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# Accelerated formation of sodium depletion layer on soda lime glass surface by corona discharge treatment in hydrogen atmosphere

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ABSTRACT

Formation of a sodium depletion layer on a soda lime glass surface was accelerated efficiently using a corona discharge treatment in $H_2$ atmosphere. One origin of such acceleration was the preferential generation of $H^+$ with a larger mobility at an anode needle end with a lower applied voltage than that in air. The second origin was the applied voltage across the glass plate during the corona discharge treatment, which was estimated theoretically as 2.7 times higher than that in air. These two effects doubled the depletion layer thickness compared with that in air.



## 1. Introduction

A high direct current (DC) voltage applied across an alkali-containing glass induces the migration of alkali ions from the anode side to the cathode side. Subsequently, the alkali depletion layer with a negative charge is formed at the anode side glass surface [1,2]. Such negative charge should be compensated by the penetration of $H^+$ provided by water molecules in air. When the glass surface is coated with a metal electrode, the negative charge remains in the surface layer [3–6], which was used for the second-harmonic generation (SHG) [7,8]. Okada et al. reported SHG in a glass waveguide [9] and a silica glass film [10] after corona discharge treatment, which is known as a non-contact method to apply a high DC voltage to a polymer [11] or a glass [12] without coating any electrode on those materials. The origin of SHG was also regarded as formation of charged defects in the material surface layer.

In our previous study, the corona discharge was used for the formation of surface relief gratings on a soda lime glass surface [12,13]. The glass surface was treated using the corona discharge through a template of self-assembled hexagonally close-packed polystyrene particles [13]. The diffraction efficiency increased with the treatment time immediately before the damage of polystyrene particles. Additionally, we recently revealed the formation of sodium depletion layer by the injection of $H^+$ to the $Na^+$ sites by the corona discharge treatment [14], which is expected to be closely related to the formation of the alkali depletion pattern with a low refractive index according to the polystyrene template. The diffraction efficiency might increase with the alkali depletion layer thickness. This report describes the effect of $H_2$ gas on accelerating the formation of alkali depletion layer on the glass surface by the corona discharge treatment. Characteristics of the $H^+$ injection from the anode side and the alkali migration to the cathode side in a $H_2$ atmosphere were investigated and discussed quantitatively.

## 2. Experimental

Commercially available soda lime glass plate of 1 mm thickness (AS glass, Tg = 555 °C; Asahi Glass Co. Ltd.) was used for the corona discharge treatment. The main glass components were $SiO_2$, $Na_2O$, CaO, with inclusion of small amounts of other alkali and alkali earth metal oxides. The $Na_2O$ concentration is 13 mol%. The corona discharge treatment was performed in an atmosphere of ambient air or 5 N purity $N_2$ and/or $H_2$. Fig. 1 shows the experimental set up. The

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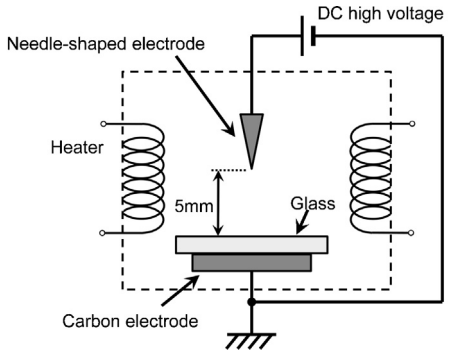


**Fig. 1.** Experimental setup for corona discharge treatment in air and $N_2$–$H_2$ atmospheres.

glass was placed on the cathode of a carbon plate. The anode was a Pt coated steel needle. The end point of needle was located 5 mm above the glass surface. The anode was connected to a DC voltage supplier (AKTB-010K1PN/S, Touwakeisoku Co. Ltd.) and the cathode was grounded. The treatment temperature was kept at 200 °C. The DC voltage applied to the anode needle was increased up to 4 kV with an increasing rate of 0.5 kV/min. The current in the circuit during the corona discharge treatment was measured using a data logger (midi Logger GL220, Graphtec Corp.).

The glass surface after the corona discharge treatment was analyzed using an inductive coupled plasma atomic emission spectrometer (ICP-AES; ICPE-9000, Shimadzu Corp.) and a Raman spectrometer (in Via Reflex, Renishaw Plc.). The cross-section of the glass was observed using an optical microscope (BX60F5, OLYMPUS Corp.). The chemical composition of the treated glass surface was investigated using an energy dispersive X-ray spectroscopy (EDS; JED-2300, JEOL Ltd.). The OH concentration of the glass was determined from the infrared (IR) absorption spectra measured by a Fourier transform IR spectrometer (FT-IR; Affinity-1, Shimadzu Corp.).

## 3. Results

Fig. 2 portrays the relation between the applied voltage and the current in the early stage of corona discharge treatment in air and $N_2$–$H_2$ atmospheres. The current increased gradually with the voltage after the corona discharge occurred at the anode needle point. The current–voltage slope increased steeply with the volume fraction of $H_2$, which reflects the efficient replacement of $Na^+$ by $H^+$ at the anode side surface and their migration to the cathode side. The current measured during the treatment in air is also shown in the figure, which is much lower than that in the $H_2$-containing atmosphere. The corona discharge in the $H_2$ atmosphere is therefore effective to accelerate the formation of sodium depletion layer on the anode side glass surface.

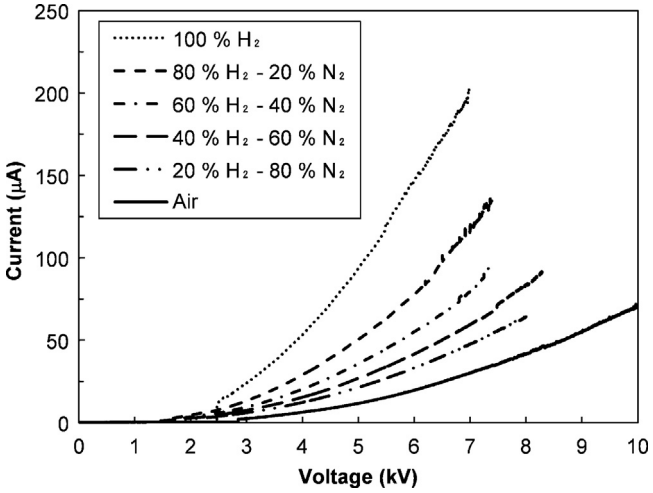


**Fig. 2.** Relation between applied voltage and current during corona discharge treatment to soda lime glass in air and $N_2$–$H_2$ atmospheres at 200 °C.

Fig. 3 shows the current variation against the corona discharge treatment time in (a) air and (b) $H_2$. The profiles of applied voltage were mutually identical. In the former case, the current decreased slightly during the treatment. By contrast, the current for the latter case increased steeply up to 53 μA, which was approximately 10 times higher than that in air. Subsequently it decreased gradually under the constant applied voltage. According to our previous study [14], $H^+$ is the predominant charge carrier in the glass during the corona discharge treatment of the soda lime glass. The mobility of $H^+$ in the glass is smaller than that of $Na^+$. Hence, the decrease in current indicates the formation of a highly resistive sodium depletion layer by the $H^+$ injection. Rather low and stable current was observed during the treatment in air, which can be attributable to the lower amount of injected $H^+$ in air compared with that in $H_2$ atmosphere.

Fig. 4 depicts photographs of the specimens after the treatment for 540 min. White precipitates were observed on the cathode side glass surface. The precipitates were identified as $Na_2CO_3$ using the

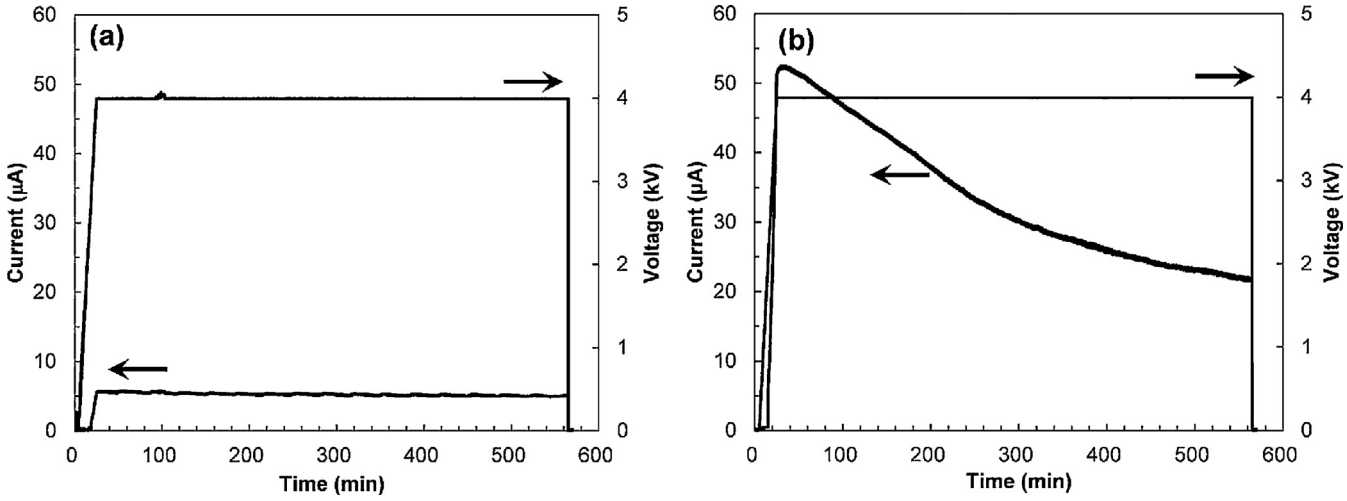


**Fig. 3.** Relation between corona discharge treatment time and current for the soda lime glass at 4 kV, 200 °C in (a) air and (b) $H_2$ atmosphere.