Bull. Inst. Chem. Res., Kyoto Univ., Vol. 49, No. 4, 1971

Electro-Crystallization of Silver in Silver Iodide Films

Makoto SHIOJIRI*, Yasuo HASEGAWA**, Yozo TSUJIKURA**
and Kazuyuki KONISHI**

Received June 18, 1971

The growth of metal silver from the cathode in β-silver iodide films across which a d-c voltage was applied was observed. The growth rate was an order of 10^{-2} mm/min at d-c 60 V at the early stage but gradually decreased. As the current direction was reversed, a rapid growth of 1 mm/min-10 mm/min took place. The process is interpreted by assuming a potential distribution with an electric double layer resulting from migration of silver ions. The developed silver crystals were composed of filament crystals.

I. INTRODUCTION

Much intensive investigations have been made on the growth and morphology of various crystals electro-deposited in solution.[1-12] There are however few reports on the growth of crystals produced by electro-decomposition of solid electrolytes.

In the present paper, the decomposition of silver iodide which is known as one of typical solid electrolytic materials and the growth of silver crystals during the decomposition are presented.

II. EXPERIMENTAL

The specimen film and the electric circuit used are schematically shown in Fig. 1. Silver (99.99%) was vacuum-deposited in width of 5 mm, in thickness of 5000Å, crossing the gold electrodes separated by 3 mm on a cover glass plate. The silver film was caused to react completely with iodine vapor of 0.14 Torr at 25°C except the regions on the gold electrodes which were covered with protective films of polyvinyl acetate. Then, the film changed to silver iodide of the β-form.[13] A d-c voltage was applied between the electrodes to cause the electro-decomposition. The applied voltage and current were measured by a voltmeter V indicating the d-c source voltage and a pen recorder Rec indicating the voltage between a standard resistance R of 100 kΩ. Silver crystals growing by the decomposition were observed under an optical microscope. Electron microscopy of the specimen films was also carried out. The films were similarly made from vacuum-deposited silver films 500Å thick and electro-crystallized, and then wet-stripped from the glass plate.

---

* 塩尻 詢 : Department of Physics, Kyoto Technical University, Sakyo-ku, Kyoto : Laboratory of Crystal and Powder Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

** 長谷川泰雄, 辻倉 陽三, 小西 和之 : Department of Physics, Kyoto Technical University, Kyoto.

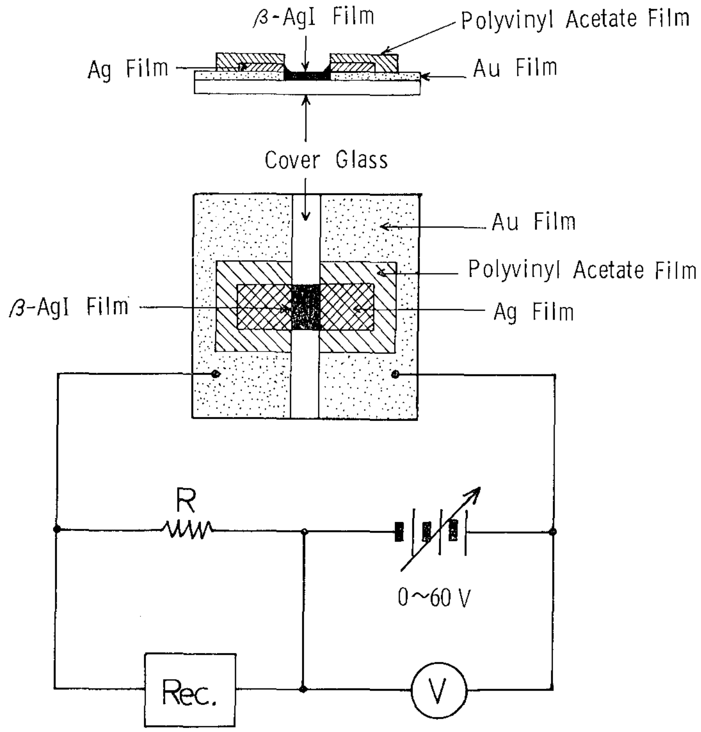
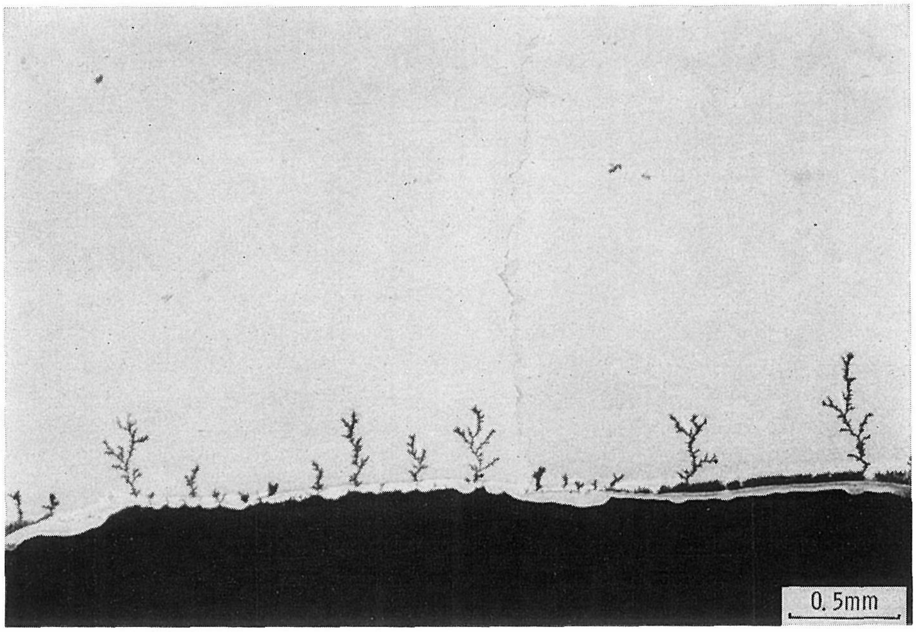


Fig. 1. A specimen film and an electric circuit used. R is a standard resistance of 100 kΩ. V and Rec represent a d-c voltmeter and a pen recorder for measuring the applied voltage and current, respectively.

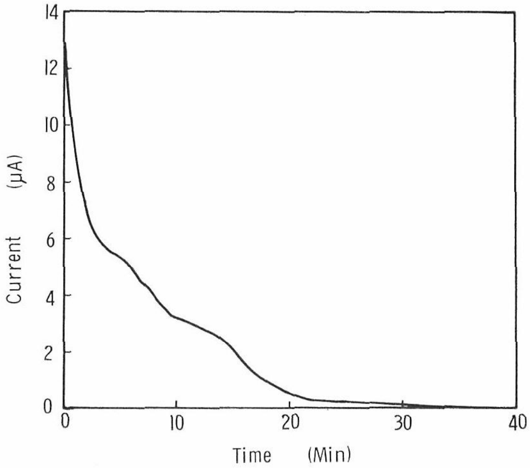
III. RESULTS AND DISCUSSION

Silver crystals grew out in the iodide films from the cathode when a d-c voltage was applied. The electrical conductivity of these β-AgI films has been reported to be about 10^{-4} ohm^{-1} cm^{-1}.[14] Figure 2 (a) shows some examples of the silver crystals decomposed at room temperature under d-c 60 V. The crystals branched out and the growth rate of the spires was an order of 10^{-2} mm/min at the initial stage of the growth. The current through the iodide film was gradually reduced as shown in Fig. 2. (b), and then the decomposition, that is, the growth of the silver crystals took place only at the spire of the most elongated branch. After about 1 hour, the current scarcely flowed and the growth stopped in a few tenth millimeters in length. The similar process appeared in the applied voltage range from 20 to 60 V, and a remarkable dependence of the growth rate on the voltage could not be detected.

The reversal of direction of the current across the specimen in which the growth of silver once declined caused a rapid growth of silver from the new cathode. The rate of this growth was of 1 mm/min-10 mm/min, which is a few hundred or thousand times the growth rate before reversing the current. The developed silver crystals were more narrow and less branched than ones before



(a)



(b)

Fig. 2. (a) : Silver crystals growing from the cathode at the bottom under the applied voltage of d-c 60 V.
(b) : Reduction of the current flow with time.

the exchange, as shown in Fig. 3. In most cases the growth of silver crystals was not retarded and the crystals reached the anode or the crystals grown from the previous cathode which was the present anode. Once such a shortcircuit was caused, many hairlike silver crystals developed along this route, as shown in Fig. 4.

If the voltage applied between the electrodes after the reversal of current direction was lower than that before the reversal, the feature was different.

Fig. 3. Silver crystals growing as the current direction was reversed after supply of d-c 60 V.

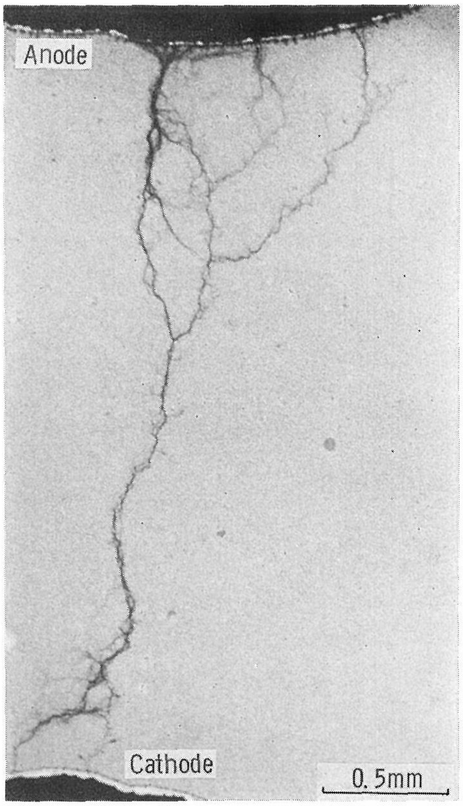
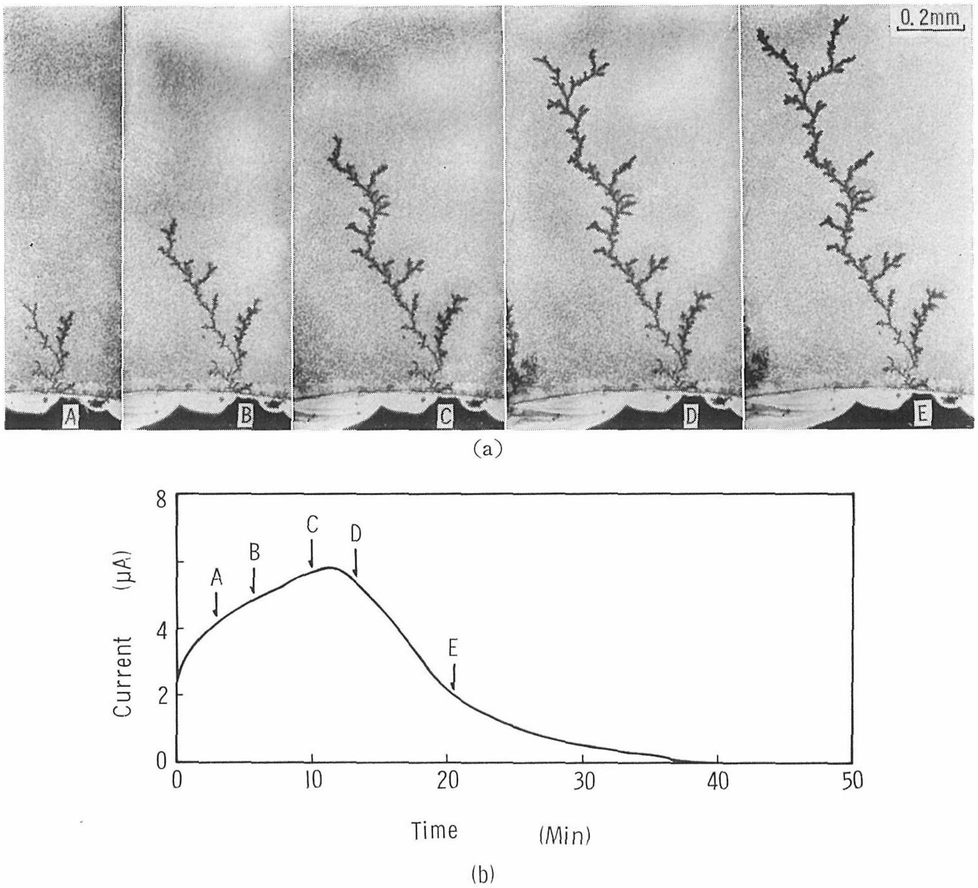


Fig. 4. Hair silver crystals resulting from shortcircuit by the silver crystal grown after the reversal. The applied voltages were both 60 V before and after the reversal of current direction.

That is, the silver crystals grown from the new cathode were rather thick and branched, and the decline of the growth rate again occurred. An example is shown in Fig. 5, in which the crystal grew under d-c 40 V after d-c 60 V was applied. The point corresponding to each photograph in Fig. 5 (a) is shown in Fig. 5 (b). The successive growth of the crystal occurred at the spire of the nearest branch to the anode, as supposed from the potential distribution in the film.

The phenomena described above may be interpreted as follow. Once the flow of current ceased, it never recovered even when the same d-c voltage was again applied in time as long as 24 hours after it was cut off. Therefore, the polarization effect is not due to the usual ionic polarization which arises from the displacement and deformation of a charged ion. The measured potential at an intermediate point between the anode at +60 V and the cathode at 0 V was nearly equal to 0 V and +60 V before and after reversing the current direction, respectively. Plausible potential distributions to which this measurement leads are shown in Fig. 6. As the d-c voltage is applied, a silver ion receives an electron on the cathode and changes into metal silver. Silver ions are succes-



(a)

(b)

Fig. 5. (a): Successive growth of a silver crystal as the applied voltage after reversing the current direction was lower than the preceding voltage. The voltage were 60 V and 40 V before and after the reversal, respectively.

(b): The change of current with time. The point at which each photograph in (a) was taken was indicated by arrow.

sively provided by migration under a given potential gradient toward the cathode through the Frenkel defects. On the contrary, iodine ions scarcely move in the film. Thus, the region in which the density of the iodine ions is relatively higher may be produced by the displacement of the silver ions. Some silver ions may be attracted near the region by its negative field. This region gradually shifts toward the anode by supplying of the silver ions from the anode side and thus the potential distribution shown in Fig. 6 (a) is realized. Since the potential distribution with an electric double layer formed in this way near the anode inside the iodide film prevents the iodide film from transmitting silver ions carrying the positive charges, it can be concluded that the decomposition of iodide and the growth of silver are gradually reduced.

Such a potential distribution as shown in Fig. 6 (b) may be realized after the reversal of direction of the current at the same voltage. Since so many silver ions having constituted the double layer exist near the new cathode as

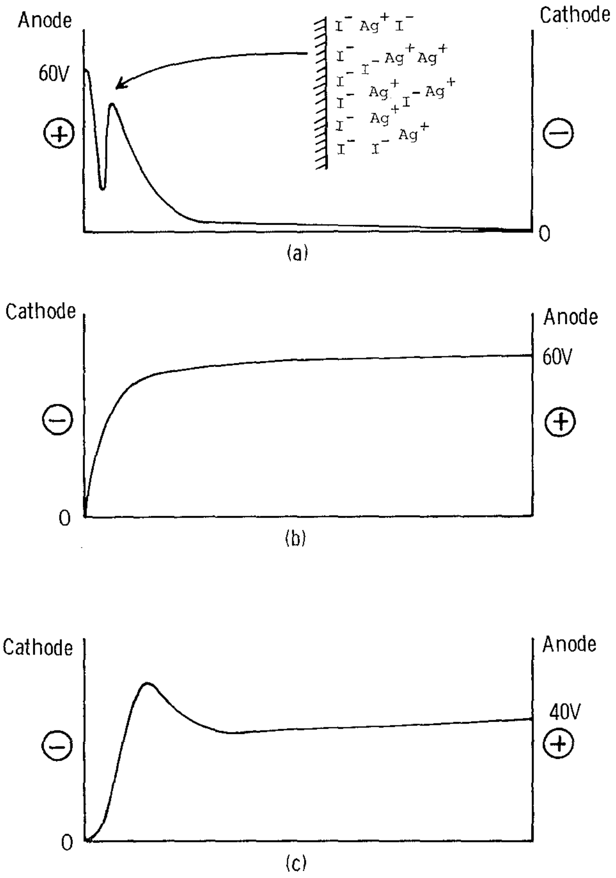
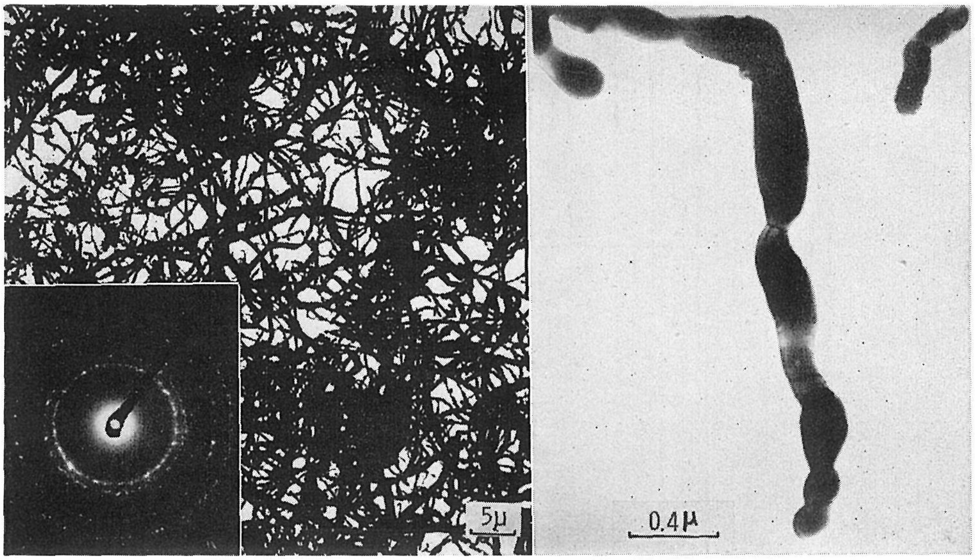


Fig. 6. Potential distributions in the silver iodide films.
(a) : at applied voltage of d-c 60 V,
(b) : at reversal voltage of d-c 60 V after d-c 60 V supply,
(c) : at reversal voltage of d-c 40 V after d-c 60 V supply.

shown in Fig. (a) that the silver ions are very easily supplied to the cathode, the growth of metal silver is very fast and silver reaches the anode before the double layer is formed near the anode.

If the reversed voltage less than the preceding voltage is applied, the field of the electric double layer may remain as a potential barrier as shown in Fig. (c). The flow of current increases with time at the early stage by easy movement of silver ions near the cathode, but it gradually decreases through the maximum as the potential barrier becomes effective. The double layer may also come to be formed near the anode in the same way as occurred before reversing the current direction.

Electron micrographs of the developed silver crystals in the same film as shown in Fig. 3 are presented in Fig. 7. They were taken by using the method that silver iodide was evaporated out by electron irradiation, since the iodide film was too thick to transmit electron beam accelerated at 100 kV. The electron diffrction pattern shows that the developed crystals were metal silver,



(a) (b)

Fig. 7. Electron micrographs of the developed silver crystals. An electron diffraction pattern due to silver was obtained as shown in (a).

and the micrographs show that the crystals were composed of many filament crystals. In Fig. (b) contrasts that may be due to twin can be seen. However, observed habits and defects may not be *a priori* in the developed crystals but may result from the electron irradiation.

Fig. 8. An electron micrographs of silver iodide film in which metal silver was electro-crystallized, taken by a 500 kV electron microscope.

Figure 8, a micrograph taken by a 500 kV electron microscope also revealed that the crystals were composed of many filament crystals. The high voltage electron microscope was useful for observing the ionic crystals without decomposing, as previously pointed.[15]

ACKNOWLEDGMENTS

The authors wish to express their thanks to Prof. E. Suito and Mr. T. Yoshida, Institute for Chemical Research, Kyoto University, for giving us a chance to use a 500 kV electron microscope, and also to Prof. H. Hashimoto, Kyoto Technical University, for his support throughout this work.

REFERENCES

(1) G. P. Tompson, *Proc. Roy. Soc.*, **133**, 1 (1931).
(2) G. I. Finch and C. H. Sun, *Trans. Faraday Soc.*, **32**, 852 (1936).
(3) W. Cochrane, *Proc. Phys.* Soc., **48**, 723 (1936).
(4) A. G. Quarrell, *ibid.*, **49**, 3 (1937).
(5) G. I. Finch and A. I. Williams, *Trans. Faraday Soc.*, **33**, 564 (1937).
(6) G. I. Finch, H. Wilman and L. Yang, *Discussion Faraday Soc.*, **1**, 144 (1947).
(7) G. I. Finch, *Z. Electrochem.*, **54**, 457 (1950).
(8) L. Yang, *J. Electrochem.*, **101**, 456 (1954).
(9) S. Ogawa, J. Mizuno, D. Watanabe and F. E. Fujita, *J. Phys. Soc. Japan*, **12**, 999 (1957).
(10) K. R. Lawless and L. B. Garmon, "5 th Intern. Congr. Electron Microscopy", Philadelphia, 1962, p. DD-7. (S. S. Bress, Jr. ed.). Academic Press, New York (1962).
(11) K. R. Lawless, "Physics of Thin Films", p. 191 (G. Hass and R. E. Thun ed.). Academic Press, New York (1967).
(12) T. Horiuchi and R. Kammel., Read at the 18th meeting of the Japanese Society of Applied Physics, March (1971).
(13) M. Shiojiri, Y. Hasegawa and Y. Tsujikura, *Japan. J. Appl. Phys.*, **10**, 143 (1971); M. Shiojiri, Y. Hasegawa and K. Konishi, to be published.
(14) M. Shiojiri, Y. Hasegawa, Y. Tsujikura and K. Konishi, *Japan. J. Appl. Phys.*, **10**, 390 (1971).
(15) M. Shiojiri, H. Morikawa and E. Suito, *Japan. J. Appl. Phys.*, **6**, 409 (1967).