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

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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.
ON OFFsw RkT 

E is the activation energy of the reduction reaction, \( V \) is the switching bias voltage, \( R_{\text{off}} \) and \( R_{\text{on}} \) are resistances with gap distances of \( x_{\text{off}} \) and \( x_{\text{on}} \), 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 \( \text{Cu}_2\text{S} \) as an example. We measured the switching time of an atomic switch made of \( \text{Cu}_2\text{S} \) 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 \( \text{Cu}_2\text{S} \) and the \( \text{Ag}_2\text{S} \) switches.

2. Experiment
The \( \text{Cu}_2\text{S} \) electrode, which was formed on a Cu substrate, was made as follows. A Cu plate (7 x 2 x 0.2 mm\(^3\)) 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 \( \text{Ag}_2\text{S} \) electrode. 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 \( \text{Cu}_2\text{S} \) 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 elsewhere. Here, we outline the procedure. In each measurement, the Pt tip was brought close to the \( \text{Cu}_2\text{S} \) 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\( \Omega \). 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\( \Omega \), which is reported to be a resistance of a single atomic contact. 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 \( \text{Ag}_2\text{S} \) switch.

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\( \Omega \) in 50 \( \mu \)s, which is the switching period we defined.

Figure 3 shows the bias dependence of the switching time of the \( \text{Cu}_2\text{S} \) atomic switch. The dependence of the \( \text{Ag}_2\text{S} \) switch is shown for comparison. As is the case of the \( \text{Ag}_2\text{S} \) switch, the
switching time of the Cu₂S atomic switch became exponentially shorter with increasing switching bias voltage.

Figure 3 indicates that the smallest switching bias voltage for the Cu₂S atomic switch (0.2 V) is a little bit larger than that for the Ag₂S 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 Cu₂S crystal is reported to be of the order of 10⁻² cm²/V sec¹⁰, which can supply more than 10⁹ ions in a nm² 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 10⁷ 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.

Ag₂S is an n-type semiconductor, and it is correctly denoted as Ag₂⁺S. Cu₂S is a p-type semiconductor, and its correct description is Cu₂⁻S. Samples of Ag₂⁺S and Cu₂⁻S have their own δ¹⁰, as a result of achieving equal chemical potentials at the interfaces of Ag₂⁺S/Ag(substrate) and Cu₂⁻S/Cu(substrate). Because the diffusion coefficient of Ag⁺ ion in Ag₂S is more 10⁰⁰ times as large as that of Cu⁺ ion in Cu₂S¹¹⁻¹², 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 Ag₂S is lower than Cu₂S, 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 Ag₂S is more easily lowered, which gives Ag₂S a larger bias dependence than that of Cu₂S. 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 Cu₂S in order to demonstrate that an atomic switch can be made from any kind of mixed conductor material. The switching time of the Cu₂S atomic switch decreases exponentially with increasing switching bias voltage, as does an Ag₂S atomic switch. However, it shows less bias dependence compared with an Ag₂S switch. This difference can be explained by taking into account the ease of increasing the density of metal ions just below the surface.
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**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$_2$S (b) and Cu$_2$S (c) was applied at $t = 0$. 