Micro-ordered periodical modification of glass composition by a staining combined with inkjet printing

Kohei KADONO,*,† Eri KUNISADA,† Tatsuya SUETSUGU*,**, and Takashi WAKASUGI*

*Division of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585
**Isuzu Glass Co., Ltd., Minami-tsumori, Nishinari-ku, Osaka 557-0063

Silver ions were incorporated into a soda-lime silicate glass substrate by applying 3 M AgNO₃–0.1 M polyethylene glycol (PEG) mixed aqueous solution on the glass and heating it at 300 °C for 12 h. The glass substrate was colorless after the heat-treatment although the refractive index at the glass surface increased by 0.04. The glass was colored red-brown by the further heat-treatment at 550 °C. The energy dispersive X-ray microanalyzer revealed that the silver migrated to around 20 μm in depth. These facts indicate that the AgNO₃ solution works as a “stain”. Since the viscosity of the AgNO₃–PEG solution was less than 2 mPa·s, it could be deposited on a glass substrate by the inkjet technique. Dot arrays were formed on the glass substrate by the inkjet deposition. The dots had around 100 μm-diameter kept clear circles and aligned with a hundreds-micrometer frequency. The silver ions were incorporated into the dot areas of the glass surface by the heat-treatment. Then, we demonstrated that a micro-ordered periodical modification in the glass composition was easily formed by the staining using the AgNO₃ aqueous solution combined with the inkjet technique.

Key-words : Staining, Ion-exchange, Inkjet, Silver, Nanoparticle, Periodical modification, Stained glass

1. Introduction

Staining is a well known glass-coloring technique, in which mixtures called as stains composed of silver or copper inorganic compounds, organic resins such as cellulose and acrylic resin, natural alcohols, and organic solvents, are applied on glass surfaces, and the glasses are heat-treated resulting in the coloration of the glasses. Some parts of yellow stained glass windows for cathedrals in medieval times, for example, were obtained by the silver staining. The mechanism for the coloration is considered as follows. During the heat-treatment, silver or copper ions in the stains are incorporated into the glasses, then reduced to atoms, and subsequently, aggregate to form nanoparticles which have intensive absorptions in the visible region. One of the important points for the staining is that the color is not owing to the inorganic pigments on the glass surfaces but to the nanoparticles inside the glasses, which means that the glasses themselves are colored. The incorporation process of the metal ions in the staining is regarded as the similar reaction to the ion-exchange which is usually performed by immersing glasses in molten salts. Therefore, the staining can be applied to fabricate graded-index optical elements based on glass substrates which are conventionally prepared by ion-exchange. Actually, we have found that optical waveguides based on soda-lime and borosilicate glasses are easily fabricated by the staining technique under heat-treatment conditions, in which the refractive indices increased by the incorporation of silver or copper ions without any coloration.

Ion-exchange in the staining occurs only at the surface where the stain is applied. Combined with the modern printing technology, therefore, the staining can incorporate ions into the localized area of glass surfaces resulting in the modification of the composition at the area without any masks which are usually formed by lithography.

Among the printing technologies, inkjet is of interest because of its easy way, high cost-performance and versatility. Particularly, computer controlled on-demand mode makes the inkjet technology not only printing technology but also one of the most important tools for various industrial processes. In order to obtain high resolution inkjet printing, properties of the ink, particularly, viscosity is very important. The viscosity of the ink should be less than 20 mPa·s. Since the stains used in the staining above mentioned are very viscous, usually having a viscosity higher than 10 Pa·s, it is necessary to develop a new “stain” for inkjet printing.

Here, we report that an AgNO₃ aqueous solution works as “stain” which has a suitable viscosity for the inkjet. Using the stain and the inkjet technique, for the first as we know, we demonstrate that a micro-ordered periodical modification of composition near the glass surface has been formed by the incorporation of silver into localized surface area of a glass substrate. The periodical modification of the composition was clearly shown by the periodical change in optical absorption; around 100 μm-dots, in which the glass itself colored yellowish, were arrayed with 500 μm frequency.

2. Experimental procedures

The stains suitable for the inkjet were prepared based on AgNO₃ aqueous solutions. In order to obtain clear dots on the glass substrate, we examined the emerging feature of the droplets and the shape of the dot deposited by the inkjet for the AgNO₃ aqueous solutions with some additives, i.e., ethylene glycol, polyethylene glycol, or sodium polyacrylate. Reagent grade AgNO₃, polyethylene glycol (molecular weight 2000), ethylene glycol, and sodium polyacrylate (molecular weight 250,000–700,000) obtained from Wako Pure Chemical Ind., Ltd., were

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used. The solutions were filtered through a cellulose acetate filter of 0.8 μm pore size to remove dusts. Commercially available soda-lime silicate glasses obtained from Schott (B270) were used as glass substrates which were cut in the size of 30 × 25 mm² and 3 mm in thickness and then both sides were optically polished.

In order to confirm that the AgNO₃–polyethylene glycol (PEG) solutions, by which clear dots were obtained, play a role of stain, we carried out the staining treatment using the solution containing 3 M AgNO₃ and 0.1 M PEG as follows. The solutions of 0.2 ml were applied on the soda-lime silicate glass substrates so that the applied area was about 750 mm². Then, the solution on the glass substrates was dried at room temperature, and subsequently the glass substrates were heat-treated at 300°C for 12 h in ambient atmosphere. The residual materials on the glass substrates were washed out by nitric acid solution and water. The silver incorporation was examined by the absorption and refractive index change. The absorption spectra of the substrates were measured using the spectrophotometer, Hitachi, Ltd., U-3000. The refractive index of the glass surfaces were measured by means of a prism coupling method, using Metricon Co., Model 2010 at 633 nm. The amounts of the incorporated silver were also determined by ICP elemental analyses. The concentration profiles of silver along the depth were measured using the energy dispersive X-ray analyzer (EDX), Horiba, Ltd., EMAX super Xerophy S–792XI.

Inkjet deposition of the solutions was carried out using a piezo-actuated inkjet device, Microjet Co., IJET–2000C. The nozzle diameter was 50 μm. The driving signals were rectangular pulses with 20–60 μs width, 114 Hz frequency, and 80–130 V amplitude. These conditions were adjusted to minimize the dot diameter and satellite droplet formation.

3. Results and discussion

3.1 Effect of the additives on the shape of the dots deposited by inkjet

We examined the effect of various additives on the emerging feature of the droplets and the shape of the dot deposited by the inkjet. The additives were ethylene glycol, polyethylene glycol, or sodium polyacrylate. The dots of all the solutions just after deposition formed clear circles. They were dried within a few seconds, and the solutes were precipitated. The dried dots of the solutions containing only AgNO₃, and AgNO₃ with ethylene glycol and sodium polyacrylate were deformed from the circular shape and the rims of the dots were not smooth. On the other hand, the dots of the solutions containing AgNO₃ with polyethylene glycol (PEG) kept the circular shape with a clear rim even after dried as shown in Fig. 1. This indicates that the AgNO₃–PEG solutions are superior in order to obtain depositions with a high spatial resolution. However, the diameters of the dots were larger than that of the nozzle used for the inkjet deposition (50 μm) because the solution spread on the glass substrate. Hereafter, we show experimental results only for the solutions containing AgNO₃ with PEG as an ink for the inkjet printing.

3.2 Staining with AgNO₃ aqueous solution

We carried out the staining treatment using the AgNO₃–PEG solutions, in order to confirm that silver ions are incorporated into the glasses. The solution of 3 M AgNO₃–0.1 M PEG were applied on the glass substrates and dried, and then the glass substrates were heat-treated. The surface of the glass substrates became slightly rough but colorless after the heat-treatment at 300°C for 12 h. The absorption spectra of the glass substrate was almost the same as that before the heat-treatment as illustrated in Fig. 2. As shown in Fig. 3, however, the refractive index of the glass surface after the staining measured by the prism coupling method increased from 1.521 to 1.563 at 633 nm. Very sharp dips were observed. This indicates that the refractive index was increased by the incorporation of silver ions into the glass surfaces resulting in the waveguide formation. 00)

Furthermore, in order to confirm the presence of silver in the
glass after the staining, we heated the glass again at 550°C for 30 min in ambient atmosphere. The glass colored red-brown and the spectrum of the glass had a large absorption at 435 nm as shown in Fig. 2. The absorption was assigned to silver nanoparticles. When the glass substrates were irradiated by UV light using a high pressure Hg lamp before the second heat-treatment, the absorption became more intense. The absorption intensity of the red-brown was decreased by polishing the glass from the colored surface step by step and disappeared after about 10 μm polishing. This indicates that the silver ions migrated at least deeper than 10 μm. Figure 4 shows the absorption coefficient at 435 nm at each depth, which was obtained from the derivative of the change in the absorption intensity with the polishing depth. This profile corresponds to the concentration profile of the silver atoms contributing to the formation of the nanoparticles. In Fig. 4 is also shown the change in the refractive index of the surface of the glass substrate, which was measured for the sample before the second heat-treatment (colorless and silver incorporated) and polished step by step. The absorption coefficient at 435 nm and the refractive index decreased along the depth and became 0 and the value of the glass substrate before the staining treatment, respectively, at about 10 μm. This indicates that the silver ions were incorporated until about 10 μm enough to form the nanoparticles and to change the refractive index. Figure 4 also depicts the silver concentration profile along the depth measured with the energy dispersive X-ray microanalyzer, indicating that the silver ions migrated until about 20 μm. These experimental results showed that the silver ions were incorporated into the glass by the staining, i.e., the first heat-treatment process at 300°C for 12 h. It was shown, therefore, that the AgNO₃–PEG aqueous solutions worked as stain solutions. The ICP elemental analysis revealed the amount of the incorporated silver was 1.4 × 10¹⁸ atom/cm². This value is 3 times larger than that of the silver incorporated by the staining using the conventional silver stain. The main reason is probably the difference of the silver concentration between the solution used in the present study and the conventional silver stain containing organic resins after applied on the substrate and dried.

3.3 Inkjet deposition
We carried out the inkjet deposition test with the AgNO₃–PEG solution. The glass substrate after the deposition was heat-treated at 300°C for 12 h and then UV-irradiated followed by the second heat-treatment at 550°C for 30 min. Although the dot arrays on the glass substrate were colorless after the first heat-treatment, they were colored yellowish after the second heat-treatment. Photographs of the three dot arrays having the different average size are shown in Figs. 5(a), (b), and (c). Depending on the inkjet conditions, the size of the dots was changed (see the figure caption). The small points beside the dots are satellites. The average diameter of the dots in (a) was 128 μm. The absor-

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Fig. 4. Depth dependence of the absorption coefficient at 435 nm (●), refractive index (○), and concentration profile of silver (solid line) measured by EDX.

Fig. 5. (a) (b) (c) Photographs of various dot arrays formed by the inkjet deposition of 3 M AgNO₃–0.1 M PEG solution on the glass substrate and the heat-treatment of the glass at 300°C for 12 h. These dots were colored yellowish after the second heat-treatment of the glass at 550°C for 30 min. The inkjet conditions were different from each other; one droplet was deposited on every dot in (a) and (b) while three droplets in (c). The small points beside the dots are satellites. The average diameters of the dots in (a) were 128 μm. (d) The absorption spectrum of the dot array shown in (a).
tion spectrum of the dot array in (a) is also illustrated in Fig. 5 (d). The absorption peak assigned to the silver nanoparticles was observed around 435 nm.

In Fig. 6 is illustrated the contour lines which indicate the intensity of the lights of 410–510 nm wavelength transmitting the dot array of the glass substrate (Fig. 5(a)). The 410–510 nm lights are selectively absorbed by the silver nanoparticles. Therefore, the absorption intensity profiles correspond to the concentration profiles of the silver atoms, which contribute to the nanoparticles. These profiles indicate that the amount of the silver atoms integrated along the depth concentrically varied from the center of the dots and it was the highest at the center part. On the other hand, the yellow dots became gradually smaller by polishing the glass substrate from the surface and were diminished when polished more than 15 μm. This indicates that the silver ions were distributed deeper at the center of the dots. The silver ions diffused by the first heat-treatment (300°C, 12 h) from the circular dots as shown in Fig. 1, where the silver ions were homogeneously distributed. This process is similar to an ion-exchange process used for the graded-index microlenses in which ions in a molten salt are introduced through a mask with circular windows of hundred-micron diameter. This can explain the distribution of the silver ions as mentioned above.

4. Conclusions

Silver ions were incorporated into soda-lime silicate glasses by applying AgNO₃–PEG aqueous solutions on the glass substrates, drying the solutions, and then heat-treatment at 300°C. The incorporation of the silver ions increased the refractive index near the surface of the glass substrates resulting in the formation of planar waveguides. Although the glass substrates were colorless after the heat-treatment, they colored red-brownish by a second heat-treatment at 550°C. The UV irradiation before the second heat-treatment made the coloration more intense. The AgNO₃–PEG solutions were deposited dot-like on the glass substrates with micro-ordered periodical structure by an inkjet device. Silver ions were selectively incorporated into the localized area of the glass substrates where the solutions were applied. Eventually, we have formed the micro-ordered periodical modifications of the composition of the glass substrate, which are observed as the periodical change in the optical absorption.

It is expected that not only the absorption but also refractive index can be modified with a micro-ordered periodicity. This technique will be applied for marking and picturing glasses and furthermore will give rise to a new optical function to glasses.

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References

3) Although metal compounds are dispersed mainly in organic media in the stains nowadays, ocher or clay were conventionally used as carrier media (literatures 1, 2).