively reduced the operating voltage and achieved improved tolerance against external stimuli

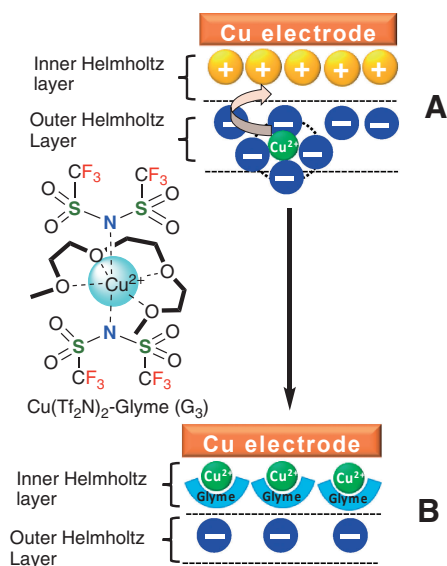


**Figure 1.** Proposed model for the forming and subsequent switching process during changes in the Cu/HfO<sub>2</sub>/Pt type CB-RAM.

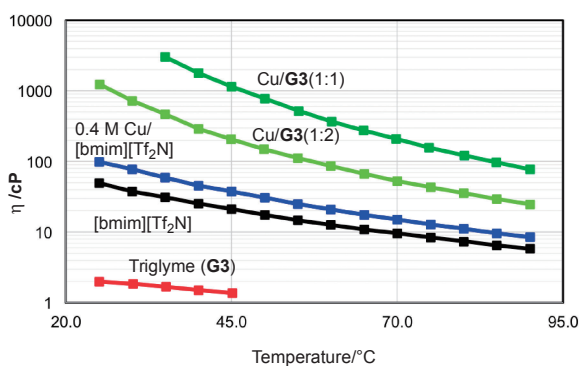
like voltage, temperature, and pressure.<sup>10</sup> We further discovered that the cycling endurance was significantly improved by the addition of Cu(Tf<sub>2</sub>N)<sub>2</sub>-doped 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([bmim][Tf<sub>2</sub>N]) to the HfO<sub>2</sub> film.<sup>11–13</sup> Although the improvement has reached a practical level,<sup>12,13</sup> a drawback still remains: the average value of  $V_{\text{set}}$  increased slightly with increasing Cu ion concentration.<sup>12,13</sup>

We hypothesize that both  $V_{\text{set}}$  and  $V_{\text{reset}}$  values during the resistive switching process in the CB-RAM may be determined by easier access of the Cu ions to the copper or platinum electrode in an adjacent area on the electrode surface. Here, “ $V_{\text{set}}$ ” is a switching voltage from high to low resistance and “ $V_{\text{reset}}$ ” indicate a switching voltage from low to high resistance during the resistive switching process. Cations of the IL may form the inner Helmholtz layer on the surface of the electrode; this may prevent Cu ions from accessing the Cu electrode and inducing increased  $V_{\text{set}}$  and  $V_{\text{reset}}$  values (A in Figure 2).

Watanabe and co-workers reported the results of extensive studies on the Glyme-Li or Na salt ionic liquids.<sup>14–22</sup> Inspired by these results, we envisioned that Cu<sup>2+</sup> ions with 2,5,8,11-tetraoxadecane (triglyme: **G3**) complexes would be arranged on the electrode surface to produce the inner Helmholtz layer that will allow easy access of the Cu<sup>2+</sup> ions to the electrode (B in Figure 2). Based on this idea, we prepared Cu(Tf<sub>2</sub>N)<sub>2</sub> solutions of **G3** with different concentrations. As expected, Cu(Tf<sub>2</sub>N)<sub>2</sub> quickly dissolved in **G3** and the TG analysis revealed that a 1:1 (Cu(Tf<sub>2</sub>N)<sub>2</sub>/**G3**) or 1:2 complex was produced (Figure S1 in the SI).



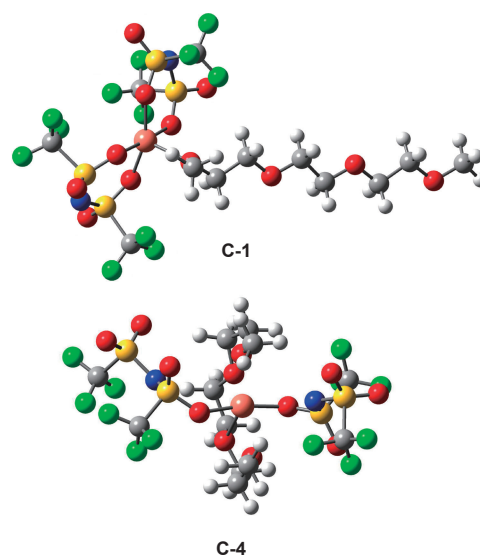
**Figure 2.** Working hypothesis of triglyme (**G3**) supported arrangement of Cu ions on the surface of the electrode.



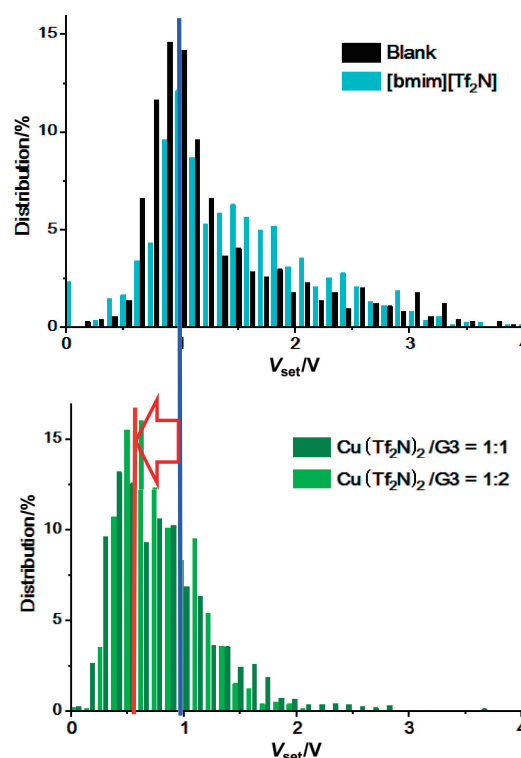
**Figure 3.** Temperature dependence of viscosity of triglyme (**G3**), [bmim][Tf<sub>2</sub>N], 0.4 M Cu(Tf<sub>2</sub>N)<sub>2</sub>/[bmim][Tf<sub>2</sub>N], Cu/**G3** (1:1), and Cu/**G3** (1:2).

However, doping Cu(Tf<sub>2</sub>N)<sub>2</sub> into **G3** led to increased viscosity: viscosity of a 1:1 molar mixture (Cu/**G3** (1:1)) at 35 °C reached 3023 cP, which was 1799-fold and 92-fold greater than that of pure **G3** and [bmim][Tf<sub>2</sub>N], respectively (Figure 3). Although the increased **G3** ratio contributed to reducing the viscosity, Cu-doped **G3** (Cu/**G3** (1:2)) still exhibited 470.1 cP at 35 °C (Table S1 in the SI). The optimized structure of Cu(Tf<sub>2</sub>N)<sub>2</sub>-**G3** (1:1) complex obtained using UB3LYP/6-311+G(d,p) calculation is shown as C-1 in Figure 4; it is assumed that a pseudo polymer comprising this complex may be formed. However, complex C-4 was electrically more stable than C-1 (Tables S1 and S2 in the SI). Therefore, it was supposed that complex C-1 changed to C-4 on the surface of the Cu electrode, as illustrated in Figure 2.

It was reported that the Cu ion diffusion ratio was inversely proportional to the viscosity.<sup>23</sup> Despite supplying such a highly viscous liquid that hindered the smooth formation of the Cu filament being a concern, we attempted to supply them to the Cu/HfO<sub>2</sub>/Pt cell (For preparing this cell, see SI and ref 10). To our surprise, unexpected good results were obtained, i.e.

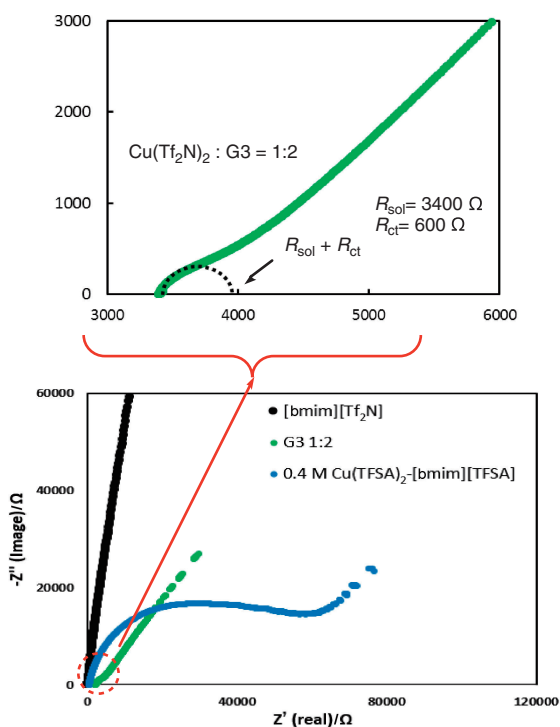


**Figure 4.** Optimized structure of Cu(Tf<sub>2</sub>N)<sub>2</sub>-**G3** (1:1) complex using UB3LYP/6-311+G(d,p) calculation.



**Figure 5.**  $V_{\text{set}}$  distributions of Cu/HfO<sub>2</sub>/Pt cells measured in the presence of [bmim][Tf<sub>2</sub>N] and Cu doped-**G3** solution. “Blank” indicates the results of the control experiment without any additive.

supplying the Cu-doped **G3** successfully reduced the  $V_{\text{set}}$  distribution rate, as shown in Figure 5. As shown in the upper graph of Figure 5,  $V_{\text{set}}$  widely disperses under the conditions of “Blank” which indicates the results of the control experiment without any additive or in the presence of pure [bmim][Tf<sub>2</sub>N]. On the other hand, the dispersions of  $V_{\text{set}}$  were minimal when we

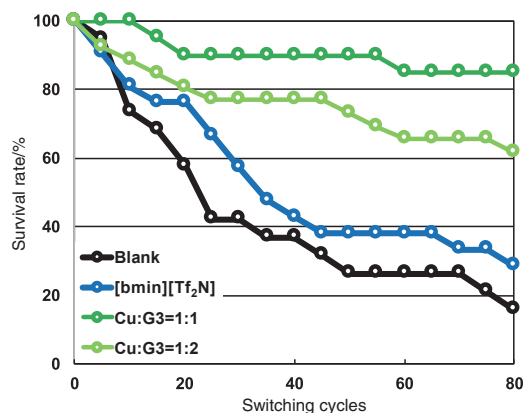


**Figure 6.** Nyquist plots of  $Z$  measured by impedance analysis of pure [bmim][Tf<sub>2</sub>N], Cu(Tf<sub>2</sub>N)<sub>2</sub>/[bmim][Tf<sub>2</sub>N] (0.4 M), and Cu-doped **G3** (Cu(Tf<sub>2</sub>N)<sub>2</sub>:**G3** = 1:2).

used 1:1 or 1:2 Cu(Tf<sub>2</sub>N)<sub>2</sub>/**G3** (the bottom in Figure 5). This indicated that the accidental generation of an anomalously high  $V_{\text{set}}$  is significantly suppressed in the presence of the Cu-doped **G3** solution. We postulate that the Cu filament would be smoothly produced at the electrode surface by the help of coordination with **G3**, while avoiding the segregation of copper ions, as illustrated in the working hypothesis (Figure 2, **B**). It was found that no significant modification was recorded for the forming voltage in the presence of Cu(Tf<sub>2</sub>N)<sub>2</sub>/**G3** (1:1) (Figure S2 in the SI). On the other hand, both  $V_{\text{set}}$  and  $V_{\text{reset}}$  values were reduced in the presence of Cu(Tf<sub>2</sub>N)<sub>2</sub>/**G3** compared to the blank conditions (Figures S3 and S4 in the SI, respectively). The results clearly indicate the importance of controlling the interface between the electrode and copper filament.

In order to investigate in more detail, we measured  $Z$  of the Cu-doped **G3** (Cu(Tf<sub>2</sub>N)<sub>2</sub>/**G3** = 1:2) by impedance analysis and compared the results to those of 0.4 M Cu(Tf<sub>2</sub>N)<sub>2</sub>/[bmim][Tf<sub>2</sub>N] (Figure 6). It was found that the Cu(Tf<sub>2</sub>N)<sub>2</sub>/**G3** (1:1) solution was too viscous to measure the  $Z$  value. However, we succeeded in obtaining results for the 0.4 M Cu(Tf<sub>2</sub>N)<sub>2</sub>/[bmim][Tf<sub>2</sub>N] and Cu(Tf<sub>2</sub>N)<sub>2</sub>/**G3** (1:2) solutions. The solution resistance ( $R_{\text{sol}}$ ) values of the 0.4 M Cu(Tf<sub>2</sub>N)<sub>2</sub>/[bmim][Tf<sub>2</sub>N] and Cu doped-**G3** (Cu(Tf<sub>2</sub>N)<sub>2</sub>/**G3** = 1:2) were determined to be 390 and 3400  $\Omega$ , respectively. On the other hand, the charge-transfer resistance ( $R_{\text{ct}}$ ) values of 0.4 M Cu(Tf<sub>2</sub>N)<sub>2</sub>/[bmim][Tf<sub>2</sub>N] and that of the Cu doped-**G3** (1:2) were estimated to be 24000 and 600  $\Omega$ , respectively (Figure 6).

Thus, the  $R_{\text{ct}}$  value of the Cu-doped **G3** was quite low compared to that of the 0.4 M Cu(Tf<sub>2</sub>N)<sub>2</sub>/[bmim][Tf<sub>2</sub>N], though the viscosity was 50-fold higher than that of the Cu-containing [bmim][Tf<sub>2</sub>N]. These results clearly indicated that the Cu ions



**Figure 7.** Survival rates of Cu/HfO<sub>2</sub>/Pt cells measured in the presence of pure [bmim][Tf<sub>2</sub>N] and Cu(Tf<sub>2</sub>N)<sub>2</sub>-doped **G3** solutions. “Blank” indicates the results of the control experiment without any additive.

can reach the electrode in the Cu doped-**G3** solution more easily than in the Cu-containing [bmim][Tf<sub>2</sub>N].

Figure 7 shows the results of the survival rate test,<sup>11</sup> which was obtained by repeating the switching processes (SET and RESET) up to 80 cycles. We found that the survival rate after 20 switching cycles was improved to 90% when the Cu doped **G3** (Cu/**G3** = 1:1) was added to the cell and ca. 85% of the cells were still active after 80 switching cycles (dark green in Figure 7). Although Cu/**G3** (1:1) is 6-fold more viscous than Cu/**G3** (1:2), better cycling endurance results were obtained (Figure 7). It has thus been established that the addition of the Cu-doped **G3** to the HfO<sub>2</sub> layer significantly improved the survival rate after repeating the switching cycle.

In summary, a significant improvement in the cycling endurance and operating voltage dispersion has been accomplished by the addition of Cu-doped triglyme (**G3**) to the HfO<sub>2</sub> film of the Cu/HfO<sub>2</sub>/Pt cell. Although the viscosity of the Cu-doped **G3** was very high, the  $V_{\text{set}}$  distributions were significantly reduced by supplying the Cu-doped **G3** to the HfO<sub>2</sub> layer of this cell. Furthermore, the charge-transfer resistance ( $R_{\text{ct}}$ ) value was also reduced compared to that of the Cu-containing [bmim][Tf<sub>2</sub>N]. These results indicate the significance of Glyme IL as an efficient additive to improve the performance of the Cu/HfO<sub>2</sub>/Pt type CB-RAM. The additive effect of the Cu-doped Glyme IL to different types of CB-RAM cells are now under investigation.

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Supporting Information is available on <http://dx.doi.org/10.1246/cl.170854>. Results of the TG analysis (Figure S1) and experimental conditions of the present CB-RAM system.

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