## Development of H+ emission gun using a proton conducting glass fiber

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Abstract—H⁺ emission from the sharpening glass fiber was successfully observed. Here, ion current density and chemical functionalization via ion irradiation are presented.

I. INTRODUCTION

Ion implantation is one important method for surface modification of materials, and has attracted considerable attention for various research fields including semiconductor industry and bio-technology. However, general ion implantation methods such as particle accelerators and ion guns have some disadvantages; e.g., huge and expensive equipment or less emission efficiency and large (a few tens mm²) irradiation area, respectively. We have studied high ion conducting glasses and those applications for fuel cell electrolytes [1,2]. One big advantage of glass is its good shapability, and we anticipate such proton conducting glasses can be applied for an emitter of portable ionic gun since the strength of the electric field is concentrated around the tip of the emitter. In this study, we prepared a proton-conducting and nano-sharpening glass fiber, and ion current density and chemical functionalization via ion irradiation are shown for the first time.

II. EXPERIMENTAL PROCEDURE

A phosphosilicate glass fiber with proton transport number \( t_H = 1 \) (10Na₂O–10K₂O–55P₂O₅–10Al₂O₃–15SiO₂, mol%) was prepared by melting method. The obtained fiber was immersed into HF solution (20 wt%) and cyclohexane mixture (volume ratio of 1:1), so-called meniscus-etching.

Fig. 1 shows the setup of the H⁺ emission current measurement. The distance between the emitter (tip of the glass fiber) and the extraction electrode was 1 cm. The ionic current was measured using a picoammeter (Keithley 6485). A correction for the secondary electron was not considered in this study, and the obtained ionic current was normalized by the pin-hole area of extraction electrode (3 mm in diameter). The chamber has two rooms; the anode reaction \( H_2 \Rightarrow 2H^+ + 2e^- \) occurs at the front chamber, and the proton is supplied for the glass fiber and a continuous ionic current can be successfully obtained using the setup.

III. RESULTS AND DISCUSSION

Some glasses show very high ionic conductivity including Na⁺, Li⁺, Cu⁺, Ag⁺, F⁻ and so on. However, preparation of a fast proton conducting glass is far difficult due to mainly following two reasons. For typical oxide glasses, the melting temperatures are higher than 1000 °C and such OH groups evaporate during the melting procedure. Thus, there are very few protons inside melting-glasses. Furthermore, the remaining -OH and H⁺ ionic pairs are strongly bonded to each other, leading to a very high dissociation energy of the proton. We recently found that proton implantation occurs and glasses with proton transport number \( t_H = 1 \) can be obtained by utilizing the mixed-alkali effect [2]. Fig. 2 shows the SEM images after the meniscus-etching for 5 h up to 72 h. A sharpening tip less than 1 μm was successfully obtained after 24 h of the etching. The nominal composition of the glass, P/Si is 7.3. The P₂O₅ component is indispensable for the proton implantation [3]. The atomic ratio of P/Si after the etching was evaluated by using energy dispersive X-ray spectroscopy (EDS), and no significant decrease (e.g. a selective dissolution of P₂O₅ component) was observed (P/Si = 6.9 to 7.1 even after 72 h).

Figure 1. Schematic illustration of the experimental setup for H⁺ emission current measurement.

Figure 2. SEM images for the glass fibers obtained by the meniscus-etching for (a) 5 h, (b) 24 h, (c) 48 h and (d) 72 h. The bar indicates 100 μm.
The obtained nano-sharpening glass fiber was connected to a Pd rod and used as the emitter in Fig. 1. High voltage up to 3.5 kV/cm was applied between the emitter and extracting electrode. Fig. 3 shows the relationship between the electric field intensity and ion current density at 550°C (1×10⁻⁵ Pa). Note that the current starts increasing around 1 kV/cm and then increases with increasing the voltage. The maximum current density of 0.3 nA/cm² was obtained in this study. The threshold voltages (the voltage at which the current increases) are plotted as a function of temperature in Fig. 4. The glass transition temperature (Tg) of the glass was estimated around 430°C using differential scanning calorimetry (DSC). Below Tg, the ionic current was not clearly observed. Above Tg, the threshold voltage decreases and the ionic current increases with increasing temperature. The current system for ion emission is very simple compared with traditional technique, e.g. no plasma is required and no additional species such as radial groups are formed.

Figure 3. The ionic current density as a function of electric field intensity measured at 550°C.

Figure 4. The electrical field intensity at start increasing the current as a function of emitter temperature.

Polyaniline shows an insulator-semiconductor transition by the implantation of H⁺ [5]. In order to confirm the species of emitted ion, ion emission for a polyaniline film was carried out. A polyaniline powder (Aldrich) was dissolved in acetone under ultrasonic dispersion, and the obtained solution was spin-coated on Si substrate. The voltage was fixed at 4 kV/cm (at 500°C), and the emission experiment was performed for approximately 5 days. Since the chamber temperature increases slightly and in order to ignore the effect of the temperature, two substrates were prepared; one is for the emission experiment, and second substrate was also set inside the chamber with a Al mask to block the ion beam.

Fig. 5 shows the FTIR spectra with and without ion irradiation for polyaniline films. Note that the bands attributed to C≡N, benzene-rings decrease, whereas those attributed to N-H and C-N increase clearly after the irradiation. It is evident from these structural changes that the emitted ion species are proton, and hydrogen addition reaction can be successfully confirmed. The assumed reaction model is also shown in the inset of Fig. 5. Further studies including Ag⁺ ion emission, emission mechanism and surface analysis after the ion irradiation will be shown at the presentation.

Figure 5. FTIR spectra for polyaniline films with and without ion irradiation.

IV. CONCLUSION

A proton-conducting and nano-sharpening glass fiber was prepared using conventional melting method, and H⁺ emission from the tip of glass fiber was successfully observed. Above glass transition temperature, the ion current increases with increasing the temperature of emitter. Our system for ion emission is very simple compared with traditional technique, and the glass fiber is a promising candidate as emitter for portable ion gun.

REFERENCES


