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Volatile and nonvolatile selective switching of a photo-assisted initialized atomic switch

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Abstract

A photo-assisted atomic switch, which has a photoconductive molecular layer in a gap of about 20 nm between an Ag₂S electrode and a Pt electrode, is set to a conventional gap-type atomic switch operation mode by light irradiation with the application of a small bias that precipitates Ag atoms from an Ag₂S electrode. After this initialization, the switch operates only with application of a bias. In this study, we also found that after the set-operation a photo-assisted initialized atomic switch shows different switching modes depending on the bias range, i.e., volatile switching when the applied bias is smaller than the threshold bias, and nonvolatile switching when the applied bias is larger than the threshold bias. These characteristics can be useful in reconfiguring a circuit such as in neural computing systems.

(Some figures may appear in colour only in the online journal)

1. Introduction

Neural computing systems have the potential to achieve highly complex computations, such as image recognition through learning processes, with high energy efficiency [1, 2]. Many studies have been conducted to develop neural computing systems [3–5], initially such as those based on software programming and/or based on complementary metal oxide semiconductor (CMOS) devices [6–12]. Such studies have demonstrated the many advantages that neural computing systems have over conventional von Neumann computers. At the same time, it was found that the energy efficiency of neural computing systems was not greatly improved when based on CMOS devices [13], because CMOS-based systems require complicated circuits just to achieve the functions that are performed by single neurons or synapses in biological systems.

Emerging memory devices, such as resistive random access memories (ReRAMs), have attracted much attention recently because of their ability to emulate synaptic functions utilizing a single device [14]. For instance, metal oxide-based ReRAMs are known to work as memristors [15, 16], which can be used as synapses in spike timing dependent potentiation (STDP)-based neural computing systems [17–22]. Learning based on short-term memory and long-term memory has also been emulated using single devices such as atomic switches [23, 24] and metal oxide-based ReRAMs [25–27]. These demonstrations suggest the near-future possibility of realizing new types of neural computing systems, which are completely different from present-day binary computing systems.

The photo-assisted atomic switch is a new type of nanodevice [28], which works with a bias application and light irradiation. Conventional gap-type atomic switches have a nanometer gap between a solid-electrolyte electrode and a counter metal electrode [29, 30]. The nanometer gap enables the flow of a tunneling current between the two electrodes, which causes the precipitation of metal atoms from the solid-electrolyte electrode to turn on the conventional gap-type atomic switch. In comparison, a photo-assisted...
atomic switch has a wider gap, in the range of tens of nanometers, but photoconductive molecules are present in the gap. These photoconductive molecules produce a photocurrent when they are illuminated by light, and the photocurrent causes a precipitation of metal atoms. After the first turning-on process in a photo-assisted atomic switch, the switch works as a conventional gap-type atomic switch, that shows nonvolatile operation, without light irradiation. On the other hand, a turning-off process with light irradiation can make a large gap again by shrinking an Ag protrusion more utilizing a photocurrent, requiring light irradiation in the subsequent turning-on process. In these switching processes, an Ag protrusion grows and shrinks in a photoconductive \( N,N' \)-diheptylperylene-tetracarboxylic diimide (PTCDI) layer by rearranging molecules, which may change the photoconductivity of the PTCDI layer, resulting in the fluctuations in current that are observed [28].

In this paper, we report that, depending on the bias range, the photo-assisted initialized atomic switch can work as both volatile and nonvolatile switches without light irradiation.

2. Experimental details

A photo-assisted atomic switch was fabricated as follows. First, nanogap electrodes were fabricated by the method previously reported (figure 1) [31]. The first and second structures, composed of Pt/Ti (50/10 nm) and Pt/Ag/Pt/Ti (5/40/5/5 nm) respectively, were made by electron beam lithography patterning and subsequent metal deposition. After a lift-off process of the second structure, the structures were annealed in a petri dish with sulfur vapor at 80 °C for 20 min to sulfurize the Ag layer in the second structure. As a result, the second structure was composed of Pt/Ag\(_2\)S/Pt/Ti. After that, a third structure of Pt/Ti (25/5 nm) was made by a shadow deposition technique, with an angle of 30°, through a metal mask having a 50 \( \mu \)m width line pattern. The gap size was controlled by the thickness of the second structure and the angle of the shadow deposition. Finally, PTCDI molecules were thermally deposited on the nanogap electrodes.

Electrical measurements were conducted using a semiconductor parameter analyzer (Keithley 4200) with a cryogenic probing station (Nagase Techno-Engineering Co., Ltd). Light irradiation to the device was conducted using a metal halide lamp (Nippon P.I. Co., Ltd) with a band-pass filter of 460–540 nm. All measurements were performed under vacuum at 298 K.

3. Results and discussion

Figure 2(a) shows the change in current flowing in an as-fabricated photo-assisted atomic switch with an
approximately 20 nm gap, under light irradiation and a bias application of 0.75 V. Light irradiation increased the current, as indicated by arrow A, meaning a photocurrent began to flow. At point B, another increase in current, up to over 1 nA, was observed. This second increase is understood as follows. The photocurrent increased the total current flowing in the photo-assisted atomic switch, which increased the bias effectively applied to the Ag$_2$S layer ($V_{\text{eff}}$ = $I \cdot R_{\text{Ag$_2$S}}$, where $I$ is the current flowing in the photo-assisted atomic switch and $R_{\text{Ag$_2$S}}$ is the resistance of the Ag$_2$S layer), enabling diffusion of Ag$^+$ cations in the Ag$_2$S layer and their precipitation at the surface, as schematically shown in figure 2(b) (center). The Ag layer formed on the surface is expected to reduce the barrier height for electronic conduction through the interface between the Ag$_2$S electrode and the PTCDI layer, which may be the cause of the increase in current at point B. The time lag between the two increases is the time taken for the diffusion of Ag$^+$ cations towards the surface [32].

Current showed a sharp increase to about 30 nA at point C, following which it showed a gradual increase to approximately 50 nA. It is expected that the growth of an Ag whisker in the gap, by the subsequent precipitation of Ag atoms, reduced the gap size between the two electrodes to about 1 nm, which enabled the flow of a tunneling current, as schematically shown in figure 2(b) (right). Specifically, the major contributor to current was a tunneling current after point C, and the sharp increase in current corresponds to the change in the major contributor from a photocurrent to a tunneling current due to a growth of an Ag whisker. Since the resistance of the gap estimated from the current was about 15 MΩ, which is much larger than that of a single atom contact, i.e., 12.9 kΩ, the Ag whisker should not have reached the counter-electrode. In other words, there should have still been a gap between the two electrodes. However, as mentioned below, the gap became small enough to cause a tunneling current to flow, and the photo-assisted atomic switch was ready to work as a conventional gap-type atomic switch.

Figure 3(a) shows the change in conductance ($\sigma$) of the photo-assisted initialized atomic switch when an applied bias was swept between ±3 V without light irradiation. Three $\sigma$–V curves measured in a series are shown. When the bias was swept from 0 to 3 V, steep increases in conductance were observed at around 2.5 V, suggesting that the Ag whisker grew further from the initial set-operation (photo-assisted initialization) shown in figure 2. The increase in conductance clearly indicates that the gap was shortened by the growth of the Ag whisker. On the other hand, conductance dropped when the bias was swept back to 0 V, suggesting that the Ag whisker had shrunk and the gap had increased. We also swept the bias in negative polarity, in which conductance did not change so much after the turning-off in the sweeping back to 0 from 3 V.

Figure 3(b) shows the distribution of set-bias ($V_{\text{on}}$) and reset-bias ($V_{\text{off}}$) measured in ten times of switching. Although they have certain distributions, the device was turned on when the bias was swept to 3 V, and it was turned off when the bias was swept back to 0 V. Since the high conductance cannot be maintained at $V = 0$, i.e., without a bias application, we categorized the operation as volatile operation. In this volatile operation, distributions of conductance both of the high conductance state and of the low conductance state were less than one order of magnitude, and the on/off ratio was about three orders of magnitude.

Because conductance at the high conductance state was still lower than that of a single atom contact, i.e., 78 µS, an Ag whisker still did not reach to the counter-electrode, and the switching schematically shown in figure 3(c) is expected to have happened.

As opposed to the volatile operation, nonvolatile switching was observed when a bias was swept up to 5 V, as shown in figure 4(a) where three $\sigma$–V$^{-1}$ curves measured in a series are shown. In addition to the steep increase in conductance to the order of sub-µS at approximately 3 V, which is similar to that observed in the volatile switching shown in figure 3(a), conductance also showed a further steep increase when the bias was swept up to 5 V and it reached a few hundred µS, which is larger than that of a single atom contact (78 µS), suggesting that the Ag whisker reached the counter-electrode, as shown in figure 4(c). A high conductance state was maintained when the bias was swept back to 0 V, and application of a negative bias was required to turn off the photo-assisted initialized atomic switch. Although the negative bias required for turning-off was sometimes very small, such as −20 mV, the device showed bi-polar switching.
Figure 3. Volatile switching of a photo-assisted atomic switch after the photo-assisted initialization shown in figure 2.
(a) Conductance–voltage ($\sigma$–$V$) characteristic when a bias was swept between 0 and 3 V, and then 0 and $-3$ V. Colored arrowheads indicate reset-bias in each bias sweeping. (b) Distributions of set-bias ($V_{on}$) and reset-bias ($V_{off}$). (c) Schematic illustrations of switching between a high conductance state and a low conductance state.

Hence, we categorized the operation as nonvolatile switching. The high conductance state has quite uniform distribution of conductance in the nonvolatile operation, but the low conductance state shows a distribution of conductance up to one order of magnitude, as shown in figure 4(b).

These results suggest that the occurrence of volatile switching or nonvolatile switching depends on the sweeping bias range. This volatile/nonvolatile selective switching and the initial operation with light irradiation can be understood as follows. In contrast to conventional gap-type atomic switches, a fairly large number of Ag atoms are required to grow an Ag whisker that reaches the counter-electrode because its gap size is much larger, e.g. 20 nm, than that of a conventional gap-type atomic switch, i.e., about 1 nm. Therefore, the decrease in concentration of Ag$^{+}$ cations in an Ag$_2$S layer is largely due to the precipitation of Ag atoms. The electrochemical potential $\mu$, in which the concentration of Ag$^{+}$ cations appears, is changed by variations in the concentration of Ag$^{+}$ cations, as follows [33]:

$$\mu = \mu_0 + RT \ln C_{Ag^+} + F\Phi$$  \hspace{1cm} (1)

where $\mu_0$, $R$, $T$, $C_{Ag^+}$, $F$, and $\Phi$ are the chemical potential of Ag$^{+}$, the gas constant, temperature, local concentration of Ag$^{+}$, Faraday’s constant, and the local electrostatic potential, respectively.

In the switching operation, bias application causes migration of Ag$^{+}$ cations towards the surface of an Ag$_2$S layer, which increases the concentration of Ag$^{+}$ cations at the subsurface, as schematically shown in figure 5(a) (left). As a result, the electrochemical potential of Ag$^{+}$ increases, and precipitation of Ag atoms occurs due to the reduction process, as shown in figure 5(a) (right). The precipitation decreases the concentration of Ag$^{+}$ cations in the Ag$_2$S layer, which decreases the electrochemical potential at the subsurface of the Ag$_2$S layer, as shown in figure 5(b), resulting in the cessation of precipitation even with the continued application of a bias. When bias application is stopped, the Ag$^{+}$ cations in the Ag$_2$S layer will have a uniform distribution. As a result, the electrochemical potential in the Ag$_2$S layer decreases further, as shown in figure 5(c), and a certain number of precipitated Ag atoms return to the Ag$_2$S layer until the electrochemical potentials between the subsurface and the surface become equal.

Phenomena explained by the abovementioned mechanism were observed in the growth of an Ag protrusion on a surface of an Ag$_2$S substrate with the use of a scanning tunneling microscope (STM) [34]. Bias application of 2 V with a tunneling current of 1 nA as a feedback condition of the STM started to grow an Ag protrusion, as indicated by dotted circle (a) in figure 5(d). However, the growth
rate gradually became small, and the growth almost stopped at last as indicated by (b), even when the bias application was continued. When we decreased the tunneling current to 0.05 nA, corresponding to the decrease in effectively applied bias to the Ag₂S substrate to 1/20 [35], the Ag protrusion shrank rapidly, as indicated by dotted circle (c) in figure 5(d). Here, the states indicated by (a), (b) and (c) in figure 5(d) correspond to the states illustrated in figures 5(a)-(c), respectively.

Figure 5(e) shows the change in height of an Ag protrusion grown on an Ag₂S substrate as a function of the tunneling bias of the STM. In the measurement, a tunneling current of 20 nA was used in order to make the effectively applied bias to an Ag₂S substrate larger, resulting in a faster growth than that observed in figure 5(d). Therefore, we can assume that figure 5(e) shows the maximum height of an Ag protrusion as a function of an applied bias with a tunneling current of 20 nA. The result clearly suggests that the maximum height of an Ag protrusion becomes larger with increase in an applied bias. Namely, the amount of Ag atoms that can be precipitated from an Ag₂S substrate is a function of an applied bias.

It should be noted that saturation can be observed when an Ag whisker grows quite long. Therefore, the use of a photo-assisted initialized atomic switch is crucial for achieving volatile and nonvolatile selective operation. Based on these experimental results, we believe that the abovementioned model is the mechanism of the volatile operation observed in the experiment shown in figure 3, where an Ag whisker grew with forward bias sweeping to 3 V and shrank with backward bias sweeping to 0 V.

When an Ag whisker reaches a counter-electrode, the Ag whisker becomes stable and retains the bridging between the two electrodes, resulting in nonvolatile switching. This mechanism has been used in demonstrating short-term and long-term memory-based learning with use of conventional gap-type atomic switches [13, 14]. Of course, the concentration of Ag⁺ cations, which is decreased in the nonvolatile-on process, should be also recovered with the bias sweeping back to 0 V. We expect that Ag⁺ cations are supplied from an Ag whisker by it thinning itself while maintaining a bridge between an Ag₂S electrode and a counter-electrode. Decrease and change in conductance, which were sometimes observed when the bias was swept from 5 to 0 V, may be caused by thinning of an Ag whisker, in which a rearrangement of Ag atoms takes place.

It is expected that the maximum number of precipitated Ag atoms also depends on the size of the Ag₂S electrode. Because the grain size of Ag₂S differs among devices, operation conditions for both volatile and nonvolatile operation have quite a wide distribution at this stage. For instance, some devices show volatile operation at around 10 V.

Figure 4. Nonvolatile switching of a photo-assisted atomic switch after the photo-assisted initialization shown in figure 2. (a) Conductance–voltage ($\sigma$–$V$) characteristic when a bias was swept between 0 and 5 V, and then 0 and $-5$ V. (b) Distributions of set-bias ($V_{on}$) and reset-bias ($V_{off}$) in the nonvolatile operations. (c) Schematic illustrations of switching between a high conductance state and a low conductance state.
Figure 5. Operating mechanism for the volatile switching shown in figure 3. (a) Precipitation of Ag atoms is caused by an increase in concentration of Ag\(^+\) cations at the subsurface. (b) Decreasing the concentration of Ag\(^+\) cations lowers the electrochemical potential at the subsurface, equalizing the electrochemical potential of the Ag\(^+\) cations at the subsurface and of the Ag atoms at the surface. (c) Re-distribution of Ag\(^+\) cations due to the cut off of bias application lowers the electrochemical potential of the Ag\(^+\) cations further, causing re-ionization of the precipitated Ag atoms. (d) Change in height of an Ag whisker grown on an Ag\(_2\)S substrate. A bias of 2 V was applied with a tunneling current of 1 nA. When the tunneling current was reduced to 0.05 nA, the Ag whisker shrank rapidly. (e) Height of an Ag whisker as a function of the tunneling bias of the STM. Bias was swept from 0 to 2 V in about 1 min. A tunneling current of 20 nA was used.

The gap size also affects the operation parameters. Therefore, the development of fabrication processes for photo-assisted atomic switches with quite a uniform size of both the Ag\(_2\)S electrode and the gap is indispensable for the future application of the volatile and nonvolatile selective operations.

4. Conclusion

We demonstrated bias range dependent, selective volatile and nonvolatile operations of a photo-assisted initialized atomic switch. The selective volatile and nonvolatile operations become available by initializing the switch with a small bias application with light irradiation. In the initialization, an Ag whisker is grown to make the gap between the Ag whisker and the counter-electrode small (about 1 nm), in which a tunneling current can flow. After the initialization, growth and shrinkage of an Ag whisker can be controlled by a bias application without light irradiation. While an Ag whisker does not reach to the counter-electrode even with the bias application, the device shows volatile operation. When an Ag whisker reaches to the counter-electrode by the bias application, the operation mode switches to nonvolatile. The selective volatile and nonvolatile switching depending on the bias range will be useful in reconfiguring logic circuits such as in neuromorphic computing systems.

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