Silver Dendrite Growth on Silver Ion Conducting Glasses

研究論文

Silver Dendrite Growth on Silver Ion Conducting Glasses*

Teruyoshi Awano**

Abstract: Growth of large silver dendrites by electron injection with a needle was observed on the surfaces of superionic conducting AgI-$AgPO_3$ glasses. The growth was strongly affected by the humidity of the surrounding atmosphere, indicating that the electron injection induced electrolysis with the support of surface water. The dendrite shapes were controlled by the surface conditions.

Keywords: AgI-$AgPO_3$ glass, superionic, surface dendrite, fractal, DLA

1 Introduction

Superionic conducting glasses have high ionic conductivity as liquids or solutions. Therefore, it is interesting to investigate phenomena in these solids on the analogy of those in liquids or solutions. It is well known that metal dendrite grows in solution by electrolysis. Fractal analysis has shown that the process of aggregation of metal ion is well explained by DLA (Diffusion Limited Aggregation) model, which is based on Brownian motion of the metal ion. Typical fractal dimension at two-dimensional DLA growth is 1.71[1]. The author has found large silver dendrite growth on a surface of superionic conducting glass $(AgI)_{0.5}(AgPO_3)_{0.5}$ by electron injection with a needle. Only a few studies of such macro-sized silver dendrite on the interface of solid and atmosphere by electrolysis was reported[2-4].

2 Experimental

$(AgI)_{0.5}(AgPO_3)_{0.5}$ glass was synthesized by heating $NH_4H_2PO_4$, $AgNO_3$ and AgI for two hours at 600 ℃, and quenching by putting it between copper blocks. Thickness of obtained glass plates were around 1 mm. A steel sewing needle was used for electron injection with voltage over 2.5 V, as shown in Fig. 1. Under 2.5 V, no dendrite growth was observed. Anode was a copper plate. The reflectivity spectrum of the dendrite showed that the dendrite was silver metal, which has characteristic spectral dip at 3.9 eV. Fractal shape analysis was executed by box-counting method[5]. Humidity of surrounding atmosphere were controlled by exposure time to water surface in a sealed container.

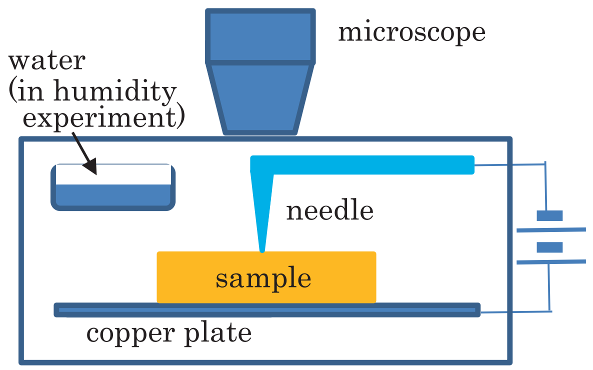

Fig. 1. Schematic diagram of the electron injection.

3 Results and discussion

3.1 Dendrite shapes

Fig. 2 shows a grown silver dendrite by electron injection at 3.0 V for 60 s. The fractal dimension of this dendrite was 1.72, which

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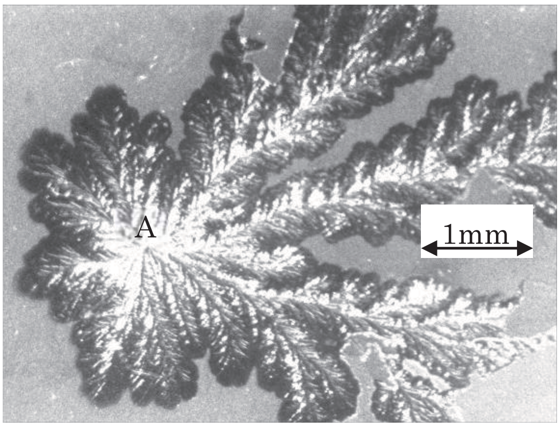
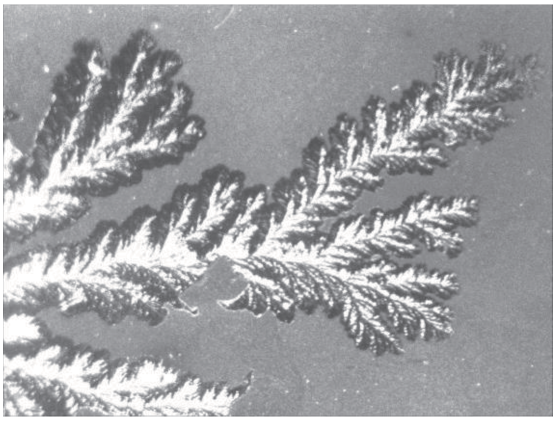


(a)



(b)

Fig.2 (a) A silver dendrite grown on $(AgI)_{0.5}(AgPO_3)_{0.5}$ glass. The injection point is shown as "A". (b) The right growth edge of the dendrite.

was in good agreement with ideal 2-d DLA model. This means that the motion of conducting silver ion in this glass is Brownian motion. Such a dendrite growth was also observed on $(AgI)_{0.25}(AgPO_3)_{0.75}$ glass as shown in Fig. 3. The growth rate was less than half of that in the $(AgI)_{0.5}(AgPO_3)_{0.5}$ glass. This seems to be due to difference of ionic conductivity. The ionic conductivity of $(AgI)_{0.25}(AgPO_3)_{0.75}$ glass is a few percent of that of $(AgI)_{0.5}(AgPO_3)_{0.5}$ glass.

Fig.3 A dendrite grown on $(AgI)_{0.25}(AgPO_3)_{0.75}$ glass. The electrode needle is seen in the upper region of the figure.

These dendrite shapes are a little different. The shapes are strongly affected by surface condition of the glasses as described below. In the fractal model, the shapes depend on microscopic movement of particle. Perfect isotropic movement of particles and growth of collected particles results in an isotropic aggregation (Eden model). Anisotropy of particle movement and growth of the aggregate particle results in IP, DLA and CCA models[1)]. Small part of difference of the dendrite shape seems to be due to such microscopic difference of silver ion conduction.

3.2 Influence of surface conditions

Such a growth of silver dendrite was strongly affected by surface condition. The shapes of grown silver metal were various at various surface conditions as humidity or roughness. Fig. 4 shows growth rate dependence of the dendrite on the humidity of surrounding atmosphere. The growth rate is proportional with the humidity excess 30%.

Anisotropic growth along with grooves on the glass surface was observed as shown in Fig. 5. The dendrite grew rapidly along with grooves which had been induced on the glass surface at quenching of the glass. Fig. 6 shows

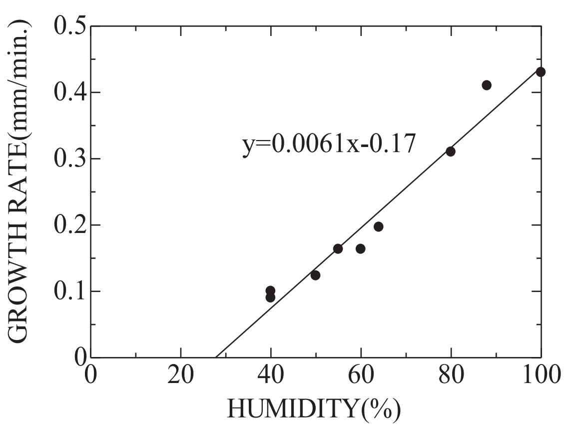


Fig.4 Growth rate dependence on humidity of surrounding atmosphere. The temperature was 25 ℃.

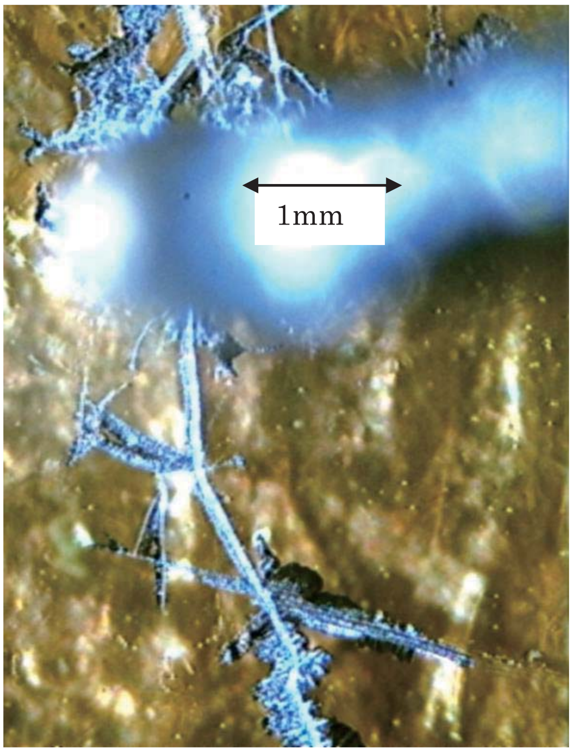


Fig.5 Anisotropic growth of the silver along with grooves on a surface of $(AgI)_{0.5}(AgPO_3)_{0.5}$ glass.

such dendrite growth along with an artificially induced groove on the glass surface by a blade. The dendrite had grown along with the groove from right side of the figure and reached to the arrow indicated point. Such anisotropic growth along with grooves seems to be due to an effect of adsorbed water in the grooves. To the contrary, a wide groove prevents dendrite growth beyond it. Fig. 7 shows dendrite growth between two wide grooves. The grooves stopped the dendrite growth.

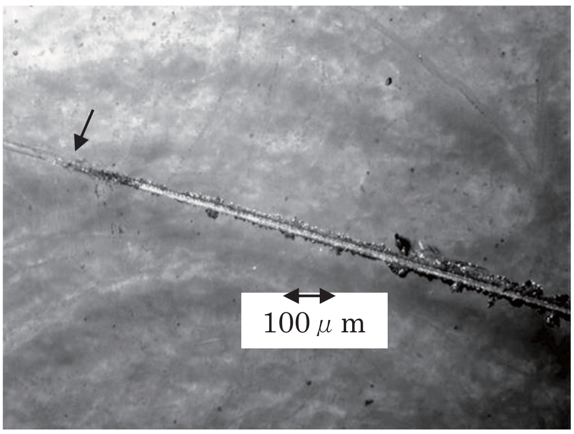


Fig.6 Anisotropic growth of the silver along with an artificial groove on a surface of $(AgI)_{0.5}(AgPO_3)_{0.5}$ glass.

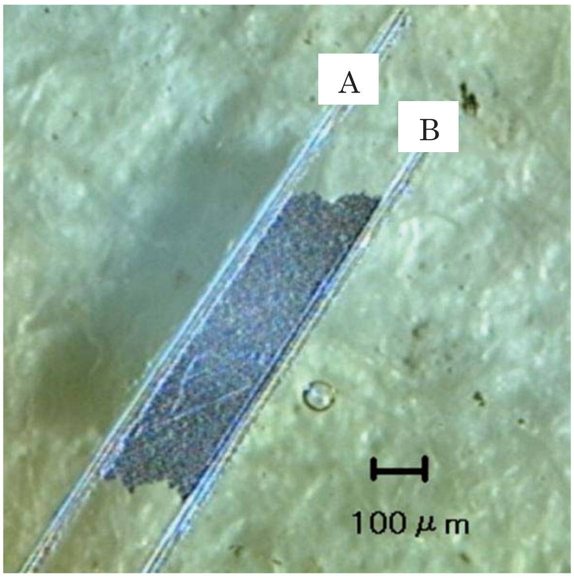


Fig.7 Anisotropic growth of the silver between two grooves (width = A: 20μm, B: 17μm) on surface of a $(AgI)_{0.5}(AgPO_3)_{0.5}$ glass.

3.3 Appling reverse voltage

Drastic change was observed when the polarity of electrode needle was inverted. The grown silver metal rapidly moved to the opposite side of the glass (the surface on anode). This change was reproducible. Another inversion of polarity of electrodes caused instantly the movement of silver metal again. Fig. 8(a) shows a glass surface with cathode needle immediately after the inversion of polarity of the applied voltage. The silver metal moved to the opposite side of the glass. Fig. 8(b) shows the same surface immediately after the inversion of polarity of the applied voltage again. The silver metal came back on the cathode side again. This phenomenon seems to be due to electrolysis of Ag_2O which is generated by water vapor adsorption on the glass, as described below.

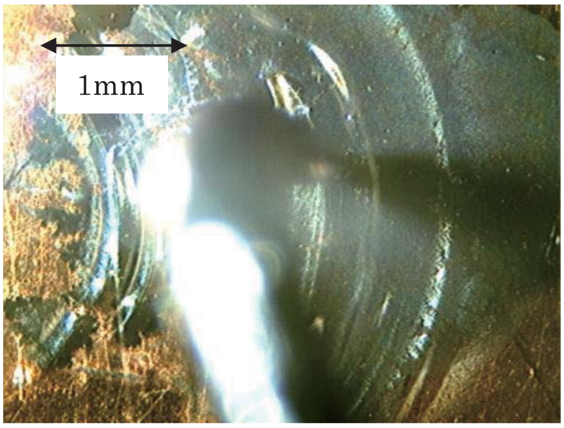
At first, water vapor in atmosphere induces silver dioxide;

$$2Ag^+ + 2OH^- \rightarrow Ag_2O + H_2O \quad (1)$$

Subsequently, electrolysis occurs by electric current;

$$\text{Cathode: } Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^- \quad (2)$$

$$\text{Anode: } Ag_2O + 4I^- + H_2O \rightarrow 2AgI + I_2 + 2OH^- + 2e^- \quad (3)$$



(a)

(b)

Fig.8 (a) Rapid "moving" of silver after the reverse voltage was applied. (b) Silver "re-moving" by reversing the voltage once more.

Potentially induced silver dioxide seems to be transformed into silver or silver iodide instantly. In the case of AgI-Ag_2MoO_4, no dendrite growth was observed even in high humidity atmosphere. This suggests that reaction (1) occurs only in the phosphate glass.

3.4 Spectroscopic study

Spectroscopic study was executed to investigate the above mentioned chemical reaction process. Fig. 9 shows reflectivity spectra of both sides of a dendrite-induced $(AgI)_{0.5}(AgPO_3)_{0.5}$ glass. The "front" (solid line) in the Fig. 9 means the dendrite (cathode) side of the glass. The dip at 3.9 eV is due to silver metal. This dip is deep in the spectrum of the front side. The peak at 2.7 eV is due to AgI. This peak is large in the spectrum of the back side. The peaks at 4.3 and 5.9 eV are due to Ag_2O. The Ag_2O peaks are observed at

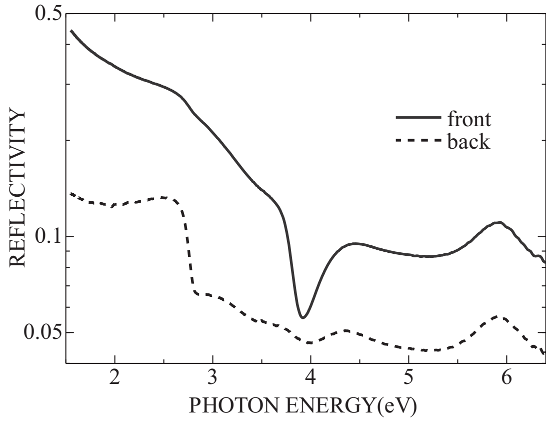


Fig.9 UV reflectivity spectra of the dendrite-induced $(AgI)_{0.5}(AgPO_3)_{0.5}$ glass. The solid line shows reflectivity spectrum of the surface of the dendrite side. The dashed line shows reflectivity spectrum of the surface of the reverse side.

equal strength in the spectra of both sides of the glass. These spectral characteristics support the above mentioned chemical reaction formula at dendrite growth.

4 Conclusions

This investigation is the first report on a macro-sized fractal metal dendrite growth on a solid electrolyte glass surface. This phenomenon seems to be strongly related with the fact that superionic conducting glasses have both natures of solids and liquids. The anisotropic growth is an important example of such double natures.

Acknowledgements

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