Electrochemical design of metal distribution in alkali silicate glass with ion-conducting microelectrodes

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Electrochemical design of silver distribution near the surface or in the bulk of alkali silicate glass for use in the preparation of optical devices was carried out using an ion-conducting microelectrode. The fundamental solid-state electrochemical cell consists of an anode (Ag)/Ag- β'' -Al₂O₃/alkali silicate glass/cathode (Ag) system, where the Ag⁺ conducting Ag- β'' -Al₂O₃ microelectrode was used as a cationic source. Ag⁺ in Ag- β'' -Al₂O₃ microelectrode under an applied electric field resulted in the fine-patterned Ag-distribution in the glass surface so that the contact radius between Ag- β'' -Al₂O₃ and glass was extremely small (about 10 µm). Furthermore, the patterned Ag distribution, which was constructed near the surface in advance, can be encapsulated within the bulk by subsequent Na⁺ injection.

Functional modification of glass surfaces is an effective method for imparting new characteristics to the original glass.¹ Wellestablished techniques include the deposition of films on the surface and the introduction of different elements into the surface region. For instance, silver or titanium coatings on the glass surfaces have already been used for IR-reflection or UV-cut glass.² The latter application corresponds to the ioninjection technique using gas phase ions at low pressure or ionexchange using molten salts.

Intended for use in conjunction with these methods, we recently proposed a new solid-state electrochemical route for introducing metal cations into glass using ion-conductors.³ In this electrochemical approach, upon application of an electric field to the solid–solid interface between cation-conducting M- β "-Al₂O₃ and alkali metal ion containing glass, the metal cations (M^{*n*+}) are injected into the glass concurrently with the substitution for alkali metal cation in the glass. A significant advantage of this technique is that it enables pinpoint doping into the desired position in the glass with the aid of a β "-Al₂O₃ microelectrode, owing to which the contact radius of the solid–solid interface is typically about 10 µm. Indeed, we have already achieved pinpoint doping into alkali borosilicate glass and/or Bi₂Sr₂CaCu₂O_y superconducting ceramics on a 10² µm scale using a β "-Al₂O₃ microelectrode.^{4,5}

There have been recent reports on the application of the microelectrode technique to solid-state fabrication of metal micro- or nano-structures. Fleig et al. have reported on electromechanical writing of Ag microstructures (lines and letters) on the surface of a Ag⁺-conducting AgCl single crystal, where cathodic deposition of Ag occurred selectively along the mechanical tracks scratched by a tungsten needle in advance.⁶ Terabe et al. have prepared silver nanowires between a Ag₂S microanode and Pt cathode, which were set 1 nm apart by a cathodic solid-state electrochemical reaction where the Ag⁺ ions arriving at the cathodic surface of Ag₂S react with the tunneling electrons generated from the Pt cathode under an electrical bias.7-9 They mention that the fabricated Ag nanowires can easily dissociate by applying the reverse field, and that the formation-dissociation reactions can occur at a rapid field frequency of above 1 kHz. Iliescu et al. reported that silver-sweeping of α -quartz causes the growth of silver

microwires inside the quartz crystals by electrodiffusion from the anodic AgNO₃ layer using tungsten microcathodes.¹⁰

Our method would conceivably enable micropatterning of dopants in glass if the β "-Al₂O₃ microelectrode were to be moved along the glass surface during doping. The technique could be used to prepare optical devices, such as photowaveguides and microlenses, since pinpoint or patterned doping induces selective refractive index profiles in glass. In the present contribution, we have devised an electrochemical method for achieving metal cation distribution in the surface and interior of alkali silicate glass by manipulating a Ag- β "-Al₂O₃ microelectrode under an electric field.

Experimental

Electrochemical cation doping was undertaken using the experimental setup shown schematically in Fig. 1a. Ag- β'' - Al_2O_3 was used as a Ag^+ conductor. The $Ag\mathchar`\beta''\mathchar`Al_2O_3$ microelectrode was prepared by the substitution of Ag for Na in Na-β"-Al₂O₃. A Na-β"-Al₂O₃ polycrystalline pellet (Nihon Tokushu Togyo Co.; thickness: 2 mm, diameter: 7 mm) was immersed in AgNO₃ molten salt for over 24 h. Electron probe microanalysis (EPMA) performed on the cross section of β'' -Al₂O₃ revealed that the Na was completely exchanged. The resultant Ag- β'' -Al₂O₃ was polished with emery paper to form a quadrangular pyramid-like microelectrode. Assuming a hemispherical microcontact between $Ag\mathchar`spherical_3$ and the doping target, the contact radius would typically be about 10 µm. An alkali silicate glass (12Na₂O-1K₂O-5MgO-9CaO-1Al₂O₃-72SiO₂ in mol%) was used as a doping target. Cation doping was performed at a constant current or voltage with a regulated DC power supply at 403–673 K in air, where the Ag- β'' -Al₂O₃ microelectrode was scanned using a PC-operated, automated *XYZ* microstage (scan rate: 0 (fixed) $\sim 1 \text{ mm s}^{-1}$). The change in applied voltage during electrolysis was monitored using a digital multimeter. It was checked that no doping occurred in the absence of the electric field at these temperatures. After doping, the distribution state of the dopant in the anodic surface and the cross section of the doping target was analyzed by EPMA.





Fig. 1 (a) Experimental setup and (b) the cation migration model of Ag doping using a Ag- β'' - Al_2O_3 microelectrode.

Results and discussion

The basic cation migration mechanism in the present system for pinpoint Ag doping into glass is illustrated in Fig. 1b. Ag was electrochemically oxidized to Ag^+ at the Ag (anode)/Ag- β'' -Al₂O₃ interface, and then injected into the glass. Na⁺ migrated from the glass to the cathode side to maintain the electrical neutrality in the glass. Na was deposited at the glass/Ag (cathode) interface and immediately reacted with the O₂ and CO₂ in air to form Na₂CO₃.¹¹ Hence, Ag⁺ was substituted for Na⁺ in the glass under an electrical field,¹² where the K⁺ sites in the glass may be also attacked by Ag⁺ because the glass used in this study contains a trace amount of potassium oxide. Thus, this doping scheme corresponds to an "electrosubstitution" mechanism.

Fig. 2 shows optical micrographs of the anodic surface and the cross section of the glass (1 mm³ cube) that was Ag-doped under a constant voltage of 30 V for 60 min at 673 K, where the Ag- β'' -Al₂O₃ microelectrode was fixed onto the glass surface during electrolysis (*i.e.*, scan rate = 0 mm s⁻¹). According to the EPMA measurement, it is confirmed that silver is present only in the brown areas in these micrographs, where a small amount of the whole silver doped in the glass may exist as thermally produced Ag colloidal particles with optical absorption in the visible region (Ag_n⁰; pale yellow to amber).^{13,14} However, most silver in the glass is in an isolated ionic state (Ag⁺; colorless). In fact, the silver distribution area after doping at low temperature (below 473 K) was colorless. From



Fig. 2 Micrographs of the anodic surface and cross section of the glass after pinpoint Ag doping under a constant voltage of 30 V at 673 K for 60 min.



Fig. 3 Time evolution of the applied voltage under a constant current of 10 μ A at 473 K with and without tracing the Ag- β'' -Al₂O₃ microelectrode.

our previous studies,^{4,5} we know that the silver doping results in a hemispherical dopant distribution centered on the microcontact between β'' -Al₂O₃ and the glass. In addition, the distribution diameter of the dopant on the anodic surface depended on the current density and/or the doping time, which reflect the amount of Ag doping.¹⁵ The distribution state of the dopant may be dominated by the potential distribution around the point contact electrode. The equipotential surfaces between the microelectrode and the planar electrode exhibit a hemispherical shape with their center at the microcontact.¹⁶⁻¹⁸ Thus, it can be concluded that Ag⁺ diffused radially from the Ag- β'' -Al₂O₃/glass microcontact during doping. As a result, a hemispherical distribution of silver was obtained by this method. We have confirmed that various monovalent cations (K⁺, Li⁺, Cs⁺) besides Ag⁺ can be doped according to the same mechanism.

Fig. 3 shows the time evolution of applied voltage under a constant current of 10 µA at 473 K with and without tracing the Ag- β'' -Al₂O₃ microelectrode along the glass surface. When the microelectrode was fixed on the glass surface, the applied voltage decreased rapidly during the initial stage of electrolysis (<0.5 min) and remained at a nearly steady state after 0.5 min, corresponding to the slight voltage reduction. The effect of the cathodic Na₂CO₃ deposition, mentioned above in the description of the doping mechanism, on the total applied voltage can be neglected in the present method because the current density at the glass/Ag (cathode) interface would be negligible compared with that at the microcontact. Others have reported that the voltage response in the ion-conducting microelectrode technique depends on ionic conductivity only in the small region near the microcontact.^{19,20} Taking into account the much larger ionic conductivity in Ag-\beta"-Al_2O_3 compared to that in the alkali glass, the voltage drop occurs mainly within the glass. Thus, the decrease in voltage under constant current suggests that the ionic conductivity in the glass around the microcontact increased with the substitution of Ag⁺ for Na⁺ in the silicate glass during the initial stage of electrolysis. This is mainly due to the higher ionic conductivity of Ag^+ in the amorphous glass network as compared to that of Na^+ .^{12,21} By contrast, when the Ag-B"-Al₂O₃ was scanned during electrolysis, the applied voltage remained almost constant throughout the duration of electrolysis, except for some variations that may have been due to the surface roughness of the glass. In this case, the Ag⁺ injection always proceeded from the original glass surface, which contained only Na⁺ as a charge carrier. That is, the chemical composition reflected by the ionic conductivity near the microcontact remained constant during doping.

EPMA elemental distribution maps of the anodic surface of



Fig. 4 (a) EPMA elemental distribution maps of the anodic surface of Ag-doped glass on scanning the Ag- β'' -Al₂O₃ microelectrode in a single direction at 403 K (scan rate: 1 mm s⁻¹ (upper line) and 0.1 mm s⁻¹ (lower line)). (b) More complex Ag patterns sketched in the glass surface.

Ag-doped glass on scanning an Ag-B"-Al2O3 microelectrode in a single direction at 403 K are shown in Fig. 4a. The scan rates of the microelectrode were 1 mm s^{-1} (upper line) and 0.1 mm s^{-1} (lower line). These results indicate that Ag was dispersed in a line along the path of the microcontact, and that the line width was easily controlled by the electric charge per unit area, i.e., scan rate and/or current. According to the elemental distribution map of the cross section of the Ag-line drawn on glass, a semicircular Ag dispersion was observed, as in the case of the fixed microelectrode. Since the Ag- β'' -Al₂O₃ microelectrode is attached to the automated XYZ stage (Fig. 1a), we can draw various silver patterns in the glass surface, not only simple structures (points and lines) but also more complicated forms (Fig. 4b). The lowest patterned Ag line width achieved to date is about 10 µm. However, the use of a microelectrode with a smaller contact radius and/or lower constant current (applied voltage) may enable the fabrication of finer and/or more complex patterns at the nanometer scale.

Expanding the present technique, we can control the glass composition not only in the surface region, but also in the bulk glass. In other words, the electrochemical design of glass composition is also possible in three dimensions. More specifically, following Ag patterning in the glass surface, Na⁺ generated by the electrochemical decomposition of the Na₂CO₃ planar anode is re-injected into the Ag-doped glass in a direction that is parallel to the anodic surface as shown schematically in Fig. 5a. EPMA elemental maps of the cross section of the rectangular glass $(1 \times 1 \times 10 \text{ mm}^3)$ containing the Ag distribution are shown in Fig. 5b. In this case, first, Ag was doped using a fixed Ag- β'' -Al₂O₃ microelectrode under 1 μ A, for 60 min at 573 K. This was followed by Na⁺ doping at 1 mA for 15 h at 673 K. Thanks to this two-step doping process, the Ag distribution is encapsulated within the glass sample by the Na⁺ doping, during which it retains its hemispherical shape. It was found that the Ag concentration increased toward the direction of ion migration. Again, this is due to the larger ionic conductivity of Ag⁺ in the glass compared with that of Na⁺. As expected, the penetration depth



Fig. 5 (a) Schematic method for encapsulating the Ag-distribution inside the glass. (b) Ag mapping after Na⁺ re-injection at 1 mA and 673 K for 15 h, following pinpoint Ag doping at 1 μ A and 573 K for 60 min.

of the Ag distribution depended on the electric charge of Na⁺ doping in the second step. It was also confirmed that the line patterned Ag dispersion could exist only within the glass. Qiu *et al.* have substantiated the possibility of selectively inducing a change of valence state of metal ions on a micrometer scale inside a glass sample by using a focused pulsed laser.^{22–24} By contrast, our electrochemical technique can cause a space-selective change of chemical composition inside the glass.

Conclusion

In this contribution, we have investigated the possibility of the electrochemical design of metal distribution in alkali silicate glass using a β'' -Al₂O₃ microelectrode. Various patterns of Ag distribution were constructed near the surface or in the bulk. The size and shape of these patterns could be easily controlled by adjusting electrolysis conditions. The patterning of metal distribution in the glass surface can also be achieved by ionexchange in molten metal salts, a most effective and convenient method. However, multiple steps (masking to write a pattern, ion-exchange, washing, and etching of mask) have to be performed to obtain the desired structure.²⁵ Although the ion injection technique makes selective patterning possible by focusing the ion beam, it requires high energy (10^3-10^6 eV) for ion acceleration in a vacuum system, and the doping occurs only in the surface region of the substrate $(<10^{-6} \text{ m})$.^{14,26} By contrast, the present technique allows single step fabrication of patterned glass since various forms can be drawn directly via the solid-solid interface between β'' -Al₂O₃ and glass under ambient atmosphere at a low-medium temperature range below the glass transition point. Furthermore, encapsulation of the metal distribution within the glass is one of the important features of the present electrochemical method. A variety of metal ion conducting solid electrolytes have been developed to date. Thus, this method can be employed to introduce many different kinds of metal ions into glass to impart it with new functions. The technique is expected to provide a new and simple route for fabricating photowaveguides and/or microlens

arrays; the optical characteristics of such optical devices would help evaluate the effectiveness of the technique.

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References

- 1 S. Tanaka, Bull. Ceram. Soc. Jpn., 1990, 25, 532–535.
- 2 H. Murakami, Bull. Ceram. Soc. Jpn., 1995, 30, 677-680.
- 3 Y. Matsumoto, Solid State Ionics, 1997, 100, 165-168.
- 4 K. Kamada, S. Udo and Y. Matsumoto, *Electrochem. Solid-State Lett.*, 2002, 5, J1–J3.
- 5 K. Kamada, S. Udo, S. Yamashita and Y. Matsumoto, *Solid State Ionics*, 2002, **146**, 387–392.
- 6 A. Spangenberg, J. Fleig and J. Maier, Adv. Mater., 2001, 13, 1466-1468.
- 7 K. Terabe, T. Hasegawa, T. Nakayama and M. Aono, *RIKEN Rev.*, 2001, **37**, 7–8.
- 8 K. Terabe, T. Nakayama, T. Hasegawa and M. Aono, *Appl. Phys. Lett.*, 2002, **80**, 4009–4011.
- 9 K. Terabe, T. Nakayama, T. Hasegawa and M. Aono, J. Appl. Phys., 2002, **90**, 10110–10114.
- 10 I. Enculescu, B. Iliescu and V. Teodorescu, Solid State Ionics, 2001, 138, 315–321.

- 11 Y. Matsumoto, K. Akagami and K. Kamada, J. Solid State Chem., 1999, 143, 111–114.
- 12 C. Thévenin-Annequin, M. Levy and T. Pagnier, Solid State Ionics, 1995, 80, 175–179.
- 13 M. A. Villegas, J. M. Fernandez Navarro, S. E. Paje and J. Llopis, *Phys. Chem. Glasses*, 1996, 37, 248–253.
- 14 M. Antonello, G. W. Arnold, G. Battaglin, R. Bertoncello, E. Cattaruzza, P. Colombo, G. Mattei, P. Mazzoldi and F. Trivillin, J. Mater. Chem., 1998, 8, 457–461.
- 15 K. Kamada, S. Udo, S. Yamashita, Y. Tsutsumi and Y. Matsumoto, *Solid State Ionics*, in press.
- 16 J. Fleig and J. Maier, *Electrochim. Acta*, 1996, 41, 1003–1009.
- 17 J. Fleig, P. Pham, P. Sztulzaft and J. Maier, *Solid State Ionics*, 1998, **113–115**, 739–747.
- 18 J. Fleig, S. Rodewald and J. Maier, Solid State Ionics, 2000, 136– 137, 905–911.
- 19 H.-D. Wiemhöfer, Ber. Bunsen-Ges. Phys. Chem., 1993, 97, 461– 469.
- 20 W. Zipprich, S. Waschilewski, F. Rocholl and H.-D. Wiemhöfer, Solid State Ionics, 1997, 101–103, 1015–1023.
- 21 K. Matushita, M. Ito, K. Kamiya and S. Sakka, *Yogyo Kyokaishi*, 1976, **84**, 496–508.
- 22 J. Qiu, C. Zhu, T. Nakaya, J. Si, K. Kojima, F. Ogura and K. Hirao, *Appl. Phys. Lett.*, 2001, **79**, 3567–3569.
- 23 K. Miura, J. Qiu, S. Fujiwara, S. Sakaguchi and K. Hirao, *Appl. Phys. Lett.*, 2002, 80, 2263–2265.
- 24 J. Qiu, M. Shirai, T. Nakaya, J. Si, X. Jiang, C. Zhu and K. Hirao, *Appl. Phys. Lett.*, 2002, **81**, 3040–3042.
- 25 C. R. Lavers, K. Itoh, S. C. Wu, M. Murabayashi, I. Mauchline, G. Stewart and T. Stout, *Sens. Actuators, B*, 2000, **69**, 85–95.
- 26 G. W. Arnold and J. A. Borders, J. Appl. Phys., 1977, 48, 1488– 1496.