# Solid-electrolyte nanometer switch

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## 1. Introduction

We have investigated a solid-electrolyte switch that comprises a Cu<sub>2</sub>S film sandwiched by two metals. The Cu<sub>2</sub>S film is a mixed Cu-ionic and electronic conductor. The switch has two conducting states (ON/OFF states), which are altered by applying a positive or negative voltage to the metal and persist without a power supply [1]. Here, we have demonstrated that the switch can be scaled down to 30 nm or less and that the formation of a conducting filament is involved in the conductance switching. We also show that this switch is an attractive alternative for non-volatile memory.

#### 2. Device fabrication and IV characteristics

The device structure is depicted in Fig. 1(a). The top layer is a Au/Pt/Ti electrode, which electrically contacts with the  $Cu_2S/Cu$  film through a hole in the insulating layer. The fabrication sequence is as follows (Fig. 1(b)). A 120-nm-thick Cu film on  $Si_2O/Si$  is deposited. The surface of the Cu film is electrochemically sulfidized using an anodic polarization technique. From its molar ratio we deduce that the phase of the sulfidized layer is a chalcocite Cu<sub>2</sub>S, which is a Cu-ionic conductor and also a p-type semiconductor. After sulfidization, an insulating layer with a hole is made from a chloromethylated calixarene film, which is an electron beam (EB) negative resist. The diameter of the hole ranges from 0.03 to  $0.3 \,\mu\mathrm{m}$ , and this hole defines the contact area of the Cu<sub>2</sub>S film with the top electrode. Finally, the top electrode of the Au/Pt/Ti is formed. Figure 1(c) shows the top view of the fabricated device with a hole 0.03  $\mu$ m in diameter.

Figure 2 shows the IV characteristics of the fabricated device at room temperature with a hole 0.03  $\mu$ m in diameter. The top electrode is connected to a voltage source and the applied voltage (V<sub>IN</sub>) to the electrode is monitored. The Cu electrode is grounded through the current amplifier, which monitors the output current (I<sub>OUT</sub>). Before the voltage is biased, the conductance is very low (< 10 nS). By sweeping V<sub>IN</sub> to negative values, the conductance suddenly increases (20 mS) at -0.28 V, and an ON state of the device is achieved. As the conductance changes, V<sub>IN</sub> decreases because of the voltage drops in measurement instruments and parasitic circuits. Subsequently sweeping V<sub>IN</sub> back to positive values suddenly decreases the conductance at 0.066 V and the state is

switched to OFF. The ON/OFF ratio is larger than  $10^5$ . This conductance switching is repeatable, and each state persists in the low voltage regime. The retention time of each state is more than one month. The ON-state conductance increases by about 10% at an ambient temperature of 77 K. This suggests that a metallic current path is involved in carrier transport. The ON conductance does not depend on the hole diameter (Fig. 3).

Switching operation of a device with a 0.03- $\mu$ mdiameter hole is made by biasing the pulse voltage (Fig. 4). A negative voltage pulse of -0.3 V drives the device into the ON state. The pulse width is 1 ms. The switching time is less than 100  $\mu$ s and depends on the pulse amplitude. To read the state -0.1 V is applied, and to switch the device to the OFF state +0.3 V is applied. This switching behavior is repeatedly observed up to about  $3 \times 10^3$  cycles (Fig. 5). For devices with a hole diameter of 0.3  $\mu$ m, the cycling number is an order of  $10^5$ . The switching failure is originated from a change in the threshold voltage. Feedback-controlled writing operation can improve the cycling number and also regulate the ON or OFF conductance (Fig. 6). For testing the operation we use a personal computer (PC) to control  $V_{IN}$ . While biasing  $V_{IN}(=\pm 1 V)$  to switch the conducting states, the PC determines whether the voltage continues to be biased or not, according to output voltage. Thus, switching failure can be excluded. When an ON-chip driver is substituted for the PC, the switching time can be improved.

### 4. Operation Principle

The ON-state current dependence on hole diameter suggests that the conductive area is localized in holes smaller than 30 nm. The plausible explanation for this is that conducting filaments smaller than 30 nm are formed in the Cu<sub>2</sub>S film. Before applying voltages, there are no conducting filaments in the Cu<sub>2</sub>S film, and the conductance is low. By applying a negative voltage to the top electrode, Cu ions migrate toward it and can be neutralized by electrons flowing from it. Precipitated Cu in the Cu<sub>2</sub>S film can form conducting filaments between the Cu and the electrodes, and these filaments can explain the observed electrical characteristics of metals such as the linear IV characteristics and a negative temperature coefficient of conductance. However, by applying a positive voltage to the electrode the Cu can be ionized and dissolved into the  $Cu_2S$  film. The Cu electrode plays an important role because the switching is not observed when the electrode is replaced by a Pt electrode. The Cu electrode can supply the Cu ions to the  $Cu_2S$  film.

## 5. Conclusions

The conductance switching can be explained by the creation and annihilation of a conducting filament inside the Cu<sub>2</sub>S film. Feedback control prevents switching failure and improves the operation of our devices. These solid-electrolyte switches are promising for non-volatile memory elements because of their advantages of scalability (< 30 nm), low voltage operation (~ 0.3 V), and high ON/OFF ratio (> 10<sup>5</sup>).

## References

T. Sakamoto *et al.*, *Appl. Phys. Lett.* **82**, 3032 (2003).;
T. Sakamoto *et al.*, *SSDM Abst.*, 264 (2002).



Figure 1: (a) Schematic view of solid electrolyte nanometer switch composed of a  $Cu_2S$  film sandwiched between Cu film and top electrode (Au/Pt/Ti). (b) Fabrication sequence of our device. (b) Plane view of top electrode around a hole.



Figure 2: Current-voltage characteristics of the device with a 0.03  $\mu$ m hole.



Figure 3: ON- or OFF-state current dependence on hole diameter.



Figure 4: Switching by applying voltage pulse for a device with a 0.03- $\mu$ m-diameter hole.



Figure 5: Cycling endurance of a device with a 0.03- $\mu$ m hole.



Figure 6: Feedback-controlled operation for a device with a 0.3- $\mu$ m-diameter hole. Load resistance (~ 1k $\Omega$ ) is connected to the switch in series.