Extended Abstracts of the 2016 International Conference on Solid State Devices and Materials, Tsukuba, 2016, pp739-740

PS-4-09(Late News)

Improvement of Switching Endurance of Conducting-Bridge Random Access Memory by Addition of Metal Ion-Containing Ionic Liquid

Kentaro Kinoshita[1, 2], Akinori Harada[1], Hiroki Yamaoka[1], Kouhei Watanabe[3], Satoru Kishida[1, 2], Yukinobu Fukaya,[2] Toshiki Nokami,[1,3] and Toshiyuki Itoh[1, 3]

[1]Tottori University, 4-101 Koyama-Minami, Tottori 680-8552, Japan
[2]Tottori Integrated Frontier Research Center (TiFREC), 4-101 Koyama-Minami, Tottori 680-8552, Japan
[3]Center for Research on Green Sustainable Chemistry, Graduate School of Engineering, Tottori University, 4-101 Koyama-minami, Tottori 680-8552

Phone: +81-857-31-5244, E-mail: kinoshita@ele.tottori-u.ac.jp

ABSTRACT

Remarkable improvement of cycling endurance was achieved by the addition of a trace amount of an ionic liquid ([bmim][Tf_2N]) that contains $Cu(Tf_2N)_2$ to the HfO_2 layer of a CB-RAM with a Cu/HfO_2/Pt structure. The improvemet was brought about by the significant improvement of the dispersion of a set voltage owing to the smooth diffusion of Cu ions in ionic liquids.

1. INTRODUCTION

We reported that the reduction of switching voltages and the improvement of an tolerance against external stimuli such as voltage and temperature can be achieved by supplying ionic liquid (IL) to the memory layer of conductive-bridge random access memory (CBRAM) [1]. On the other hand, it was reported that doping of Cu to the memory layer reduced switching voltages and improved the dispersion of the switching voltage and data retention [2,3]. However, the data endurance, at the same time, worsened with increasing the doped Cu concentration, due to the formation of filaments that are too thick to be ruptured for reset [3]. Inspired by these results, we hypothesized that the addition of an appropriate Cu salt solution of IL would improve a cycling endurance as well as the switching voltages and the data retention of CB-RAM. This hypothesis is based on the expectation that the segregation of Cu, which is a main factor causing reset failure, could be avoided in liquids as compared to in solids. In this paper, we investigated the additive effect of Cu containing IL on the switching endurance and dispersion of switching voltages.

2. Experiment

A HfO_2 layer with a thickness of 12 nm was deposited on a Pt(100nm)/ Ti(20nm)/SiO_2(100nm)/Si(650μm) substrate using the RF sputtering method. By contacting the surface of the HfO_2 film with a Cu-probe, a Cu-probe/HfO_2/Pt structure was created at the contact region (Fig. 1(a)). The voltage was applied to the Cu-probe with the Pt-electrode grounded. A drop of IL was added to the surface of the HfO_2 film (Fig. 1(b)) and then the Cu-probe was brought into contact with the surface through the droplet of IL. Current-voltage (*I-V*) characteristics were measured using a semiconductor parameter analyzer (Agilent 4155C) in DC sweep mode and a current compliance value at which a current flowing through CB-RAM structures is limited, was fixed at 100 μA for forming and set processes.

We prepared [bmim][Tf_2N] solution containing $Cu(Tf_2N)_2$ (Cu-IL) with the Cu concentrations of 0, 0.2, 0.4 M, and added them to the HfO_2 layer of Cu/HfO_2/Pt cells.

3. RESULTS AND DISCUSSION

3. 1 Addition effect of Cu-IL on a cycling endurance

Fig.2 shows survival rates of Cu/HfO_2/Pt devices measured in the presence of pure IL and Cu-IL, where the survival rate is defined as the percentage of cells that can still work after each switching cycle. The result for the control experiment without any additive is also shown for comparison. The survival rate of the IL-non-added samples decreased to 30% after 100 switching cycles. On the other hand, the cycling endurance was improved significantly by the addition of Cu-IL. The survival rate after 100 switching cycles was increased with increasing the Cu concentration and reached 70% and 90% for the Cu concentration of 0.2 and 0.4 M, respectively.

3. 2 Addition effect of Cu-IL on the dispersion of switching voltages

Figs. 3(a)-(d) show probability densities of V_{set} for Cu/HfO_2/Pt devices measured in the absence of IL, in the presence of pure IL, and in the presence of Cu-IL of the Cu concentration of 0.2 and 0.4 M, respectively. The dispersion of V_{set} decreases with increasing the Cu concentration. The dispersions of V_{set} are fit well to Gaussian functions (solid curves in Figs. 3) with the small standard deviation of 0.33 and 0.31 V respectively for the Cu concentration of 0.2 and 0.4 M, whereas the deviations from Gaussian functions are significantly large for IL-non-added and pure IL-added samples. The vertical lines in Figs. 3 indicate V_{set}'s immediately before the subsequent reset errors, suggesting that reset errors is caused mainly due to the occurrence of anomalously large V_{set}. It is expected that the smooth diffusion of Cu ions in ILs reduces the mean V_{set} value and its dispersion, and prevents the segregation of Cu. The superior survival rate and V_{set} dispersion of Cu-IL-added devices suggest that Cu ions which are contained originally in the Cu-IL contribute dominantly to the resistive switching. The dispersion of V_{reset} was also improved by the addition of Cu-IL as shown in Fig. 4.

4. Summary

Significant improvements of the cycling endurance and dispersion of switching voltages were accomplished by the addition of Cu-IL to the HfO_2 layer of the Cu/HfO_2/Pt device.

References

[1] A. Harada *et al*., J. Mater. Chem. C 3, 6966(2015).
[2] J. Park *et al*., IEEE Electron Device Lett. 33, 646(2012).
[3] F.-T. Chin *et al*., Solid-State Electron. 103, 190(2015).

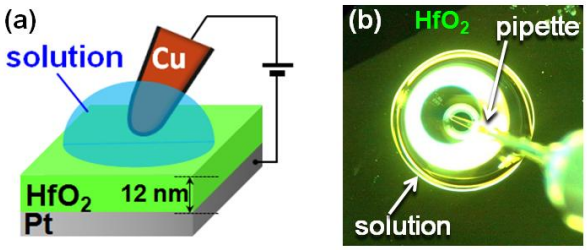

Fig. 1 (a) Cu-probe/HfO_2/Pt device structure.
(b) Measurement of addition effect of Cu-IL.

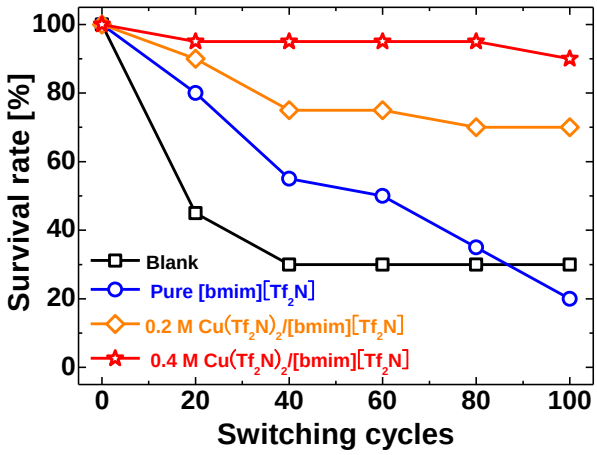

Fig. 2 Survival rates of Cu/HfO_2/Pt devices measured in the presence of pure [bmim][Tf_2N] and Cu(Tf_2N)$_2$/[bmim][Tf_2N] (Cu: 0.1, 0.2, and 0.4 M). "Blank" indicates the results for the control experiment without any additive.

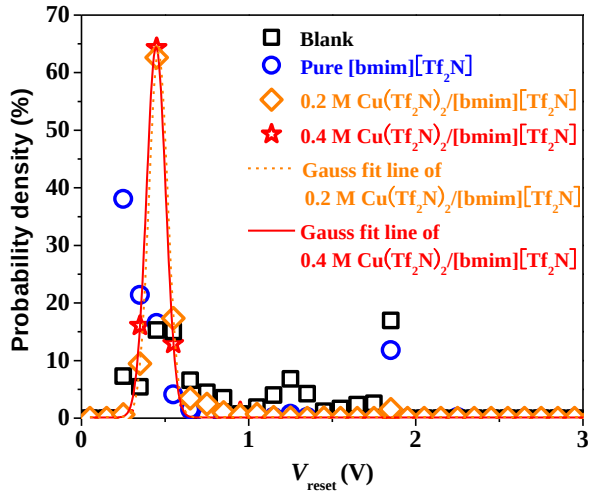

Fig. 4 Probability densities of V_{reset} for Cu/HfO2/Pt devices measured in the presence of pure [bmim][Tf2N] and Cu(Tf_2N)$_2$/[bmim][Tf_2N] (Cu: 0.1, 0.2, and 0.4 M).

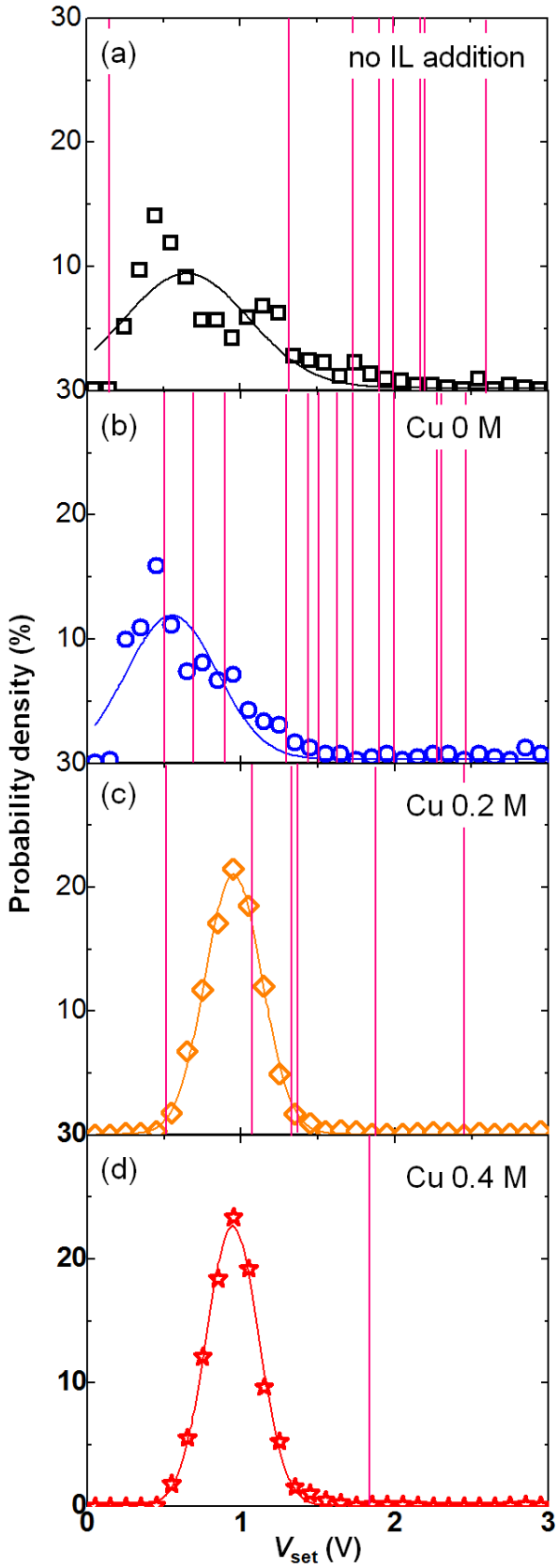

Fig. 3 Probability densities of V_{set} for Cu/HfO_2/Pt devices measured (a) in the absence of IL, (b) in the presence of pure IL, and in the presence of Cu-IL of the Cu concentration of (c) 0.2 and (d) 0.4 M. The vertical lines indicate V_{set}'s immediately before the subsequent reset errors.