Laser micro-machinability of borosilicate glass surface-modified by electric field-assisted ion-exchange method

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Abstract. In order to improve the laser micro-machinability of borosilicate glass, the glass surface was doped with metal (silver or copper) ions by an electric field-assisted ion-exchange method. Doped ions drifted and diffused into the glass substrate under a DC electric field. The concentration of metal ions within the doped area was approximately constant because the ion penetration was caused by substitution between dopant metal and inherent sodium ions. Nanosecond ultraviolet laser irradiation of metal-containing regions produced flat, smooth and defect-free holes. However, the shapes of holes were degraded when the processed hole bottoms reached ion penetration depths. A numerical analysis of ionic drift-diffusion behaviour in glass material under an electric field was also carried out. The calculated results for penetration depth and ionic flux showed good agreement with the measured values.

1. Introduction
It is well known that glass materials have excellent mechanical hardness, chemical stability and optical transparency. Micro-machining of glass materials, therefore, has become a key technology for various applications such as micro-machines, micro-opto-electro-mechanical systems (MOEMS) and analytical chemistry. However, mechanical or laser micro-machining of glass materials faces some problems with processing quality due to their brittleness and optical transparency. Therefore, chemical wet-etching techniques using hydrofluoric acid (HF) are frequently adopted in glass processing industries. As it is widely known, hydrofluoric acid is very harmful to human bodies and recycling of waste solutions is also difficult. For the reduction of the environmental burden, a novel processing method for glass materials is necessary.

The improvement of laser machinability is a promising approach for precise processing of glass materials. In fact, some research on the development of laser machinable glass has been carried out [1-5]. Typical laser machinable glass contains nanometer-sized metal clusters, such as silver or copper, in the glass matrix. Metal nano-clusters play two important roles during laser irradiation; they cause an increase in light absorption and mechanical strengthening of glass materials. This kind of laser machinable glass is usually prepared by an ion-exchange process in a molten salt bath that contains silver or copper ions. This ‘wet’ ion-exchange method is very simple and provides excellent laser micro-machinability to glass materials [1-4]. However, a long exchange time is required to obtain a large penetration depth of metal ions, because the process is driven by the substitution between alkali and metal ions at the glass surface. Also, penetrating metal ions are non-uniformly distributed in glass materials because the penetration is caused only by their ionic self-diffusion [4,6].
In the present study, the authors propose a method for improving the laser micro-machinability of glass materials by electric field-assisted ion-exchange (FAIE). In the FAIE process, metal ions are supplied from a metal foil or film placed on the glass surface under an applied DC voltage. Because the process is electrically driven, metal penetration is more rapid and deep in comparison with the conventional wet ion-exchange process in a molten salt bath. In this report, the penetration behaviour of metal ions is experimentally and numerically examined. The laser micro-machinability of silver- and copper-doped borosilicate glasses prepared by FAIE is also investigated.

2. Experimental

Borosilicate glass slides (Schott, BOROFLOAT 33, 25 mm x 25 mm x 1.1 mm) and pure silver or copper foils (> 99.9 %, 20 mm x 20 mm x 10 μm) were used in the experiment. The glass slides and metal foils were rinsed in acetone, ethanol and distilled water before the experiment. A glass slide and metal foil were placed between two copper electrodes in a high vacuum chamber (<10⁻³Pa). The experimental setup for ion-exchange is shown in Figure 1. After the evacuation and temperature elevation, a DC voltage was applied using the metal foil as the anode. The applied voltage, ion-exchange temperature and time were 100 V, 623 K and 3.6 ~ 21.6 ks, respectively. After the ion-exchange process, the glass slide was detached from the metal foil and rinsed in distilled water. The penetration depth and cross-sectional distributions of metal ions were measured by electron probe micro-analysis (EPMA: JEOL, JXA8900).

The laser micro-machining system consisted of a fourth harmonic generator of a Nd:YAG laser (Continuum, Surelite I-20, wavelength: 266 nm) and a PC-controlled translation stage (Suruga Seiki, KS201-20HD). In Figure 2, the laser micro-machining system is illustrated. The pulse duration and repetition rate of the laser beam were 6 ns and 20 Hz, respectively. All samples were irradiated on the front (ion-exchanged) surfaces by defocusing the laser beam to produce a spatially uniform (flat-top) energy distribution in atmosphere. The shapes and cross-sectional profiles of the processed holes were examined by scanning electron microscopy (SEM: JEOL, JSM-840A) and confocal laser scanning microscopy (Keyence, VK-8500), respectively.

3. Numerical analysis

We assume that only two mobile species A and B exist in the glass material, both of which are univalent cations. Symbols A and B denote metal (silver or copper) and sodium ions, respectively. When a DC electric field \( E \) is applied along the x-axis, the one-dimensional ionic drift-diffusion behaviour is expressed by the Nernst-Planck equation [6-8],

\[
J_i = -D_i \frac{q}{kT} E C_i - D_i \frac{\partial C_i}{\partial x} \quad (i = A, B),
\]

where \( J \) is the ion flux, \( D \) is the self-diffusion coefficient, \( C \) is the ion concentration and \( q \) is the ionic charge. Because of local electrical neutrality, the total mobile cation concentration is assumed to be constant \( C_0 \), which is equal to the sodium ion concentration in un-doped glass, so that
Assuming that the potential drops at electrode-glass interfaces are negligible, the applied voltage $V_0$ between two electrodes is expressed by eq. (3),
$$\int_0^h E\,dx = V_0,$$
where $h$ is the thickness of the glass slide and $V_0$ is the applied DC voltage. Equations (1) and (2) were numerically solved under boundary condition (3) by the standard explicit finite-difference method. Material and physical properties used in the calculation are listed in Table 1. For simplicity, the concentration dependence of the self-diffusion coefficients was not taken into consideration in this calculation.

### 4. Results and discussion

#### 4.1. Penetration behaviour of metal ions into glass substrates

Figure 3 shows typical silver and sodium ion distributions in the glass surface region obtained by EPMA. The field-assisted ion-exchange time of this sample was 21.6 ks. It is clearly indicated that the

![Figure 3](image-url)

**Figure 3.** Cross-sectional ion distributions of (a) silver and (b) sodium in glass substrate measured by EPMA. Ion-exchange time was 21.6 ks.
silver concentration is approximately constant over the penetration area, and this is quite a contrast to that in silver-doped glass prepared by the wet ion-exchange method [4]. In the case of wet ion-exchanged glasses, the laser ablation rate (removed depth per laser shot) gradually decreased with distance from surface, because of the non-uniformities in ion concentration [4]. On the other hand, a constant ablation rate is expected for the ion-exchanged glasses produced by FAIE, because of their uniform ion distributions. Figure 3 also shows that a sodium depletion layer was formed at the glass surface, and its depth accurately accorded with the silver-doped depth. This result suggests that sodium ions in the glass substrate were fully substituted by penetrating silver ions. Although not shown here, similar results were obtained for copper-doped glasses.

The penetration depths of silver and copper ions for various exchange times obtained from EPMA profiles are indicated by white and black circles in Figure 4. Because the ionic mobility of silver in glass materials is much larger than that of copper [8], a difference in their penetration depths is seen in Figure 4. In a previous letter [5], we reported that the penetration depth of copper after 21.6 ks under similar experimental conditions was 27.2 μm, and this value is about half of the present value. The reason for the increase in penetration depth was the improvement of our experimental procedure, that is, surface cleaning and mirror polishing of two electrodes (anode and cathode) before every experiment. According to our previous result [5], the penetration depth of silver in wet ion-exchanged glass prepared in 1.0 % AgNO₃-NaNO₃ at 623 K after 21.6 ks was 8.8 μm, which was about one twentieth of that by FAIE after the same exchange time. This result suggests that the applied electric field is very effective for increasing the penetration depth, and therefore, for reducing the ion-exchange time.

In order to understand the penetration behaviour of silver and copper ions, the numerical analysis described in section 3 was carried out. The calculated penetration depths of silver and copper are shown by solid lines in Figure 4. As shown in Figure 4, the calculated results show good agreement with measured penetration depths. Especially, it should be noted that the geometrical difference between two penetration curves, i.e., linearly-increasing behaviour for silver and gradual saturation for copper, were accurately expressed by a simple simulation. Although the reason for the difference between the two penetration curves is now under investigation, we consider that the self-diffusion coefficient ratios $M_i = D_i/D_{Na}$ ($i = Ag$ or $Cu$) have a large influence on the penetration behaviour. For validation of the calculation model, the numerically calculated and experimentally measured ionic fluxes after 21.6 ks were compared as listed in Table 2. The analytic and experimental ionic fluxes have comparable values within the range of experimental error, and therefore, the present calculation can reasonably describe the ion penetration behaviour.

![Figure 4. Change in ion penetration depths with exchange time.](image-url)
4.2. Laser micro-machinability of metal-doped glasses

Figure 5 shows front views of laser ablated holes on silver- and copper-doped glasses, when the beam diameter and irradiated energy density were 300 μm and 10 J/cm², respectively. Cross-sectional profiles between the two white arrows are also shown in these micrographs. As shown in Figure 5, the bottoms of the ablated holes are remarkably flat and smooth before 680 irradiation pulses for silver and 200 pulses for copper-doped glasses. These flat bottom faces were assumed to be caused by the spatially uniform energy distribution of the laser beam. In Figure 5(a) to (c) and (d) to (f), the area of the flat bottom face decreased with increasing shot number. This is due to a decrease in the beam spot diameter with the progress of hole drilling, because the focal position of the laser beam was inside the glass substrate, i.e., the beam was underfocused. No large cracks or chips, which are often observed for laser irradiated un-exchanged glasses [5], were found in these holes. These results suggested that the input laser energy was effectively absorbed in the vicinity of the glass surface and rapid ablation of the surface layer occurred. On the other hand, the shapes of the 700 pulse hole for silver and 220 pulse hole for copper-doped glass were obviously different. The flat and smooth bottom faces were severely damaged and irregular-shaped structures appeared. As shown by the cross-sectional profiles in Figure 5, such deterioration of the bottom faces occurred at depths of 150 μm for silver and 60 μm for copper-doped glasses. These values approximately accorded with the penetration depths of silver and copper ions shown in Figure 4. Therefore, it was suggested that the defective structures at the hole bottoms were caused by the inherent brittleness of un-exchanged glass materials.

Table 2. Comparison between numerically calculated and experimentally measured results for ionic flux after 21.6 ks of ion-exchange time.

| Ionic flux [ions/m²s] | Silver | Copper |
|-----------------------|--------|--------|
| Numerically calculated | 1.00 x 10¹⁹ | 2.95 x 10¹⁸ |
| Experimentally measured | 1.09 x 10¹⁹ | 2.04 x 10¹⁸ |

Figure 5. SEM micrographs of laser-ablated holes on metal-doped glasses. (a) 200, (b) 680 and (c) 700 irradiation shots on silver-doped glass. (d) 160, (e) 200 and (f) 220 shots on copper-doped glass. Irradiated energy density was 10 J/cm².
Figure 6. Change in removed depth with laser shot number for silver- and copper-doped glasses. Irradiated energy density was 10 J/cm².

Figure 6 shows the change in removed depth with laser shot number for silver and copper-doped glasses. As shown in Figure 6, the removed depths increased linearly with shot number, i.e., constant ablation rates (0.21 μm/pulse for silver and 0.28 μm/pulse for copper-doped glasses) were maintained over the ion penetrated area. We consider that these results are due to the constant ion concentrations using the FAIE process.

5. Conclusions
In the present study, a method of improving the laser micro-machinability of borosilicate glass by FAIE was proposed. UV nanosecond laser irradiation of silver or copper-doped glasses produced flat, smooth and defect-free holes. It was therefore found that metal doping of the glass surface was very effective for the improvement of laser micro-machinability. The concentrations of doped metal ions were approximately constant, and constant laser ablation rates were therefore achieved. However, the shapes of holes were degraded when the processed hole bottoms reached ion penetration depths. Therefore, a precise prediction method of ion penetration depth was strongly required for the high-accuracy fabrication of micro-optoelectronic devices. A simple numerical calculation using the finite-difference method was found to be sufficient to describe the ionic drift-diffusion behaviour in glass materials.

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References
[1] Tsunetomo K and Koyama T 1997 Opt. Lett. 22 411
[2] Koyama T and Tsunetomo K 1997 Jpn. J. Appl. Phys. 36 L244
[3] Rosenbluh M, Antonov I, Iafets D, Kaganovskii Y and Lipovskii A. 2003 Opt. Mater. 24 401
[4] Matsusaka S and Watanabe T 2008 J. Mat. Proc. Tech. 202 514
[5] Matsusaka S and Watanabe T 2010 Scripta Mater. 62 141
[6] Quaranta A and Gonella F 1995 J. Non-Cryst. Solids 192 & 193 334
[7] Abou el leil M and Cooper A R 1979 J. Am. Ceram. Soc. 62 390
[8] Oven R 2007 J. Appl. Phys. 101 113113