

OPEN ACCESS

Material dependence of switching speed of atomic switches made from silver sulfide and from copper sulfide

To cite this article: T Tamura *et al* 2007 *J. Phys.: Conf. Ser.* **61** 1157

View the [article online](#) for updates and enhancements.

You may also like

- [The Electrical Conductivity, and the Thermodynamic and Structural Properties of Molten AgCl - Ag₂S Mixtures: II. Electrical Conductivities](#)
M. C. Bell and S. N. Flengas
- [Nanoscale neuromorphic networks and criticality: a perspective](#)
Christopher S Dunham, Sam Lilak, Joel Hochstetter et al.
- [Nanoarchitectonics Intelligence with atomic switch and neuromorphic network system](#)
Takashi Tsuchiya, Tomonobu Nakayama and Katsuhiko Ariga



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Material dependence of switching speed of atomic switches made from silver sulfide and from copper sulfide

T Tamura^{1,2,3}, T Hasegawa^{2,3}, K Terabe^{2,3}, T Nakayama^{2,3}, T Sakamoto^{3,4}, H Sunamura^{3,4}, H Kawaura^{3,4}, S Hosaka¹ and M Aono^{2,3}

¹Department of Nano-Material Systems, Gunma University, 1-5-1 Tenjincho, Kiryu, Gunma 376-8515, Japan

²National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

³JST/ICORP, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

⁴Fundamental and Environmental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan

E-mail: TAMURA.Takuro@nims.go.jp

Abstract. We developed an atomic switch consisting of an ionic and electronic mixed conductor electrode and a counter metal electrode, having a space of about 1 nm between them. Formation and annihilation of a conductive atomic bridge is controlled using a solid electrochemical reaction, which is caused by applying a certain bias voltage between the electrodes. In this study, we measured the switching time of atomic switches made of silver sulfide and copper sulfide. The switching times were different, and this difference can be attributed to the different activation energies and chemical potentials of the materials.

1. Introduction

Recently, we developed a conceptually new nanodevice, called an ‘atomic switch’¹⁻⁴, using a solid electrochemical reaction⁵ in order to overcome the downsizing limits of present-day semiconductor devices. The atomic switch consists of an ionic and electronic mixed conductor electrode and a counter metal electrode with a nanometer gap between them. Switching is achieved by using a solid electrochemical reaction to form and annihilate a metal atomic bridge between the electrodes. That is, applying a positive bias to the mixed conductor electrode reduces the number of metal ions in the electrode, resulting in formation of the bridge. By applying the opposite bias, the precipitated metal atoms are oxidized, resulting in annihilation of the bridge.

The measured switching time of an atomic switch made of Ag₂S becomes exponentially shorter with increasing switching bias voltage⁶. This exponential relation suggests that the switching time is determined by the rate of the solid electrochemical reaction. We estimated the switching time by using a simple theoretical model as follows.

$$t_{sw} = \int \frac{dt}{dx} dx = F(V) \cdot \left[R_{OFF} \cdot \exp\left(\frac{DV(x_{OFF} - x_{ON})}{kT}\right) - R_{ON} \right],$$

where

$$F(V) = \frac{1}{CV} \cdot \frac{kT}{DV + kTB} \cdot \exp\left(\frac{E - DV(x_0 - x_{ON})}{kT}\right).$$

E is the activation energy of the reduction reaction, V is the switching bias voltage, R_{off} and R_{on} are resistances with gap distances of x_{off} and x_{on} , respectively. The equation reproduces the main features of the measured switching time. In addition, the equation suggests that the change in activation energy due to the use of different materials will cause a change in the switching time.

In this study, we demonstrate that an atomic switch can be made from any kind of mixed conductor material, by using Cu_2S as an example. We measured the switching time of an atomic switch made of Cu_2S and found that the equation accounts for the main features of the switching time. In addition, we found an unexpected difference in the switching properties of the Cu_2S and the Ag_2S switches.

2. Experiment

The Cu_2S electrode, which was formed on a Cu substrate, was made as follows. A Cu plate (7 x 2 x 0.2 mm³) was sulfurized at 150 °C with sulfur vapor for five minutes in an evacuated glass ampoule. The sulfurization time was much shorter and the temperature lower much than in the case of making the Ag_2S electrode⁵. This is because Cu is more easily sulfurized than Ag under the experimental conditions. After sulfurization, the sample was slowly cooled to room temperature. This prevents the melting metal ions from precipitating at the surface, due to the solubility difference according to temperature.

We used a scanning tunneling microscope to make the atomic switch configuration, i.e., a Pt tip was brought sufficiently close to the Cu_2S sample; then, after the tip position was fixed, the switching operation was performed by changing the bias voltage between the tip and the sample.

The procedure for measuring the time for turning on the switch is described in detail elsewhere⁶. Here, we outline the procedure. In each measurement, the Pt tip was brought close to the Cu_2S sample with a certain bias voltage that was high enough to eliminate Cu atoms precipitated by any previous measurement. The Pt tip was then fixed with a bias voltage of -5 mV and a tunneling current of 50 nA. Namely, the switch was set to the OFF state with a resistance of 100 k Ω . After that, a switching bias voltage was applied to turn on the switch. We defined the switching time as the time interval over which the resistance decreases to 12.9 k Ω , which is reported to be a resistance of a single atomic contact⁷⁻⁹. All the measurements were carried out in vacuum at room temperature.

3. Results and Discussion

Figure 1 shows the change in resistance of the switch that was measured by sweeping the bias voltage applied to the Pt electrode. The switch was turned on with a bias voltage of -0.28 V, as can be seen in the figure. The resistance suddenly decreased to a certain ON resistance when the conductive atomic bridge formed between the electrodes. By sweeping the bias voltage to a positive value, the resistance suddenly increased to a certain OFF resistance at 0.27 V when the atomic bridge disappeared. Although the figure shows only one switching cycle, we confirmed long-term continuous operation like that of the Ag_2S switch^{1,2}.

Figure 2 shows a typical change from OFF to ON resistance by applying a bias voltage of 0.2 V. After applying the bias voltage, the resistance decreased exponentially, and it became 12.9 k Ω in 50 μs , which is the switching period we defined.

Figure 3 shows the bias dependence of the switching time of the Cu_2S atomic switch. The dependence of the Ag_2S switch is shown for comparison. As is the case of the Ag_2S switch, the

switching time of the Cu_2S atomic switch became exponentially shorter with increasing switching bias voltage.

Figure 3 indicates that the smallest switching bias voltage for the Cu_2S atomic switch (0.2 V) is a little bit larger than that for the Ag_2S atomic switch (0.05 V). This difference can be attributed to the different activation energies for the chemical reactions of the materials. However, the difference in the slopes cannot be understood in terms of this activation energy difference, which only shifts the curve in the graph without changing its slope.

The mobility of Cu^+ ions in a Cu_2S crystal is reported to be of the order of $10^{-2} \text{ cm}^2/\text{Vsec}^{10}$, which can supply more than 10^9 ions in a nm^2 area of the surface. On the other hand, the experimental results indicate that the reaction rate of the reduction process for switching ON is at most of the order of 10^7 reactions/sec. Therefore, we believe that enough Cu^+ ions always exist in the reaction area, and the rate of the reduction process determines the switching speed.

The rate of the reduction process is dominated by the activation energy of the material and also by an effective barrier height change due to the applied bias voltage (the latter term is denoted by DV in the equation). Because the change in the activation energy cannot cause the difference in the slope of the switching curve, we believe that the bias dependence of DV differs between the materials.

In the switching process, metal ions diffuse through the materials towards the surface, resulting in more metal ions just below the surface where the chemical reaction occurs. The metal ion increase lowers the potential barrier height for the chemical reaction in terms of the electrical and chemical potentials. Therefore, the change in metal ion concentration directly relates to the change in the reaction rate. The difference between the metal ion increases can be explained as follows.

Ag_2S is an n-type semiconductor, and it is correctly denoted as $\text{Ag}_{2+\delta}\text{S}$. Cu_2S is a p-type semiconductor, and its correct description is $\text{Cu}_{2-\delta}\text{S}$. Samples of $\text{Ag}_{2+\delta}\text{S}$ and $\text{Cu}_{2-\delta}\text{S}$ have their own δ^{10} , as a result of achieving equal chemical potentials at the interfaces of $\text{Ag}_{2+\delta}\text{S}/\text{Ag}(\text{substrate})$ and $\text{Cu}_{2-\delta}\text{S}/\text{Cu}(\text{substrate})$. Because the diffusion coefficient of Ag^+ ion in Ag_2S is more 10000 times as large as that of Cu^+ ion in $\text{Cu}_2\text{S}^{11-12}$, it is thought that activation energy for diffusion of Ag^+ ion is lower than Cu^+ ion. We assumed that, as in the case of metal ion migration to the defect, the energy for metal ion migration which increases the metal ion concentration of Ag_2S is lower than Cu_2S , as shown in Fig. 4a. The characteristics shown in Fig. 4a, it is much easier to increase the density of Ag^+ ions than it is to increase the density of Cu^+ ions, which causes the difference in Fig. 4b and c. Consequently, the potential barrier height of Ag_2S is more easily lowered, which gives Ag_2S a larger bias dependence than that of Cu_2S . Although further experimental and theoretical work is needed to confirm this explanation, it seems to explain all of the switching behaviors we observed.

4. Conclusion

An atomic switch was made from Cu_2S in order to demonstrate that an atomic switch can be made from any kind of mixed conductor material. The switching time of the Cu_2S atomic switch decreases exponentially with increasing switching bias voltage, as does an Ag_2S atomic switch. However, it shows less bias dependence compared with an Ag_2S switch. This difference can be explained by taking into account the ease of increasing the density of metal ions just below the surface.

References

- [1] K Terabe, T Hasegawa, T Nakayama and M Aono 2002 *Riken Rev.* **37** 7
- [2] K Terabe, T Hasegawa, T Nakayama and M Aono 2005 *Nature* **433** 47
- [3] T Sakamoto, H Sunamura, H Kawaura, T Hasegawa, T Nakayama and M Aono 2003 *Appl. Phys. Lett.* **82** 3032
- [4] S Kaeriyama, T Sakamoto, H Sunamura, M Mizuno, H Kawaura, T Hasegawa, K Terabe, T Nakayama and M Aono 2005 *IEEE J Solid-State Circuits* **40** 168
- [5] K Terabe, T Nakayama, T Hasegawa and M Aono 2002 *J. Appl. Phys.* **91** 10110
- [6] T Tamura, T Hasegawa, K Terabe, T Nakayama, T Sakamoto, H Sunamura, H kawaura, S Hosaka and M Aono 2006 *Jpn. J. Appl. Phys.* **45** 364
- [7] H Ohnishi, Y Kondo and K Takayanagi 1998 *Nature* **395** 780
- [8] A Enomoto, S Kurosawa and A Sakai 2002 *Phys. Rev. B* **65** 125410
- [9] V Rodrigues, J Bettini, A R Rocha, L G C Rego and D Ugrate 2002 *Phys. Rev. B* **65** 153402
- [10] T Kudo and K Fueki, *Solid State Ionics*, Kodansha-VCH (1990)
- [11] G P Power, I M Ritchie and M T Wylie 1981 *Electrochim. Acta* **26** 1633
- [12] S Sanchez, S Cassaignon, J Vedel and H G Meier 1996 *Electrochim. Acta* **41** 1331

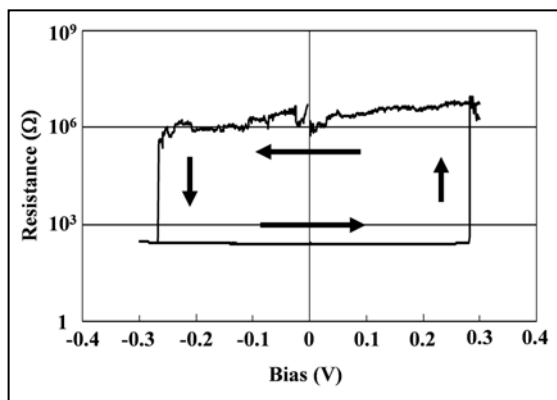


Figure 1. Resistance-voltage characteristics of atomic switch.

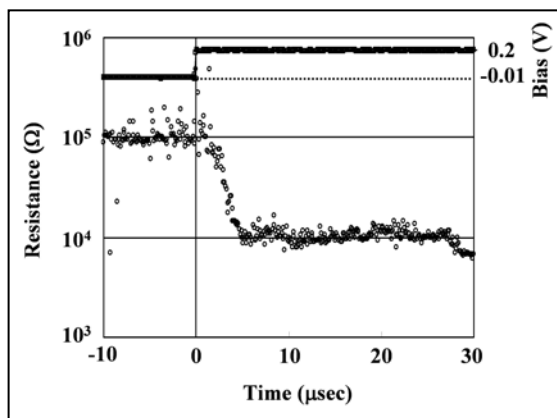


Figure 2. Example of the change in resistance. A switching bias voltage of 0.2

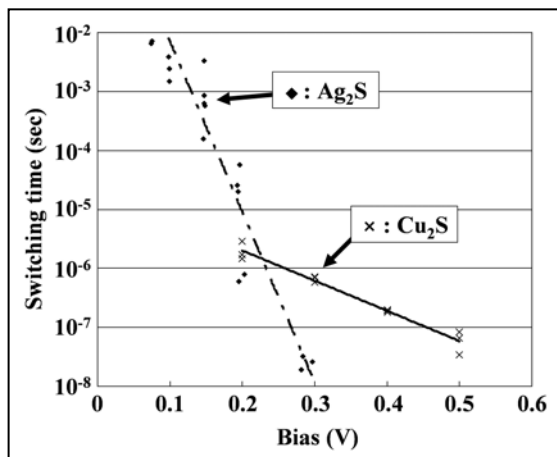


Figure 3. Materials dependence of the switching time.

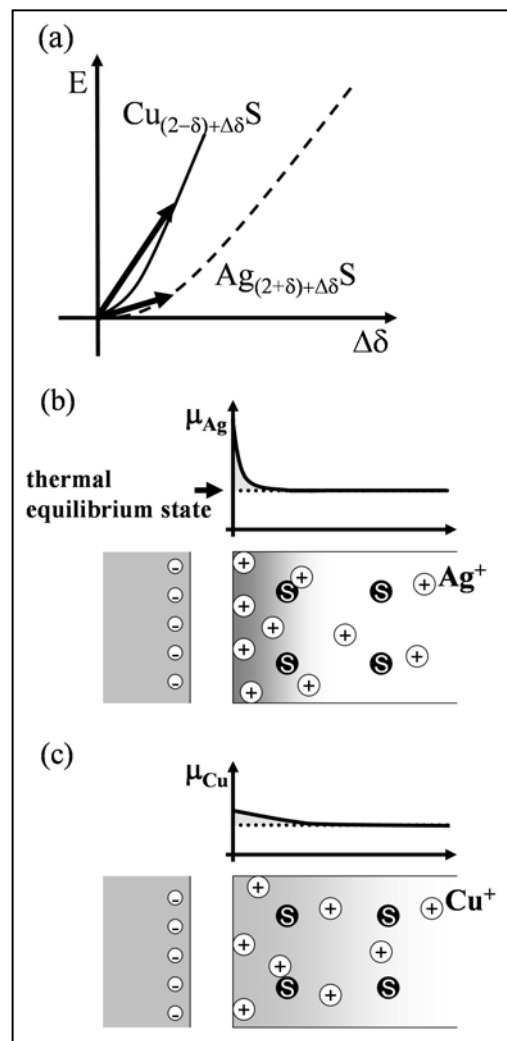


Figure 4. Metal ion redistribution due to the switching. (a): energy diagram in terms of $\Delta\delta$, and schematic diagrams of chemical potential and ionic distribution for Ag_2S (b) and Cu_2S (c) was applied at $t = 0$.