BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3662—3665 (1973)

The Photo-Erasable Memory Switching Effect of Ag Photo-Doped Chalcogenide Glasses

Isamu SHIMIZU, Hiroshi KOKADO, and Eiichi INOUE

Imaging Science and Engineering Laboratory, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152

(Received May 1, 1973)

The electric conductivity of the chalcogenide glass increased with an increase in the amount of Ag which had been photo-doped. By applying the electric field to the electrodes which were set on the surface of the Ag photo-doped chalcogenide glass film, a conductive path was grown from the cathode to the anode. As a result of the connection of the electrodes with the path, the electric resistance of the cell abruptly decreased (ON state). The path was made of the metal silver reduced by electrolysis and was diminished by irradiation with light. As the path was erased, the cell was turned into the resistant state (OFF state). The cycles were repeatable many times. There was a delay time (t_d) in turning the cell from the OFF to the ON state by applying the electric field (E). It was empirically described by the following equation for the Ag photo-doped chalcogenide glasses:

$$t_d = a\exp(-b\cdot E)$$

When a binary layer of metal and chalcogenide glass was exposed to light with the fundamental absorption band of the glass, the metal was doped into the glass layer. The term "photo-doping"[1] was given to the phenomenon on analogy with the doping of the foreign materials into the semiconductors.

As the electric field was applied to a pair of electrodes set on the surface of the Ag photo-doped chalcognide glass film, a conductive path was grown from the cathode to the anode. When the electrodes were connected with the path, the electric conductivity of the cell abruptly increased (ON state). The path remained stable even if the field was removed, while it could be erased at will by irradiation with light. As the path was erased, the cell returned to the resistant OFF state. These cycles were repeatable many times and were similar to the memory-switching effect[2] in the chalcogenide glass film. This phenomenon, however, was characteristic because of the following facts. In an ordinary case, the transition between the OFF and the ON state caused by applying a field is due to the phase transition between the vitreous and crystalline states. On the contrary, in this case

---

[1] H. Sakuma, I. Shimizu, H. Kokado, and E. Inoue, Proc. 3rd Conf. Solid States Devices, Japan, *Supplement to Oyo Butsuri*, **41**, 76 (1972).

[2] E. J. Evance, J. H. Helbers, and S. R. Ovsihnsky, *J. Non-crystalline Solids*, **2**, 334 (1970).

a migration of the silver ion in the glasses by applying the field takes place and the silver ions are reduced to the metal at the cathode, thus forming the conductive path. Moreover, the path can be erased by illumination at will.

The delay time (t_d) for the conductivity change from the OFF to the ON state under the field (E) was measured for the Ag photo-doped chalcogenide glasses. An empirical relation was obtained between t_d and E.

$$t_d = a \exp(-b\,E) \tag{1}$$

Here, a and b are constant.

Experimental

The chalcogenide glasses were prepared by the methods described in a previous paper.[3] The binary layers of Ag-chalcogenide glass were made on a substratum (slide glass) by successive vacuum evaporation (10^{-5} Torr). The silver layer on the chalcogenide glass was completely doped by irradiation with light. A high-pressure mercury lamp (Ushio-USH 250 W) fitted with an IR cut filter was used as the source. When the silver layer was completely photo-doped, the optical absorption of the metal silver at the wavelength longer than the absorption edge of the chalcogenide glass disappeared. The completion of the photo-doping of the silver layer was confirmed by the above measurement.

Two types of electric cells were used for the electric measurement (see Fig. 1). In the type (a) cell, a pair of the Au electrodes was formed on the surface of the photo-doped glass by vacuum evaporation. In the type (b) cell, an Au electrode was used as the anode and a tungsten pin electrode, as the cathode. An electric resistor of 500 KΩ was connected with the sample in series to prevent the cell from breaking because of the excessive current in the conductive ON state. A regulated power supply (Showa Electronics R-700) was used as the electric source. The electric current of the specimen was measured by means of a micro-ammeter (Takeda Riken TR-8651). To measure a t_d value of less than 1 s., a square wave pulse was used as the source and the change in the current flowing through the cell was traced with a synchroscope as the voltage drop through the series resistance.

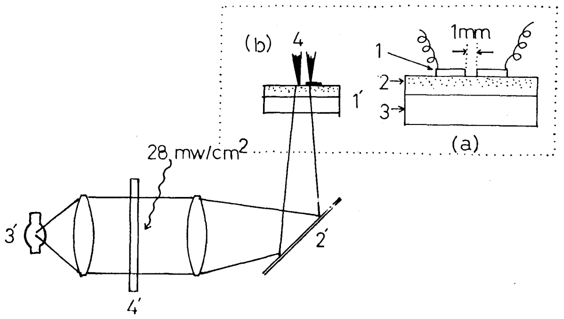

Fig. 1. Sketch of electric cells and the apparatus to measure the photo-erasing of the conductive path.
1: Au electrode, 2: Ag photo-doped chalcogenide glass, 3: substratum, 4: tungsten pin electrode, 1′: specimen, 2′: mirror, 3′: mercury lamp, 4′: IR cut filter.

Results and Discussion

As a result of the photo-doping of Ag into the chalcogenide glasses, the electric conductivity of the surface of the glass films increased with an increase in the photo-doped silver. When the electric field was applied to the cell (type (a)) on an Ag photo-doped chalcogenide glass film, the conductive path was grown from the cathode to the anode, as is shown in Fig. 2. As a result of tracing with an EMX(electron probe X-ray micro-analyser), it was confirmed that the path was made of silver dendrite. On the basis of these facts, we may suppose that the photo-doped silver was

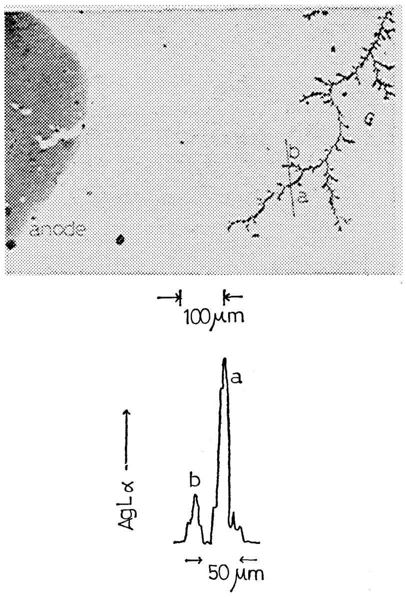

Fig. 2. Micrograph of conductive path grown from cathode to anode and EMX profile traced along a-b.

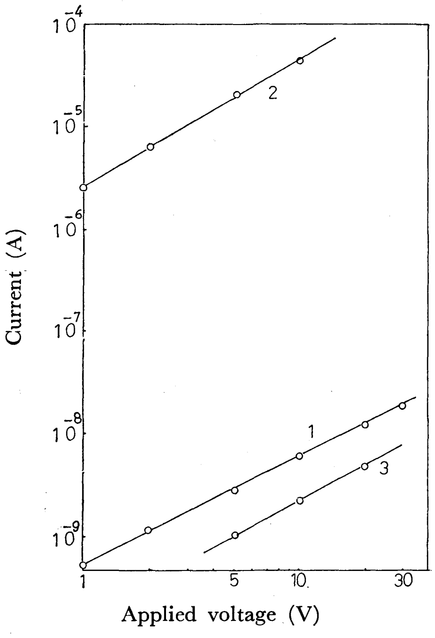

Fig. 3. Typical I-V characteristic curves of Ag (1000A) photodoped chalcogenide glass ($As_{16}S_{80}Te$) showing the photoerasable memory effect.
Type (a) cell was used. 1: OFF state, 2: ON state, 3; after irradiation of (2) with light

---

[3] I. Shimizu, H. Sakuma, H. Kokado, and E. Inoue, This Bulletin, **46**, 1291 (1973).

moved through the chalcogenide glass as the silver ion by applying the electric field and that the metal silver was reduced as a result of electrolysis at the cathode. The presence of the Ag ion has been supposed from studies of the electric properties of the chalcogenide glasses containing silver.[4)] The electric conductivity of the specimen changed a very little before the path reached the anode. As the electrodes were shorted with the path, however, the conductivity of the cell absuptly increased. Figure 3 shows the current-voltage characteristic of the Ag(1000 A in thickness) photo-doped chalcogenide glass ($As_{16}S_{80}Te_4$) film in the OFF and ON states. The path was diminished by irradiation with light. When the path was erased, the cell returned to the OFF state, as is shown by Curve 3 in Fig. 3. These cycles were repeated many times unless the specimen was damaged by the passege of an excessive current through the cell in the ON state.

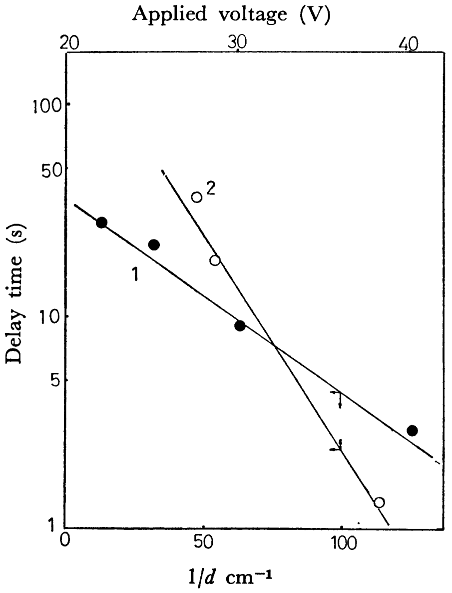

Fig. 4. Delay time plotted against applied field.
1: t_d *versus* V at constant d (1.3×10^{-2} cm), 2: t_d *versus* $1/d$ at constant V (30 volt) for Ag(500A) photo-doped $As_{30}S_{50}Se_{20}$

To regulate the position at which the path was generated, the type (b) cell was used and the delay time (t_d) was measured by changing the applied voltage (V) and the electrode distance (d). When the tungsten pin electrode was used as the cathode, the growth of the path was difficult because of its high contact resistance. Figure 4 shows the curve of the log t_d plotted against the applied voltage at the constant electrode distance ($d=1.3\times10^{-2}$ cm), and also the curve of the log t_d against the reciprocal of the electrode distance at a constant applied voltage (V=30 volt) for the Ag (500 A in thickness) photo-doped glass ($As_{30}S_{50}Se_{20}$) 0.5 μm thick. From these results, the relation between t_d and the electric field ($E=V/d$ V/cm) was described as follows:

$$\log t_d = \log A - B\cdot E. \qquad (2)$$

Table 1. A and B values obtained from the relation of the Eq. (2) for Ag photo-doped chalcogenide glasses

Chalcogenide glass	Thickness of photo-doped Ag (A)	A (s)	B (V/cm)$^{-1}$
$As_{30}S_{50}Se_{20}$	50	360$^{a)}$ 360$^{b)}$	7×10^{-4} $^{a)}$ 7×10^{-4} $^{b)}$
$As_{40}S_{60}$	400	290$^{a)}$ 290$^{b)}$	3×10^{-4} $^{a)}$ 2×10^{-4} $^{b)}$
$As_{14}S_{55}Te_{26}$	500	240$^{a)}$ 240$^{b)}$	6×10^{-4} $^{a)}$ 4×10^{-4} $^{b)}$

a) The values obtained from the curve log t_d *versus* V under the constant electrode distance.
b) The values obtained from the curve log t_d *versus* $1/d$. Respective value for a) and b) coincided with each other within the experimental errors.

Table 2. A and B values obtained from the relation of the Eq. (2) for Ag photo-doped (As_2S_3)·I

Photo-doped Ag (A)	A (s)	B (V/cm)$^{-1}$
200		0.93×10^{-3}
400	580	3.1×10^{-3}
600		3.7×10^{-3}
500$^{a)}$	4.8	1.5×10^{-3}

a) The values A and B presented in the bottom were the ones obtained in high electric field.

Here, A and B are constants. The A and B values for the Ag photo-doped chalcogenide glasses are summarized in Table 1.

The conductive path was easily grown under the lower electric field when iodine was included in the Ag photo-doped chalcogenide glass. Under a constant electric field, the t_d value decreased with an increase in the amount of photo-doped silver. The values for A and B obtained from the results are shown in Table 2. In this case, the decrease in t_d corresponded closely to the increase in the B value for the heavier doped glass. Under a high electric field, we obtained a linear relation different from that obtained under a low field for the same specimen, as is shown in Table 2. In this case, both A and B values were smaller than that obtained under the low electric field. The growth of the conductive path from the cathode to the anode proceeded rapidly under the low electric field, while it became slow in the vicinity to the anode. The change in the growth rate must be due to a scarcity of the silver ions in the vicinity of the anode. No change in the growth rate was, however, observed in the high electric field, because the path arrived at the anode before the depletion zone at the anode was formed. The fact that the conductive path was easily grown in the Ag photo-doped (As_2S_3)–I system may be explained as follows:

(1) A greater amount of silver was ionized in the glass by forming the ionic bond with the iodine.

(2) The migration of the silver ion in the glass easily took place in the same way as that of the silver ion through the ionic crystals, such as α-Ag_2S or AgI.[5)]

---

4) K. Arai, T. Kuwahata, H. Namikawa, and S. Saito, *Japan. J. Appl. Phys.*, **11**, 1080 (1972).

5) C. M. Perrott, *J. Phys. Chem. Solids*, **31**, 2709 (1970).

Though the Ag photo-doped glasses in this work were confirmed by X-ray diffraction patterns to be retained in the vitreous state, micro-crystallization could occur locally in the glass.

The conductive path was retained for a long time after the electric field was removed, and the cell could be memorized in the ON state. When the cell was exposed to light, the conductive path disappeared and the cell returned to the OFF state. Figure 5 shows the relation between t_d and the exposure time needed to turn the cell into the OFF state for the Ag photo-dopes $(As_2S_3) \cdot I$ system. The experimental conditions are shown in Fig. 1. The OFF state formed by a short illumination was turned into the ON state with a short t_d. In this case, the conductive path is partially diminished. The t_d was recovered to the value for the virgin sample when the specimen was exposed to light for enough time. This implied that the path could be erased completely.

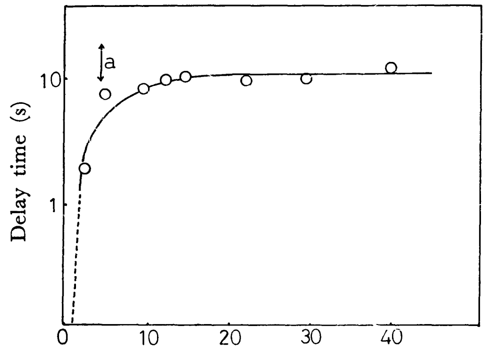

Fig. 5. Delay time plotted against exposure time for Ag-(400A) photo-doped $(As_2S_3) \cdot I$.
Applied field (7.7×10^2 v/cm); (a) shows the t_d for the virgin sample.

Conclusion

An electric memory-switching effect was found in the Ag photo-doped chalcogenide glass. It is different from the memory-switching effect observed in the chalcogenide glass films, such as the As–Ge–Te system, in which the effect is due to the phase transition between the vitreous and crystalline states. The properties of this memory-switching effect were as follows:

(1) In the Ag photo-doped chalcogenide glass, the silver ion was moved by the applied electric field, and the metal silver was reduced by electrolysis at the cathode and formed the conductive path.

(2) The ON state could be reverted to the OFF state at will by exposure to light.