

Dendritic growth of silver nanowires in borosilicate glass formed by field-assisted solid-state ion exchange

Hiroki Aoyama, Souta Matsusaka*, Hirofumi Kawamura, Hirofumi Hidai, Akira Chiba, Noboru Morita, Takaomi Itoi

Department of Mechanical Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba, 263-8522, Japan

HIGHLIGHTS

- The voltage application provided silver nanowires in Ag/Na ion-exchanged glass.
- Nanowires dendritically developed from glass surface to doped/un-doped interface.
- The precipitates changed the growth direction and expanded along the interface.
- The generation of silver precipitates was not derived from a thermodynamic process.
- Electrochemical interaction was a dominant factor for the silver precipitation.

ARTICLE INFO

Keywords:

Solid-state ion exchange
Borosilicate glass
Silver nanowire precipitation
Dendritic growth
Electrochemical reduction

ABSTRACT

The additive voltage application provides silver nanowires in silver-doped glass prepared by electric field-assisted solid-state ion exchange. We experimentally investigate the growth behavior of silver nanowires in a glass substrate. It was found that silver nucleation was initiated at the silver-doped surface contacted with the cathode, and the precipitates dendritically developed toward the doped/un-doped interface as the time of voltage application was increased. After the precipitates reached the interface, the growth direction changed and extended along the interface. Transmission electron microscopy (TEM) observation suggested that the precipitation did not arise from the aggregation or growth of nanoparticles formed in the silver doping process. The experimental results, where the precipitation occurred just below the contacted cathode and was independent of cathode material, indicated that the precipitation resulted from the electrochemical interaction between doped silver ions and supplied electrons. From these findings, we are able to control the silver nucleation area by the arrangement of the cathode configuration.

1. Introduction

Ion exchange is a commonly used method for the metal doping of alkali-silicate glasses [1]. In this method, metal doping is achieved by the replacement of alkali ions in a glass substrate with supplied metal cations. Conventionally, the wet exchange process, in which a glass substrate is immersed in a molten salt bath that contains metal ions (e.g., silver [2] or copper [3]), was adopted. In addition, a solid-state process assisted by a voltage application has also been widely used. In the latter case, metal ions (e.g., silver [1], copper [4], chromium [5], gold and cobalt [6]) are doped from a film or a foil placed on the glass substrate by an electric field using the dopant metal as the anode. In both processes, doped metal ions aggregate and form nanoparticles

(~10 nm in diameter) in the glass matrix that provide the glass substrates with peculiar optical and mechanical characteristics [3,7]. Because of the simplicity and versatility of the process, many research efforts on wet/solid-state processes have been made for applications such as planer waveguides and optical switching devices [3,4,8] as well as microfluidic devices [9].

Most recently, some studies on the post-exchange technique have been conducted for the control of the nanoparticle size, configuration, distribution and composition, as these characteristics strongly influence the optical and mechanical characteristics of ion-exchanged glasses. For example, Manikandan et al. [10] reported that the core-shell structured nanoparticles were formed by sequential ion exchange using silver and copper followed by furnace annealing. Their glasses exhibited

* Corresponding author.

E-mail address: matusaka@faculty.chiba-u.jp (S. Matsusaka).

<https://doi.org/10.1016/j.matchemphys.2018.08.002>

Received 14 July 2017; Received in revised form 31 July 2018; Accepted 1 August 2018

Available online 04 August 2018

0254-0584/ © 2018 Elsevier B.V. All rights reserved.

characteristic absorption spectra with two surface plasmon resonance peaks at approximately 410 and 565 nm. Additionally, it was shown that repeated nanosecond laser irradiation on silver-sodium ion-exchanged glasses induced a particle growth up to 50 nm in diameter, resulting in an increase of the optical absorption at a specific wavelength of 400–420 nm [11]. In another study, it was reported that the post-exchange treatment on silver-doped glasses, such as ultraviolet nanosecond laser irradiation [12] or annealing in a reducing hydrogen atmosphere [13], triggered the out-diffusion of silver from the glass substrates, and nanoparticles or nano-islands were formed on the glass surfaces.

Additionally, we have previously reported interesting phenomena during silver doping to borosilicate glass by solid-state ion exchange with different methods of electric field-assistance [14]. In our process, after silver doping of glass by conventional field-assisted ion exchange (*i.e.*, a silver foil was used as the anode; referred to as the forward voltage), the voltage with an opposite direction to the case of doping (*i.e.*, the silver foil acted as the cathode; referred to as the reverse voltage) was applied. As a result, networked silver nanowires appeared at the bottom of the silver-doped area. The diameter of the precipitated nanowires was up to 300 nm, and this value was obviously larger than that of the nanoparticles (~10 nm in diameter) formed by application of only the forward voltage. Here, two questions arise, these are, how and why do the large precipitates suddenly appear at the bottom of the silver-doped area with the reverse voltage application. In this study, we observe the precipitation process of the silver nanowires with a focus on the initiation and growth of precipitates when the application time of the reverse voltage was varied. Additionally, the control of the silver nucleation area was examined. We also discuss the electrochemical precipitation mechanism of silver nanowires.

2. Experimental

The substrate was a borosilicate glass slide (Borofloat 33, $25 \times 25 \times 1.1 \text{ mm}^3$, Schott, Mainz, Germany) with a composition (wt. %) of 81 SiO₂, 13 B₂O₃, 4 Na₂O/K₂O, and 2 Al₂O₃. A pure silver foil (> 99.9%, $20 \times 20 \times 0.01/25 \times 25 \times 0.01 \text{ mm}^3$, Nilaco, Tokyo, Japan) was used as the dopant. The silver foil, glass slide, and an aluminum foil (> 99.9%, $25 \times 25 \times 0.01 \text{ mm}^3$, Nilaco) were placed between two copper electrodes in a vacuum chamber (< 10^{-3} Pa). The aluminum foil was used for the improvement of close contact between the lower electrode and glass slide. Fig. 1 shows the experimental setup for the ion exchange. After evacuation of the chamber and increasing the temperature, a direct current (DC) voltage was applied using silver foil as the anode (*i.e.*, forward voltage application). The applied forward voltage, ion-exchange temperature, and time were 200 V, 623 K, and 10.8 ks (3 h), respectively. Under these conditions, the silver penetration depths were in the range of 90–120 μm. The reason of discrepancy in penetration depths between our previous [14] and present

results was considered in Appendix A. In Appendix A, the temperature dependence of silver doping process was also shown. After doping the glass substrate with silver, an additive DC voltage was applied using silver foil as the cathode (*i.e.*, reverse voltage application). Because slower precipitation was preferable for the observation of silver growth, lower value (100 V) was adopted as reverse voltage. For the time-series observation, the ion-exchange time was varied from 30 s to 10.8 ks. The ion-exchange temperature was the same as the forward-voltage case. After the experiment, the glass slides were detached from the remaining silver foil and rinsed in distilled water. The cross-sections of the glass slides were observed using an optical microscope (ME600, Nikon, Tokyo, Japan) and a transmission electron microscope (TEM; JEM-2100F, JEOL, Tokyo, Japan). The cross-sectional chemical compositions were examined by an electron probe micro-analyzer (EPMA; JXA-8900, JEOL).

3. Results and discussion

3.1. Growth of silver nanowires with application of reverse voltage

Fig. 2 shows the surface appearances and cross-sectional views of the glass samples when the application time of reverse voltage was varied from 30 s to 10.8 ks. As shown in Fig. 2(a), very small precipitates were observed on a glass surface (a magnified photograph is also shown in Fig. 2(a)). As the application time of the reverse voltage was increased, many dendritic precipitates randomly appeared and connected with one another (Fig. 2(b)). After sufficient time for the precipitation, a silver layer was formed in the glass substrate as shown in Fig. 2(c). The cross-sectional photographs using transmitted light (Fig. 2(d)–(g)) indicated that the precipitates generated at the glass surface dendritically developed towards the depth direction with the application of reverse voltage. After the precipitates reached the silver doped/un-doped interface, they continuously expanded along the interface without penetrating into the un-doped area. This means the silver layer observed in Fig. 2(c) was just on the interface. Additionally, it was found that the buried silver layer was formed by the linkage of many silver branches. This fact is in agreement with the TEM observation results [14] that showed the silver layer had a nanowire network structure. In our previous letter [14], we reported that the precipitation layer was embedded in a glass substrate and it was exposed only at the glass surface around the outer edge of the doped area. However, this was our misunderstanding, and there were in fact some connections to the glass surface through vertically developed precipitates.

Fig. 3 shows the change in the precipitation depth (see Fig. 2(d)) with the application time of reverse voltage from 30 s to 10.8 ks. In this figure, maximum, minimum and averaged values obtained by nine measured depths in one glass sample for every time condition are shown using error bars and filled circle. As shown in Fig. 3, the maximum depth of the precipitates increased with time and was saturated at approximately 90–120 μm, which was the silver penetration depth under the present doping conditions. Surprisingly, the fastest growing precipitate reached the doped/un-doped interface after 300 s of the application of reverse voltage. The reason why the minimum depth hardly changed with time arose from the continuous nucleation and precipitation of silver at the glass surface. The obtained results in this section are summarized by the schematic illustration shown in Fig. 4. It is worth noting that the outer edges of the silver foil cathode and precipitation layer were slightly mismatched, because doped ions diffused in the glass matrix driven by the electric field and concentration gradient of silver [15].

3.2. TEM observation around silver precipitates

The next question is why the large precipitates suddenly appeared in the silver-doped area with the application of reverse voltage. We

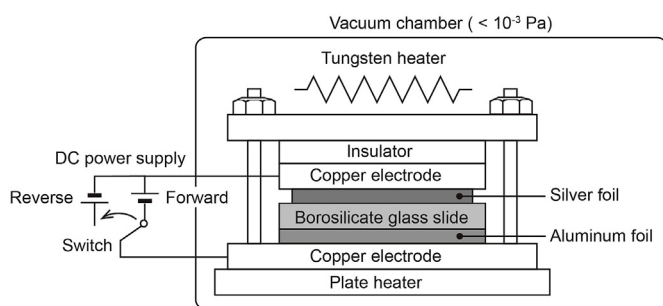


Fig. 1. Experimental setup for field-assisted solid-state ion exchange. The silver foil, glass slide, and aluminum foil were placed between two copper electrodes. The sample temperature was measured and controlled using a neighbor dummy sample (not shown in this figure).

Download English Version:

<https://daneshyari.com/en/article/7921136>

Download Persian Version:

<https://daneshyari.com/article/7921136>

[Daneshyari.com](https://daneshyari.com)