Transmittance properties and TEM observation of metal doped glass by field-assisted ion exchange

Souta Matsusaka, Taketsugu Nomura, Hirofumi Hidai, Akira Chiba and Noboru Morita
Department of Mechanical Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba-shi, Chiba, 263-8522, Japan
E-mail: matusaka@faculty.chiba-u.jp

Abstract. Metal (silver or copper) ions were doped into borosilicate glass using an electric field-assisted ion exchange method. The optical transmittance of the metal doped glass was measured to determine why the doped glass exhibited an excellent laser micro-machinability. The doped metal ions were found to have enhanced the optical absorption of the glass, especially in the ultraviolet range. This in turn facilitated the efficient absorption of incident laser irradiation, and hence improved laser machinability of the glass. The metal doped glass also exhibited some absorption in the visible range, leading to a slight yellow-brown coloration. Transmission electron microscope (TEM) observations indicated that the metal ions had penetrated the glass and therein formed nanometer-sized (~6 nm) fine particles. In an attempt to control the optical characteristics in the ultraviolet-visible range, metal doped glass was heat-treated following the ion exchange doping step. In the case of silver-doped glass with heat treatment at 723 K, silver nanoparticles aggregated locally yielding an inhomogeneous structure. The heat-treated samples had a high optical absorption in the ultraviolet range.

1. Introduction
Glass materials have some unique characteristics such as high transparency, mechanical hardness, and thermal and chemical stability; and are therefore widely used as substrates for micro-machines, micro-electro-mechanical systems (MEMS) and devices in analytical chemistry. However, the laser micro-machining of glass materials has proven to be difficult. Some recent studies have considered the development of laser-machinable glass [1-4]. Typically, laser-machinable glass was prepared by metal (usually silver or copper) doping to glass surfaces using an ion exchange technique. The resulting glasses, showed excellent laser micro-machinability, without cracking or chipping around processed area [5]. In this study, the optical characteristics of metal doped glasses were examined in order understand their enhanced laser machinability. More fundamentally, we wish to understand how the penetrating dopant ions can modify both the optical characteristics and the laser machinability of glass. Accordingly, the structure of metal doped glass was studied using a transmission electron microscope (TEM). We will discuss the relationship between the microscopic structure of the metal dopant within the glass matrix, the optical characteristics and the laser machinability of metal doped glass. Finally, in order to better control the optical characteristics of doped glass, a heat treatment method was tested.
2. Experimental procedure

Borosilicate glass slides (Schott, Borofloat 33, 25 mm × 25 mm × 1.1 mm) and pure silver or copper foils (> 99.9 mass%, 20 mm × 20 mm × 0.01 mm) were used for the ion exchange process. The glass slides and metal foils were rinsed in acetone, ethanol and distilled water before the procedure. A glass slide and a metal foil were placed between two copper electrodes in a high vacuum chamber (< 10⁻³ Pa). The experimental setup for ion exchange is illustrated in figure 1. After evacuation and temperature elevation to 623 K with a tungsten heater and a plate heater, a DC voltage was applied with the metal foil serving as the anode. The ion exchange conditions are listed in table 1. After ion exchange, the samples were heat-treated under two different sets of conditions. Some samples were heat-treated immediately after the ion exchange, i.e., the samples were held inside the vacuum chamber and heat-treated after the applied voltage was removed. The other samples were cooled in the vacuum chamber and then transferred to an electric furnace for heat treatment. The heat treatment temperatures applied in both methods were 623 K and 723 K.

Following the ion exchange and heat treatments, the glass samples were detached from the metal foil and rinsed in distilled water. The rinsed samples exhibited a slight frosted appearance on their underside due to the outflow of alkali ions. This was removed by mirror polishing of the underside only. The optical transmission spectra of the samples were then obtained using an ultraviolet-visible spectrophotometer (UV-VIS) (JASCO, V-550). The metal doped areas were examined using TEM (JEOL, JEM-2100F).

![Figure 1. Schematic illustration of the experimental setup for ion exchange.](image)

### Table 1. Ion exchange conditions.

| Doped element | Ag | Cu |
|---------------|----|----|
| Glass         | Borofloat 33 | |
| Temperature [K] | 623 | |
| Voltage [V]   | 100 | |
| Experiment time [ks] | 21.6 | |

3. Results and discussion

3.1. Optical characteristics and glass structure of the metal doped area

Figure 2 shows the optical transmittance for silver doped and copper doped glasses. The transmittance curve is clearly shifted towards the visible region with metal doping, i.e., the UV absorption of metal doped glass is greater than that of un-doped glass. The UV absorption is increased to a particularly large extent in the case of copper doped glass. Our previous report [5] on UV laser micro-machinability of metal doped glass showed that the diameter of a laser-ablated hole on copper doped glass was larger than that formed on silver doped glass under the same laser irradiation conditions. In other words, the energy threshold for laser processing in copper doped glass was lower than that for silver doped glass. The difference in UV absorption between copper doped and silver doped glass explains the higher laser-
machinability of copper doped glass. Therefore, it was suggested that the efficient absorption of incident laser irradiation contributed to the much enhanced laser micro-machinability of the metal doped material. Less desirable, however, was the slight yellow-brown coloration of the doped glasses, arising from absorption in the visible range, also illustrated in figure 2. This reduced transparency may be unacceptable for many industrial applications. The development of laser-machinable glass with both high optical absorption in the UV range and high transparency in the visible range is necessary.

In order to investigate the relationship between the structure and the optical characteristics of metal doped glass, a cross-sectional TEM image of the glass surface was obtained. Figures 3a and b show HAADF-STEM images of silver and copper doped areas, respectively. In these figures, the bright granules are metal nanoparticles. The particle size was approximately 2-6 nm for both silver and copper, with no evident size difference between the two metals. It should be noted that the apparent difference in particle density between the two glasses is due to different thicknesses of the TEM samples. It is known that metal nanoparticles embedded in a dielectric matrix exhibit a characteristic light absorption due to localized surface plasmon resonance (LSPR) [6]. We therefore attribute the absorption edge shift from the UV into the visible range, shown in figure 2, to LSPR of metal nanoparticles in the glass matrix. The LSPR frequency and wavelength depend strongly on nanoparticle size, composition and structure [6]. To achieve specific intended optical characteristics, it will be necessary to control particle size and structure precisely.

At present, the growth mechanism from ions to nanometer-sized particles is not fully understood. In the ion exchange process, however, each metal ion moves from the glass surface to its interior by ionic self-diffusion and electrical drift [5]. This means that the transition from ions to particles occurs during a cooling process after ion exchange. We therefore expect that a heat treatment following the ion exchange would be effective for controlling the metal particle size.

Figure 2. Transmittance curves of un-doped and metal doped glasses.

Figure 3. Cross-sectional HAADF-STEM images of a) silver and b) copper doped glasses.
3.2. Heat treatment of silver doped glasses

Two types of heat-treated silver doped glasses were prepared, as mentioned above. Heat treatment times were 3.6 ks for samples before cooling, and 43.2 ks for samples after cooling. Silver doped glass was selected for the heat treatment experiments because of the proximity of its UV absorption edge to the 266 nm line. Figure 2 shows the transmittance curve of silver doped glass approaching zero at around 270 nm. A 266 nm wavelength UV laser is widely used in micro-machining. A small shift of the silver doped glass transmittance curve towards the visible is expected to enhance the UV absorption by the material. Since this might be achieved by particle growth at elevated temperatures, heat treatment of silver doped glass was carried out. Correspondingly, a rapid cooling of copper doped glass may be expected to shift the transmittance curve towards the UV region. However, a rapid cooling in our vacuum chamber was not experimentally feasible because of protection of electrical heaters. Only the heat treatment results of silver doped glasses are reported here.

Figures 4a and b show transmittance curves of heat-treated silver doped glasses. Figure 4a is for the samples heat-treated before cooling and figure 4b is for heat-treated after cooling. Clearly UV absorption increases with increasing heat treatment temperature. Heat treatment at 723 K resulted in a particularly strong enhancement of UV absorption. It was also found that the transmittance curves of heat-treated samples at 723 K had a characteristic shoulder around 325 nm. These transformations in optical characteristics may be caused by a structural change in embedded nanoparticles.

![Figure 4](image_url)

**Figure 4.** Transmittance curves of silver doped glasses after heat treatment. a) heat-treated before cooling and b) heat-treated after cooling.

Figure 5 shows HAADF-STEM images of heat-treated silver doped glasses. As shown in figure 5, the obvious growth of individual silver particles was not observed in samples heat-treated at either 623 K or 723 K. However, the local aggregation of particles did occur in samples heat-treated at 723 K. In the case of heat treatment at 723 K for 3.6 ks (figure 5b), a few particles aggregated. At 723 K for 43.2 ks (figure 5e) numerous particles aggregated and formed cloudlike structures. Figure 5f is a low magnification view of figure 5e, showing an inhomogeneous structure unevenly distributed in the glass. These aggregated structures will alter the optical characteristics of glass. We believe the 325 nm shoulder feature in the transmittance curves in figure 4 was caused by the aggregation of silver particles.

As shown in figure 4, an ‘ideal’ laser-machinable glass, which has high UV absorption and high transparency in the visible range, has not yet been developed. However, thermal treatment, i.e. heat treatment or rapid cooling, is one of the promising candidates for the improvement in optical characteristics of metal doped glass. For precise control of optical characteristics, it will be necessary to clarify the growth and aggregation mechanisms of metal nanoparticles in the glass substrate.
4. Conclusions
Metal (silver or copper) ions were doped into borosilicate glass using an electric field-assisted ion exchange method. TEM imaging revealed that penetrated metal ions formed fine metal particles of diameter of 2-6 nm. These particles increased the UV absorption of the glass and led in turn to its improved laser micro-machinability. A heat treatment for controlling the optical characteristics was tested on silver doped glass. UV and visible absorption increased with increasing heat treatment temperature. TEM imaging suggested that the changed optical characteristics were not due to individual particle growth, but rather to local aggregation of particles.

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