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Reproducible current switching in copper sulfide films

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1. Introduction

Switching processes have been observed in various materials such as chalcogenide alloys [1], molecular monolayers [2], thin oxide films (Cr doped SrZrO₃ [3]), and point contacts using solid electrolytes [4]. These materials have been proposed as potential candidates for non-volatile memories.

Here, we have demonstrated that a thin copper sulfide (Cu_xS) film shows a reproducible switching in its conductance with a memory effect. Biasing a positive or negative voltage switches the conductance of Cu_xS films between a low- and a high-conductance states. The ratio between these two states is about 30. Once each state has been achieved it persists without a power connection, demonstrating the feasibility of nonvolatile memory. Memory devices using Cu_xS films are advantageous due to its simple structures, scalability, and low voltage operations.

2. Electronic properties of Cu_xS film

The Cu_xS film was prepared by anodic polarization of Cu film in aqueous solution of Na₂S. The 100 nm-thick Cu film was immersed into 0.025 M Na₂S solution. Positive voltage was biased to the Cu film while grounding the immersed Au electrode. During biasing voltages, sulfide ions were absorbed on the surface of the Cu film, and then the surface was sulfidized electrochemically. Figure 1 shows the ionic current between two electrodes during the anodic polarization. After 300 sec, the current decreased and the film was fully sulfidized (film A). The surface of Cu_xS was very rough (Fig. 1(b)). For film B, the sulfidization was interrupted after 150 sec. During the anodic polarization, total number of consumed sulfide ions for film A was $6.2 \times 10^{17} / \text{cm}^2$, that was estimated by the measured current. The molar ratio x was given by 2.8. This ratio may be corrected when the hydrolysis was considered during the anodic polarization. At room temperature, copper sulfide can form five stable phases: covellite CuS, anilite Cu_{1.75}S, digenite Cu_{1.8}S, djurleite Cu_{1.95}S and chalcocite Cu₂S [5]. We can not identify the phase of the fabricated film.

The electronic properties of the Cu_xS film was measured by using a conventional prober with W needles.

Two needles were electrically touched to the film. The conductance of film A remained low with changing voltage. On the other hand, the conductance of film B switched with biasing a positive and a negative volt-

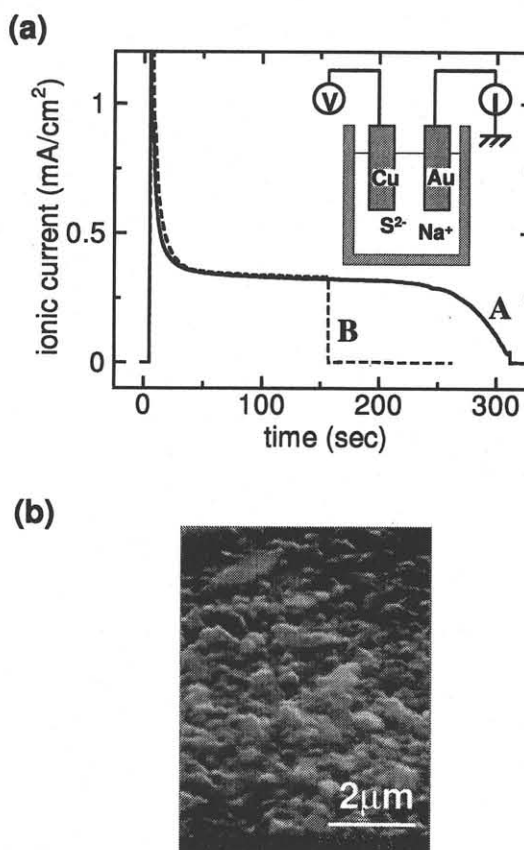


Figure 1: (a) Ionic current during anodic polarization. At $t = 5$ sec, the Cu film was immersed into an aqueous solution of Na₂S. Positive voltage ($= 0.2$ V) was biased to the Cu film. For film B (broken line), the sulfidization was interrupted after 150 sec. For film A (solid line), we took the film out from the solution when the ionic current decreased. Inset: experimental setup for anodic polarization. (b) SEM image of sulfidized Cu film.

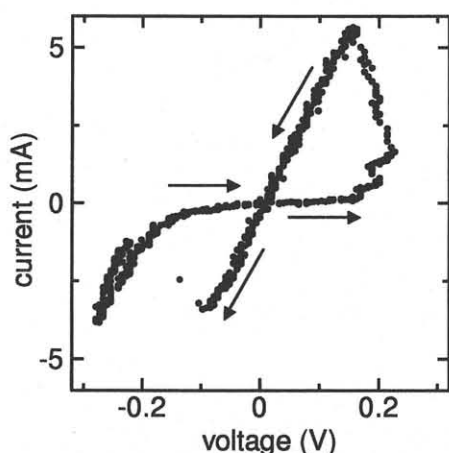


Figure 2: IV characteristics of Cu_xS film at room temperature. Two needles electrically touched to the film. One needle was connected to current amplifier, namely virtual ground, another needle to voltage source.

ages (Fig. 2). The transition from a high- to a low-conductance state occurred at -0.1 V. The ratio between two states was about 30 but could exceed three orders of magnitude.

3. Device fabrication and IV characteristics

The device structure was fabricated. The structure was very simple. The Cu_xS wire was sandwiched by Cu and a top electrode. The fabrication process is as follows. Firstly, the Cu wire was formed on a Si/SiO₂ substrate. Then, the surface of the Cu wire was sulfidized by anodic polarization (the inside of the wire was not sulfidized). The surface became rough after the sulfidization. Finally, the top electrode (Ti/Pt/Au wire) was evaporated on the Cu_xS surface (Fig. 3).

Figure 4 shows the IV characteristics of the fabricated device. With increasing a voltage, the conductance remained high (0.56×10^{-3} S). And at around 0.5 V the conductance jumped to a low conductance state (0.38×10^{-5} S). When the negative voltage was biased, the conductance changed at -0.35 V. The ratio between two states was over 10^2 . This conductance switching was recursive. And in the low bias regime, there were two stable states. When the large voltage (≥ 5 V) was biased, the bistable state disappeared and the conductance remained low.

4. Discussions

We deduce that the migration of Cu ions at the interface between Cu_xS and Ti film is responsible for the conductance switching. Cu ions easily migrate in Cu_xS , which is a solid electrolyte. When the positive voltage is biased on the top electrode, namely Ti film, Cu ions at the interface migrates into the Cu_xS film. Then, the molar ratio changes and the conductance decreases. The Cu ions can migrate recursively with changing the polarity of voltages. The Cu film plays an important role in

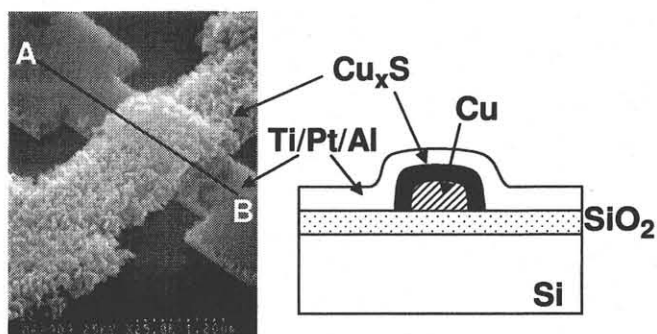


Figure 3: Device structure: SEM image and cross-sectional view along A-B. Cu_xS wire was sandwiched between top electrode (Ti/Pt/Al) and Cu.

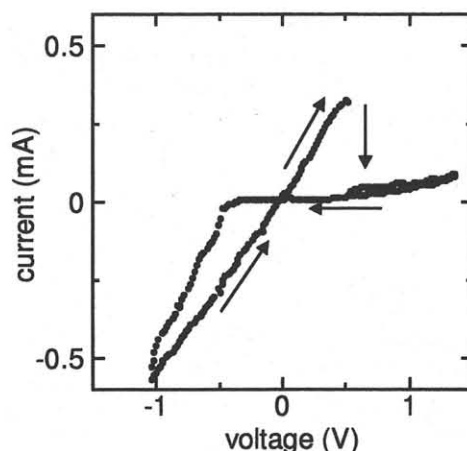


Figure 4: IV characteristics of fabricated device. Top electrode was connected to voltage source, Cu wire to current amplifier. Sweeping rate was 0.024 V/msec.

the switching, because we did not observe the switching without Cu in film A. It may work as a source of Cu ions.

5. Conclusions

We have observed a memory effect in the Cu_xS film. The Cu_xS film is fabricated by the anodic polarization of Cu film in a controllable way. We have shown that the film can be applied to the nonvolatile memory.

References

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