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# Memory Effect in Metal–Chalcogenide–Metal Structures for Ultrahigh-Density Nonvolatile Memories

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A novel memory effect in metal–chalcogenide–metal structures was observed using chalcogenide films connected by two Al electrodes. A bias polarity-dependent switching between a high (RESET) and low (SET) resistance state was observed in current–voltage characteristics of the structure when sweeping voltage in forward and backward directions. The reversible SET/RESET switching was induced by voltage pulses and their polarity. The resistances of the structure changed over a range of approximately two orders of magnitude. In readouts of the resistance, we obtained its retention time for data over 17 days at room temperature. [DOI: 10.1143/JJAP.45.4951]

KEYWORDS: switching, memory, phase change, chalcogenide, AgInSbTe, dendrite

## 1. Introduction

In the late 1960s and early 1970s, Ovshinsky *et al.* demonstrated the high-speed reversible structural transformations between amorphous (disorder) and crystalline (order) phases in chalcogenide glasses which could be induced by short laser pulses or voltages.[1–3] optical media compact disk rewritable (CD-RW) and digital versatile disk random access memory (DVD-RAM) based on the difference of optical properties between these two phases have been widely used in recent years. In the past 5 years, furthermore, many researchers focused on phase-change random access memory (PRAM) based on the large differences in electrical properties between these phases.[5–9] PRAM has been thought of as one of the candidates for next generation memories due to its promising advantages such as nonvolatile operation, DRAM speeds, no practical cycling limitations, high integration density, and low manufacturing cost over any other established technology.

The electrical switching in chalcogenides, the basis of PRAM, was characterized by symmetric current–voltage ($I$–$V$) characteristics and current-controlled effects. The switching was referred to as ovonic switching. However, in our experiment, asymmetric $I$–$V$ characteristics were observed in metal–chalcogenide–metal (MCM) structures with naturally oxidized Al electrodes in the boundaries. The electrical switching in the structure was voltage bias amplitude-related and polarity-dependent effect. In this paper a memory effect based on such switching in the structures is reported in detail.

## 2. Experimental Methods

The MCM structure connected by Al electrodes is schematically illustrated in Fig. 1. Al electrodes were naturally oxidized in air. A layer of 40-nm-thick AgInSbTe (AIST) chalcogenide was then sputtered on the electrodes. A 30-nm-thick capping layer of $ZnS–SiO_2$ was finally sputtered onto the chalcogenide material to protect it from oxidation and mechanical damage. The chalcogenide material was effectively crystallized by annealing before electrical measurements were performed. An Agilent 4155B semiconductor parameter analyzer was used to measure electrical properties of these samples in air at room temperature. Single voltage pulses with a width of 90 ms were employed in the measurements.

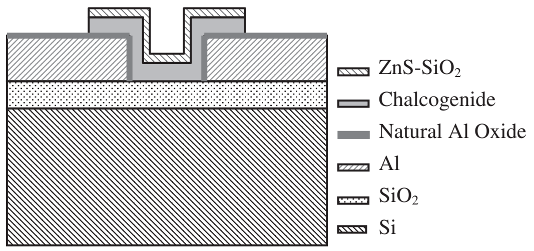


Fig. 1. Schematic diagram of the MCM structure with naturally oxidized Al electrodes.

## 3. Results

### 3.1 $I$–$V$ characteristics

The $I$–$V$ characteristics of these structures were obtained by sweeping from a negative bias voltage to a positive bias voltage and back. Figure 2 shows an example of typical $I$–$V$ characteristics of samples. There is a turning point from a low-resistance state (LS or SET) to a high-resistance state (HS or RESET) at a voltage of +11 V in the forward

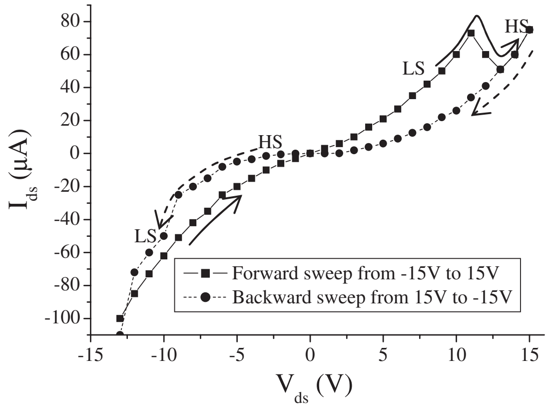


Fig. 2. $I$–$V$ characteristics of a sample. Turning points in $I$–$V$ characteristics mean switching between low and high resistance states. "HS" and "LS" beside the turning points represent the high and low resistance states, respectively. The sweeping directions of bias voltage from −15 to +15 V and backward to −15 V are indicated by arrows.

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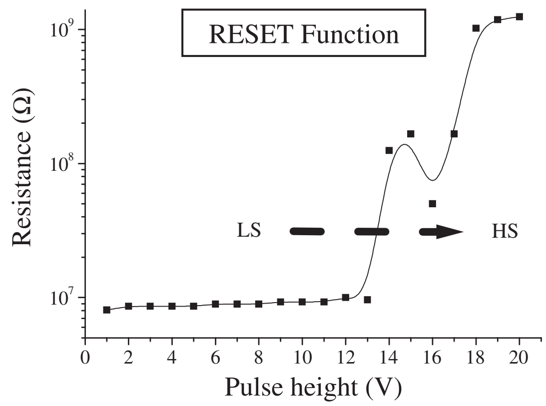
direction, while the resulting HS does not reverse to LS until the bias voltage reaches $-9$ V in the backward direction. At lower voltage values of both bias polarities, states do not change at all. On the contrary, no obvious turning point could be observed when the bias voltage was swept only at the same polarity all the time. *I–V* characteristics of the structures hence show asymmetry with respect to the polarity of bias. The LS state can be switched to another state HS at higher than a certain positive voltage (threshold voltage $V_{\text{thl-h}}$), while the resulting state HS can only be reversed to the former state LS at lower than a certain negative voltage (threshold voltage $V_{\text{thh-l}}$). Here we call the phenomenon the bias polarity-dependent switching effect.

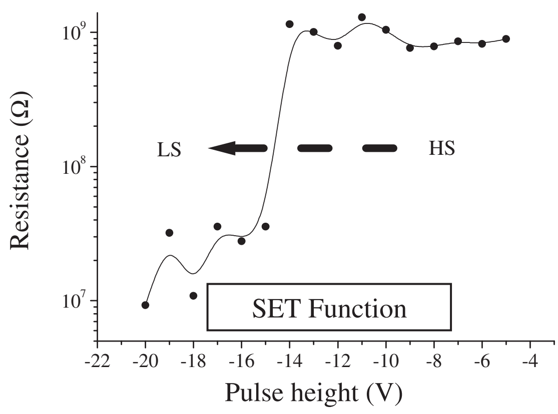
### 3.2 Switching by voltage pulses

According to the *I–V* characteristics of the structure, LS and HS can be reversed by application of bias voltage, while the resulting state can be maintained even after switching. The two states are available for a memory device. It is very easy and stable to reverse between HS and LS and read out the two states by applying high and low voltage pulses, respectively.

The typical changes in resistance of RESET and SET functions after application of voltage pulses are shown in Figs. 3(a) and 3(b), respectively. The sample began with LS. Positive voltage pulses were first applied and resistances were read at $-0.25$ V after the application of each pulse. The pulse height gradually increased from $+1$ to $+20$ V. The LS remained at low voltage pulses below $+13$ V. Resistance increased suddenly from approximately $10^7$ to approximately $10^8\ \Omega$ after applying a $+14$ V voltage pulse and further increased from approximately $10^8$ to approximately $10^9\ \Omega$ after application of a $+18$ V voltage pulse. The LS hence can be successfully switched to HS by applying a relatively high positive voltage pulse as shown in Fig. 3(a). Then negative voltage pulses were applied to the structure and resistances were measured at $-0.25$ V after the application of each pulse. The pulse height gradually changed from $-4$ to $-20$ V. The LS remained until a $-15$ V voltage pulse was applied, and the resistance decreased suddenly from approximately $10^9$ to approximately $10^7\ \Omega$. Thus by the application of a relatively high negative voltage pulse, the HS can be reversed to LS as shown in Fig. 3(b).




(a)




(b)

Fig. 3. Resistance of a sample as a function of pulse height with a pulse width of ~90 ms. The (a) RESET and (b) SET functions were realized by applying relatively high voltage pulses with two opposite polarities. Resistance was read at $-0.25$ V after application of a pulse.

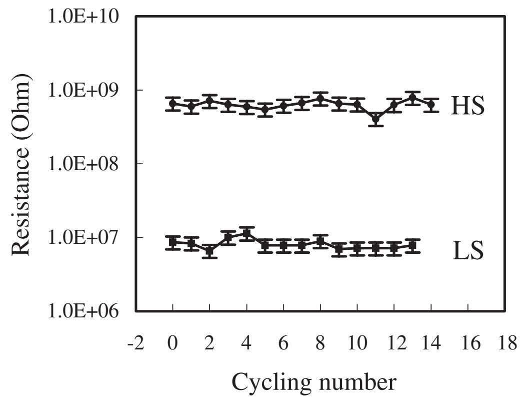



Fig. 4. Resistances of the sample after applying $+20$ and $-20$ V voltage pulses as a function of cycling number. The resistance of the HS is about $10^2$ times as high as that of the LS.

Figure 4 illustrates a reversible pulse polarity-dependent switching effect of the structure. The resistance was read at $-0.25$ V after applying each high voltage pulse. A resistance of approximately $10^9\ \Omega$ of the HS, shown as rounded dots, was obtained after applying a $+20$ V voltage pulse, while resistance dropped to approximately $10^7\ \Omega$ of LS, indicated as square dots, after applying $-20$ V voltage pulse. In this experiment, the reversible switching effect induced by $\pm 20$ V voltage pulses was recorded 14 times.

Consequently, for the SET function to attain the LS, a high negative pulse must be applied, while for the RESET function to attain the HS, a high positive pulse must be applied. A READ function can be realized in the structure by the application of a small signal pulse.

### 3.3 Retention behavior of structures

In order to determine the retention behavior of the MCM structures in this study, the current of the LS induced by the voltage pulse as a function of time was measured at room temperature. Typical behavior is shown in Fig. 5. The $I_{\text{ON}}$ and $I_{\text{OFF}}$ currents of the LS and HS at $+1$ V immediately after applying $-20$ and $+20$ V pulses were first measured and they were about 450 and 10 nA, respectively. Then the current of the LS at $+1$ V after the application of a $-20$ V voltage pulse was measured over time. The $I_{\text{ON}}$ current first dropped quickly in a few minutes after application of the

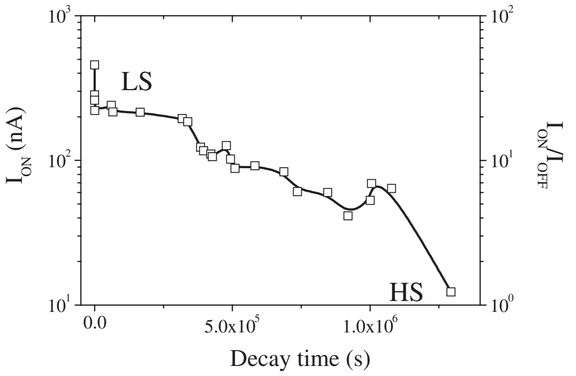



Fig. 5. Current as a function of decay time of a sample. $I_{ON}$ and $I_{OFF}$ are the currents at 1 V of LS and RS.

pulse; next remained relatively stable, then gradually decreased, and finally dropped suddenly to a value of approximately $I_{OFF}$. The ratio of $I_{ON}/I_{OFF}$ reduces to unity about $1.5 \times 10^6$ s after the pulse. In other words, states of the MCM structures can be kept for about $1.5 \times 10^6$ s (over 17 days) at room temperature.

## 4. Discussion

*I–V* characteristics and switching effects exhibited in MCM structures with naturally oxidized Al electrodes are characterized by reversible polarity-dependent behavior. The resistance ratio of HS to LS is as high as $10^2$ and thus the states can be easily read out and stored for a long time.

The memory effect reported in this paper is very different from that of PRAM. First, ovonic switching, the basis of PRAM, is a current-controlled effect, while the switching here is voltage-controlled. Second, ovonic switching is symmetric, since it depends strongly on energy applied to the PRAM cell.[5–9] On the contrary, the *I–V* curves in MCM structures here exhibit asymmetry. Third, ovonic switching depends on structural transformation, and thus resulting LS crystalline states can be readily kept long enough for nonvolatile memory. However, the LS state here obviously decayed with time, and the data can be kept for over 17 days at room temperature.

The cause of the polarity-dependent switching and memory phenomenon might be related to solid-state electrochemical reactions in the chalcogenide channel and formation and rupture of a dendrite filament along the channel.[10–12] On the basis of electrochemical reactions, when a negative bias pulse is applied to the drain electrode as shown in Fig. 6(a), neutral atoms (e.g., Ag), after losing an electron, could become mobile cations. The resulting cations migrate toward the negative electrode and a filament of Ag dendrite (low resistive) might finally form along the channel via the combination of $Ag^+$ cations and electrons.[12] A low-resistance state could consequently be obtained after the Ag dendrite filament forms. On the other hand, when a positive bias is applied to the drain electrode as shown Fig. 6(b), parts of the existing Ag dendrites disappear by forming mobile $Ag^+$ cations and electrons, especially in the channel adjacent to the drain electrode, while new Ag dendrites form at other positions via electrochemical reactions. Thus, the formerly existing Ag dendrite filament might become obviously discontinuous as illustrated in Fig. 6(b) by

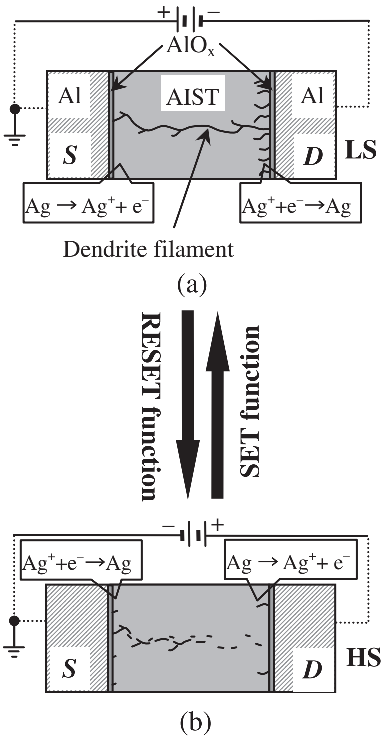



Fig. 6. Schematic diagrams of the polarity-dependent switching between (a) LS and (b) HS states on the basis of solid-state electrochemical reactions and formation and rupture of a dendrite filament along the channel.

application of a bias higher than the threshold voltage $V_{thl-h}$, resulting in a high-resistance state. As a result, polarity-dependent switching as shown in Figs. 2–4 might be attributed to the formation and rupture of dendrite filaments along the channel.

The Ag dendrite induced by an electrical pulse might be not sufficiently stable. After we apply a negative bias pulse to the drain electrodes, a dendrite filament forms, which results in a low-resistance state. Many vacancies exist in the chalcogenides according to the literature.[13] Atoms in a dendrite might move and enter into these vacancies due to thermal fluctuations. The dendrite filament would gradually become discontinuous with time. As a consequence, a low-resistance state might finally decay into a high-resistance state as illustrated in Fig. 5.

The polarity-dependent switching and memory effect reported here is reproducible; 16 identical samples were prepared and similar experimental results were obtained. The switching threshold voltage varied from about 6 to about 15 V. The cycles for polarity-dependent switching of these samples are different from sample to sample and are currently in the range from 10 to 100 times. Higher switching voltages (e.g., 20 V) usually facilitate higher reliability.

The minimum pulse height for switching reported here was nearly 15 V, which is higher than the voltage used in memories today. To define the mechanism of the observed behavior in detail, reduce the switching voltage pulse height, and prolong the retention time, electrical properties using different materials for the channel and electrodes and samples with different channel lengths and channel widths are under investigation.

## 5. Conclusion

We investigated the electrical properties of metal–chalcogenide–metal structures and demonstrated a memory effect. The following conclusions can be drawn. (1) *I–V* characteristics exhibited a bias polarity-dependent switching between high and low resistance states. (2) The electrical switching induced by voltage pulses was characterized by changes in resistance up to approximately $10^2$ times. (3) SET/RESET and READ functions were available by applying voltage pulses of different polarity and heights. (4) The current as a function of decay time indicated that the retention time of data is over 17 days at room temperature.

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