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Effect of ion diffusion on switching voltage of solid-electrolyte nanometer switch

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1. Introduction

We have developed a solid-electrolyte nonvolatile switch characterized by two distinctive features: compactness (potentially $4F^2$) and low ON resistance ($<100\Omega$) [1-4]. The novel switch is composed of the solid electrolyte (here we used $Cu_{2-\alpha}S$) sandwiched between two metals (Cu and Pt). The resistance changes when a metallic bridge forms or dissolves in $Cu_{2-\alpha}S$ by biasing the negative or positive voltage of the Pt (Fig. 1). When we apply our switch to the reconfigurable switch element in the programmable logic device, the chip size or die cost can be reduced, and its performances (speed and power consumption) improved [1]. For this application, the switching voltage (V_{SW}) should be larger than the operating voltage (0.8-1.1V@hp65). But, the V_{SW} for $Cu_{2-\alpha}S$ still remains below 0.3V.

In this contribution, we discuss what process plays an important role in switching and how V_{SW} can be increased. Switching consists of two processes: Cu^+ ion migration and electrochemical reaction (Fig. 1). Because both processes can be suppressed at low ambient temperatures, we have demonstrated that the V_{SW} increases to a desired value of 1V at 5K. From the temperature dependences of the two processes, we have revealed that the migration process plays a dominant role in this improvement. Thus, to obtain a large V_{SW} of 1V at RT, we suppress the Cu migration using a solid electrolyte with a small diffusion coefficient ($<10^{-20}cm^2/sec$).

2. Temperature dependence of switching voltage

We fabricated the $Cu_{2-\alpha}S$ on the Pt bottom electrode using pulse laser deposition, where the film was 40-nm thick and the Cu/S ratio was 1.9 (Fig. 2(a)). We then deposited the top Cu electrode. The contact area of Pt with $Cu_{2-\alpha}S$ was limited to $0.036\mu m^2$, using an interlayer of calixarene. When the $Cu_{2-\alpha}S$ film touched the Cu electrode, the film changed to nearly stoichiometric Cu_2S, or chalcocite.

As shown in Figs. 2(b) and (c), both the ON/OFF (V_{OFF}) – OFF/ON (V_{ON}) switching voltage increased as the temperature decreased. This is because the migration rate of Cu^+ ions and the reaction rate are suppressed at low ambient temperatures. At 200K, the V_{ON} was about 0.7 and the V_{OFF} was 0.5V (Fig. 2(b)). At 5K, they increased to more than 1V (not shown), which is required for logic applications.

3. Limiting factors of switching

Next, we checked to see which processes contributed most to the V_{SW} increase at low temperatures. Because it is difficult to obtain the rate of electrochemical reaction independently, we compared the Cu^+ ion diffusion rate with the electrochemical reaction (D_B) to one without an electrochemical reaction (D_A).

The diffusion rate of D_A was obtained using polarization method [5]. We prepared a sample comprised of $Cu_{2-\alpha}S$ film with four Pt electrodes and a Cu electrode, placed on a plane (shown in inset of Fig. 3(a)). When an electric potential was applied across the $Cu_{2-\alpha}S$ film, the Cu^+ ions electromigrated toward the cathode, and the vacancies, which have a negative charge and act as acceptors, electromigrated towards the anode. Consequently, this resulted in an inhomogeneous hole distribution and voltage distribution. The time constant required to get stable distribution (τ_A) depends on the Cu^+ ion diffusion rate. In Fig. 3(a), the voltage difference ($|V_A-V_B|$) was measured while a constant current was applied between electrodes C and D at low value (= -0.5nA), insufficient for an electrochemical reaction.

The diffusion rate of D_B with the electrochemical reaction was obtained using a planar sample with the Cu and Pt electrodes located at each edge (shown in inset of Fig. 3(b)). When a relatively large voltage (= -0.2V) was applied to decompose the $Cu_{2-\alpha}S$ and electroplate the Cu at the cathode, the hole concentration in the film increased, resulting in a current increase. The current increases with time and approached a steady-state value with a time constant (τ_B), which depends on both the reaction rate and the Cu^+ migration rate. In Fig. 3(b), the current was measured while a positive voltage was applied to the Pt electrode.

The diffusion coefficients D_A and D_B were derived using $D = L^2/2\pi^2\tau$ (τ: τ_A or τ_B). As shown in Fig. 4, D_A was larger than D_B by two orders of magnitude. However, to compare each value, we must consider the diffusion coefficients under the same bias conditions, because D_B strongly depends on the $Cu_{2-\alpha}S$ composition, or the applied voltage, due to the change in the number of hopping sites for Cu^+ [5]. When we extrapolated the reduced D_B' from the bias voltage dependence of D_B under the same bias conditions for D_A, we found that both coefficients had similar values. This indicates that the rate of electrochemical reaction is significantly faster than the Cu^+

ion migration rate, and that the migration of the Cu^+ ions plays a dominant role in switching.

Figure 5 shows the relationship between D_B or D_B' and V_{sw}, each of which was obtained at specific temperatures. Although D_B reduced exponentially, V_{sw} increased linearly. This suggests that even if the diffusion of the Cu^+ ions is reduced exponentially, V_{sw} doesn't increase drastically. To obtain a V_{SW} of 1V, we must use a solid electrolyte with a diffusion coefficient that is smaller than that of $Cu_{2-\alpha}S$ by several tens orders of magnitude. An oxide material like SiO_2 has good potential because the diffusion coefficient for Cu^+ ions is 10^{-22}cm^2/sec [6].

References

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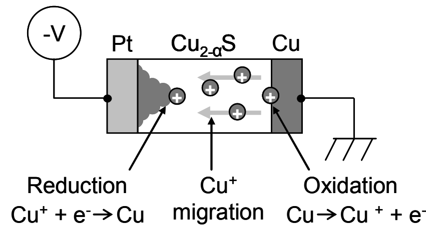

Fig. 1 Schematic view of bridge formation. When a negative voltage is applied to the Pt electrode, Cu^+ ions are produced from the Cu electrode and deposited at the Pt/$Cu_{2-\alpha}S$ interface. The deposited Cu forms conducting bridges between two electrodes.

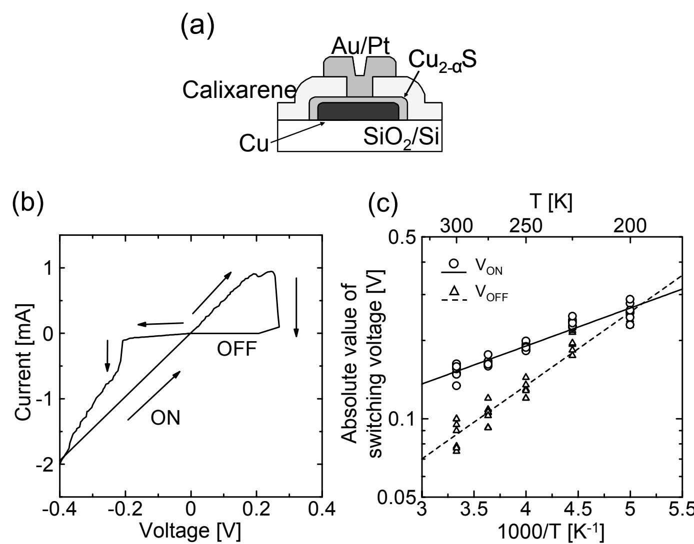

Fig. 2 (a) Schematic view of the switch. (b) Current-voltage characteristic of our novel switch at 200K. (c) Temperature dependence of switching voltage from ON to OFF (V_{OFF}) and from OFF to ON (V_{ON}).

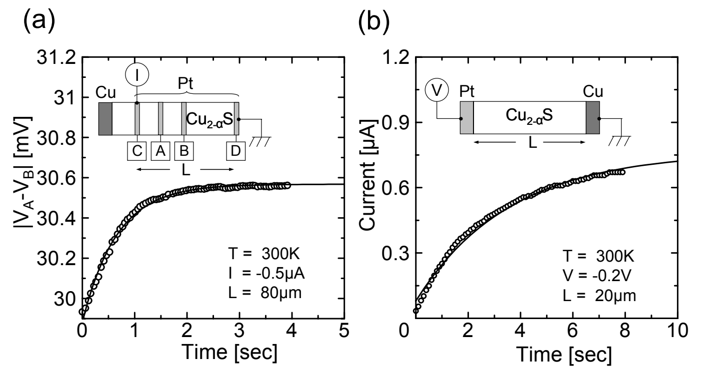

Fig. 3 (a) Voltage difference ($|V_A-V_B|$) taken over time to measure the Cu^+ migration without an electrochemical reaction. (b) Current for measuring Cu^+ migration with electrochemical reaction taken over time. Inset: schematic view of device for each experiment.

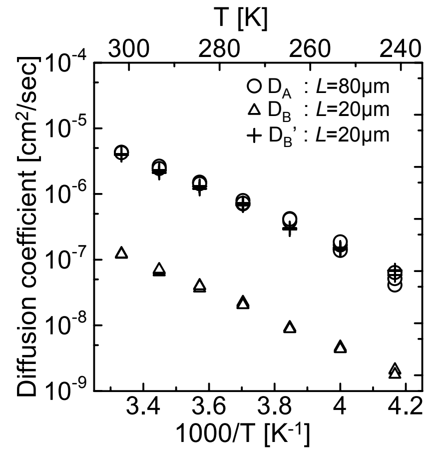

Fig. 4 Temperature dependence of diffusion coefficient with electrochemical reaction (D_B) and one without electrochemical reaction (D_A). Reduced diffusion coefficient D_B', under the same bias conditions as D_A, is extrapolated value from D_B.

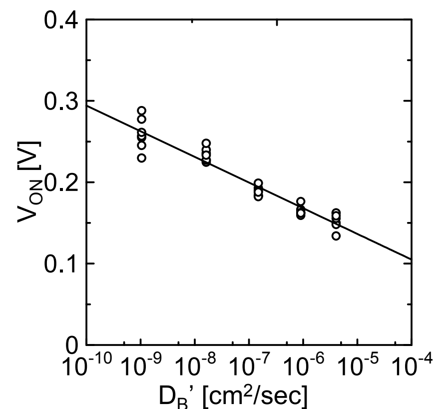

Fig. 5 Relationship between switching voltage from OFF to ON (V_{ON}) and reduced diffusion coefficient D_B'.