（様式２）

学位論文の概要及び要旨

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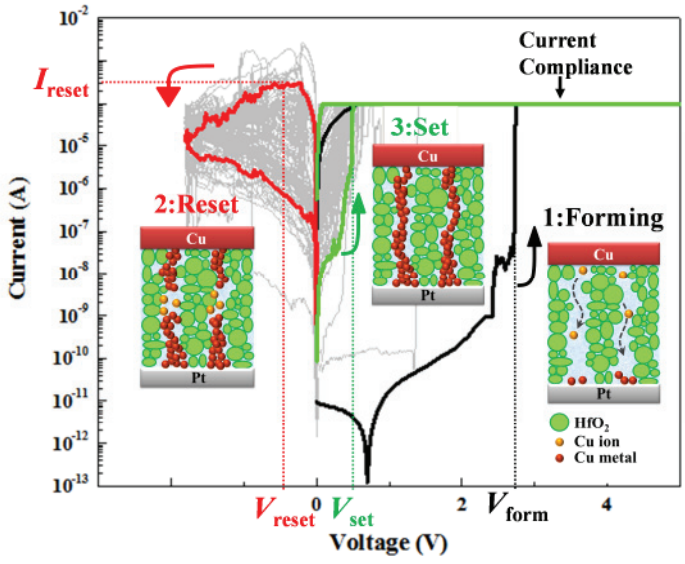
題　　目　Development of ionic liquids for the use of conducting-bridge random access memory
（導電性ブリッジメモリ用イオン液体の開発）

学位論文の概要及び要旨

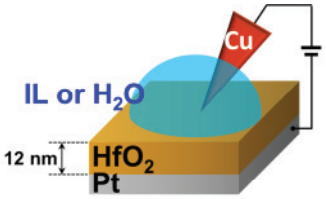
The conducting-bridge random access memory (CB-RAM) is a promising candidate for the next-generation memory. The CB-RAM displays very attractive memory properties, such as high speed, high resistance ratio, and high density, based on its simple device architecture. The present operating voltage and cycling endurance of the CB-RAM are, however, still insufficient for practical use, therefore development of an efficient means to reduce their operating voltage and high cycling endurance in the resistive switching process has been strongly desired. One of the most plausible switching mechanisms is the formation and annihilation of filamentous metal conduction paths in the solid electrolyte; the resistive switching phenomenon is therefore caused by a conductive bridge which is created by the reduction and deposition of metal ions which are eluted from the positively biased active electrode into a metal oxide (1: Forming step). Next, the conductive bridge ruptures by applying a negative bias to the active electrode, producing a high resistance state (2: Reset step). The conductive bridge is then reproduced by applying a positive bias again, resulting in a low resistance state (3: Set step). The reset and set steps are alternately repeated by applying negative and positive biases, respectively.



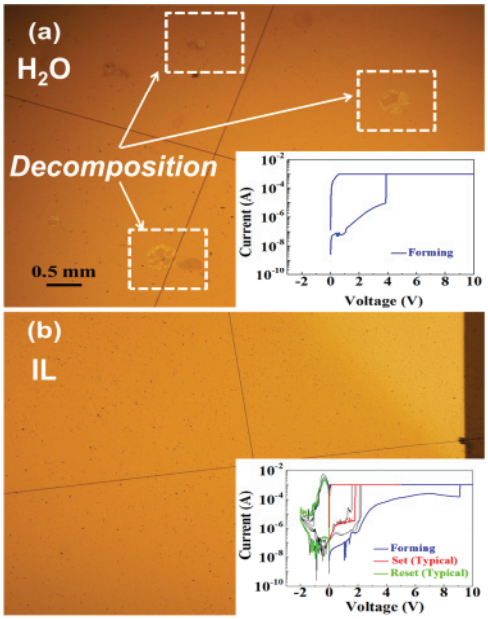
We investigated the effect of supplying water to the HfO_2 film in CB-RAM ($Cu/HfO_2/Pt$) and found that water significantly reduced the switching voltage account for the promotion of copper (Cu) ion migration. However, we encountered serious difficulty since decomposition of the HfO_2 electrolyte took place during the recycling of the resistive switching process due to the electro-chemically unstable nature of water.

Ionic liquids (ILs) are special salts that show low melting points at around room temperature and recently have attracted strong interest because of their many attractive characteristics of low-volatility, less flammable nature, high ion conductivity, and a wide potential window. For this reason, we envisioned that ILs would act as an alternative to water and improve the CB-RAM properties.

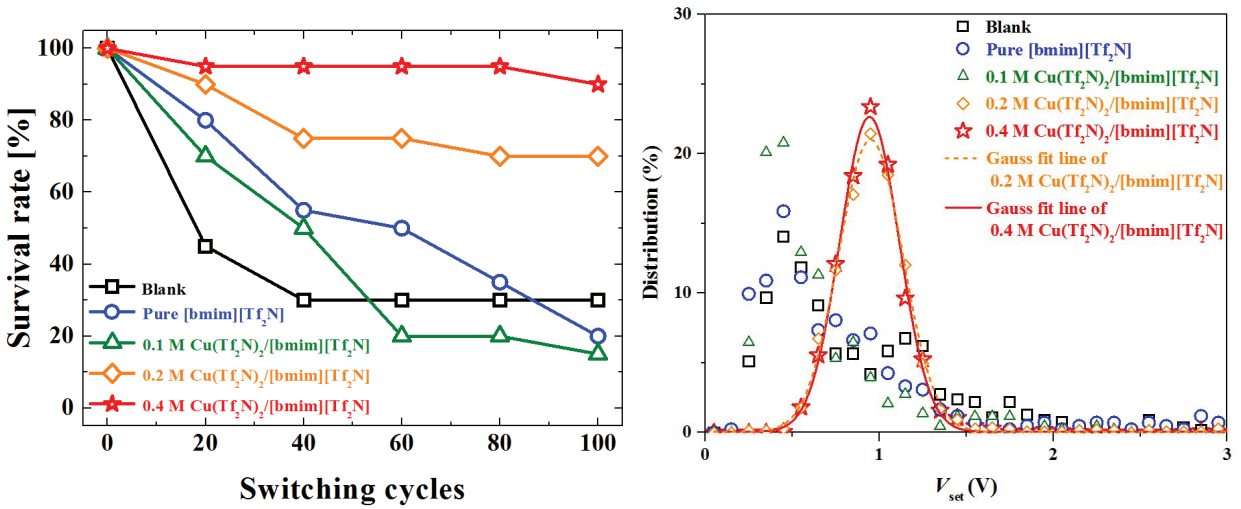
Firstly, we chose 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([bmim][Tf_2N]) as a model IL and evaluated the effect of supplying IL by the cumulative probabilities of the forming voltage (V_{form}), the set voltage (V_{set}) and the reset voltage (V_{reset}). Then, we have established the IL remarkably improved the stability of the electrolyte of a CB-RAM ($Cu/HfO_2/Pt$) and reduced the operating voltage.



	Blank	H_2O	IL
Additive	none	Ultra pure water	**[bmim][Tf_2N]**
V_{form} (average)	4.30 V	0.75 V	**3.15 V**
V_{set} (average)	0.83 V	0.65 V	**0.65 V**
V_{reset} (average)	0.60 V	0.34 V	**0.50 V**
HfO_2	remained	**decomposed**	**remained**



Next, we investigated the effect of copper ion containing ILs. We chose [bmim][Tf_2N] as a model IL and copper (II) bis(trifluoromethylsulfonyl)amide ($Cu(Tf_2N)_2$) as copper salt. We evaluated addition effect of their solution ($Cu(Tf_2N)_2$/[bmim][Tf_2N]) to the HfO_2 layer of a $Cu/HfO_2/Pt$ cell. Then, we found that remarkable improvement of cycling endurance and working voltage variance has been achieved.



Finaly, the addition effect of 18 types of ILs on the performances of the Cu/HfO_2/Pt type CB-RAM has been investigated. It was revealed that the ionic conductivity (σ_i) of the IL and the coordinating ability (β) of the anion in the IL towards the Cu ion are key competing factors that determine the voltage required for the formation of the Cu filament (V_{set}); the increase in σ_i and the decrease in β are effective in enhancing the ionization and diffusion of the Cu atoms, resulting in the reduction of V_{set}. Thus, the performance of the CB-RAM can be optimized by the adjustment of the IL, considering the balance of the competing factors revealed by the present study.

In summary, we established that the IL remarkably improved the stability of the electrolyte of a CB-RAM (Cu/HfO_2/Pt) and reduced the operating voltage, and remarkable improvement of cycling endurance and working voltage variance has been achieved by addition of a trace amount of a $Cu(Tf_2N)_2$/[bmim][Tf_2N] to the HfO_2 film layer of a CB-RAM with Cu/HfO_2/Pt structure. And we also found that ionic conductivity of the IL and the coordinating ability of the anion in the IL towards the Cu ion are key competing factors that determine the voltage required for the formation of the Cu filament. The performance of the CB-RAM can be optimized by the adjustment of the IL, considering the balance of the competing factors revealed by the present study.