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Migration behavior of network-modifier cations at glass surface during electrical poling

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ABSTRACT

X-ray photoelectron spectroscopy with C_{60}-ion sputtering (C_{60}-XPS) and electron spin resonance (ESR) revealed the migration behavior of network-modifier cations in an electrically poled soda-lime silicate glass. The Na^+-deficient layer of 700-nm thickness was confirmed at the anode side surface. The Mg^{2+} and Ca^{2+} existed in the 200-nm thick layer from the top surface were concentrated in the layer of 200–700 nm depth from the surface. Additionally the oxygen content in the 200-nm thick layer decreased by the degassing as oxygen molecules from the glass surface, which is an essential requirement for the migration of Mg^{2+} and Ca^{2+} to cathode side. The bond scission between Si–O–Si is caused by the concentrated Mg^{2+} and Ca^{2+}, resulting the formation of $\equiv SiO^-(Mg^{2+}$ or $Ca^{2+})^-OSi\equiv$ and $\equiv Si\cdot$ (Si E′ center). We have also confirmed the generation of oxygen hole center (NBOHC) and peroxy radical (POR) in the electrically poled soda-lime silicate glass.

1. Introduction

Nanoimprint technology is crucial to apply a new function on the glass surface such as diffraction, phase control, antireflection. Recently, the electrical nanoimprint was reported as a low temperature and low pressure process for the fine pattern formation on several materials [1–4]. Ikutame et al. reported that periodic structures were imprinted on a soda-lime silicate glass surface below its glass transition temperature using a carbon-coated SiO_2 mold under applying direct current (DC) voltage [4]. It was confirmed that the alkali metal ions at the anode side surface migrated to the cathode side only in the contacted area of the imprint mold [4,5]. Furthermore, the chemical etching using a KOH solution was useful for the fabrication of the fine structures on the electrically nanoimprinted glass corresponding to the mobile cations distribution. In order to optimize the periodic structure shapes, it is important to understand the migration mechanism of network-modifier cations in the glass during the DC voltage application.

Historically, many researchers have investigated the migration mechanism of the network-modifier cations in oxide glasses by the heat treatment in several kinds of glasses [6–16]. In certain condition, the inward migrations not only of Na^+ but also of Ca^{2+} were observed at the surface of a soda-lime silicate glass [11–16]. Similar investigations were conducted for the electrically poled glasses [17–21]. Krieger et al. investigated the transport phenomena of ions (Na^+, Ca^{2+}, and H^+) in a soda-lime silicate glass after the electrical poling using the Rutherford backscattering method [17]. They suggested that the formation and migration of holes are the driving force for the inward migration of Na^+ and Ca^{2+} ions in the glass surface region. In such a case, the consideration of charge balance in the poled area should be a critical issue to understand the migration behaviors of mobile ions. However, the formation of holes has not been confirmed yet in glass surface region.

This paper reports the migration behavior of network-modifier cations in the electrically poled soda-lime silicate glass surface. An X-ray photoelectron spectroscopy with C_{60}-ion sputtering (C_{60}-XPS) and an electron spin resonance (ESR) were used for the analysis. C_{60}-XPS allows a precise depth profiling of network-modifier cations with the suppression of the remigration of mobile ions during the analysis [22].

2. Experimental procedures

Commercial soda-lime silicate glass [Composition: $72SiO_2$–$12Na_2O$–$9CaO$–$6MgO$–$1Al_2O_3$ (mol%), AGC Co., Ltd.] was used for the experiment. The glass thickness was adjusted to 1 mm by polishing both glass surfaces. The anode electrode was a silica glass plate of 25 × 25 × 2 mm coated with Pt thin film of 500-nm thickness. The cathode electrode was a carbon plate. The glass plate was sandwiched between two electrodes and pressurized under 3 MPa. The electrical poling was conducted at 450 °C for 90 s in an N_2 atmosphere under the application of DC voltages. The DC voltage was changed between 25–400 V to obtain the different thickness of the treated surface layer. Fig. 1 presents a typical current profile during the electrical poling to the soda-lime silicate glass under the applied voltage of 400 V.

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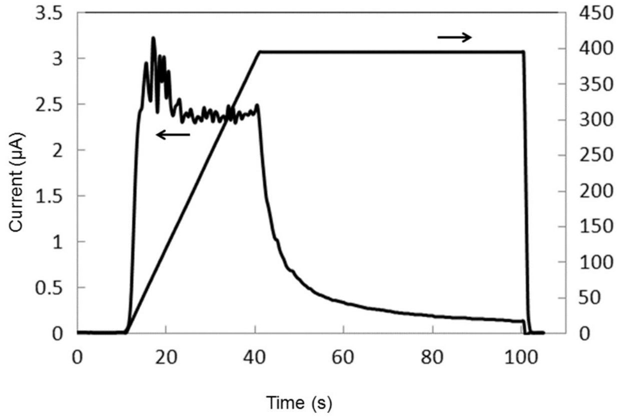

Fig. 1. Time dependence of applied voltage and current during electrical poling of soda-lime silicate glass at 450 °C, 400 V under the press of 3 MPa.

For the measurements of the C_{60}-XPS depth profiles, an ESCA-5500 (Physical Electronics, Chanhassen, MN) was used with a C_{60} ion gun (Ion Optika 06-C_{60} type; Chandlers Ford, Hampshire, UK); the detection angle was 75° using the monochromatic Al–Kα line ($h\nu = 1486.6$ eV). The irradiation conditions were optimized as 10 kV, 10 nA, and an incident angle of 37° for the C_{60} ion beam. Neutralization of the surface charge was performed using low-energy electrons in all measurements. Quantification of selected peak areas was performed using the MultiPak (Ulvac-Phi, Chigasaki, Japan) software. The depth of craters was eroded by the sputter or the primary ion beam was measured using a stylus profilometer to calibrate the depth scales with respect to sputtering time for the C_{60}-XPS.

ESR measurements were conducted using a JES-TE300 (JEOL, Akishima, Japan) to obtain the X-band spectra of the soda-lime silicate glasses with and without the electrical poling. In order to detect the ESR signal with high sensitivity, the stripe-shape glass plate was piled up in the silica glass tube of 4-mm internal diameter. The ESR signal of Fe^{3+} located at $g = 4.3$ for the glasses before and after the electrical poling was measured at the room temperature under the microwave power of 4 mW and the magnetic field of 150 ± 50 mT. The ESR signals located at $g \fallingdotseq 2.0$, which are attributed to hole center and/or Si E′ center, were measured at the liquid nitrogen temperature (77 K) under the microwave power of 1 mW and the magnetic field of 327 ± 5 mT.

3. Results

Fig. 2 shows the C_{60}-XPS depth profiles of the anode side cross section of soda-lime silicate glass after the electrical poling at 450 °C, 400 V under the pressure of 3 MPa. The deficient layer of network-modifier elements including alkaline-earth metal cations was formed at the surface. Such deficient layers were not recognized at the as-polished glass surface. There are two discriminative points in the profiles; (1) homogeneously deficient layer of mobile elements, and (2) concentrated layers of Mg and Ca.

(1) Homogeneously deficient layer

The concentrations of Na, Mg and Ca in the near surface area were lower than the detection limit of our XPS. Such deficient layer thicknesses were respectively 650 nm for Na, 200 nm for Mg and approximately 300 nm for Ca. The difference in thickness is closely related with the relative mobility of each element, which is expected to be in the order of $Na^+ > Ca^{2+} > Mg^{2+}$. Shilo et al. reported the same tendency in a lead–zinc–borosilicate glass [23]. Although the migration of cation with high valence state such as Nb^{5+} was reported in an electrically poled Nb_2O_5–TeO_2 glass [18], no such evidence was recognized for Al and Si in the soda-lime silicate glass because of their covalent bonding character with surrounding oxygens [24].

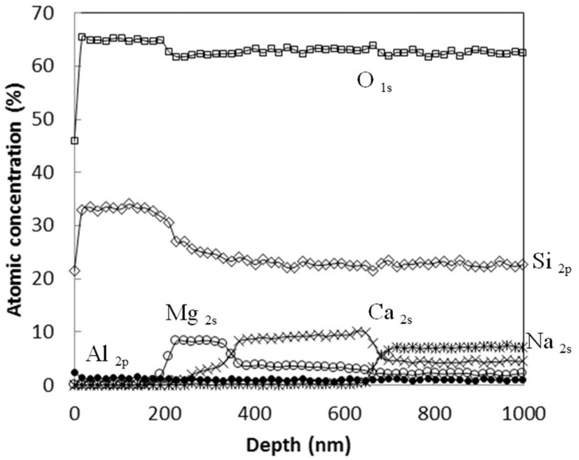

Fig. 2. C_{60}-XPS depth profile of the surface layer for soda-lime silicate glass after electrical poling at 450 °C, 400 V under pressure of 3 MPa. Concentrations of O, Si, Na, Mg, Ca and Al were monitored by the signals of O_{1s} (□), Si_{2p} (◇), Na_{2s} (*), Mg_{2s} (○), Ca_{2s} (×) and Al_{2p} (●).

(2) Concentrated layer of Mg and Ca

A concentered layer was confirmed independently in the 200–350 nm region for Mg and 350–650 nm region for Ca. Such layer was not observed in the depth profile of Na and other network former elements. The local condensation of Mg and Ca is difficult to explain by a simple replacement of Na^+ to Mg^{2+} or Ca^{2+}. In the following, we focused on the behavior of oxygen in the altered layer during the poling.

Fig. 3 shows the O/Si ratio against the depth of the electrically poled glass. The O/Si ratio in the surface layer of 200 nm thickness was lower than that of the deeper region, suggesting that an oxygen deficient layer was formed in the anode side surface during the electrical poling [25]. Fig. 4 shows the relationship between the total charge during the electrical poling and the deficient layer thickness estimated using the C_{60}-XPS. It is confirmed that the deficient layer thicknesses of Na, Mg, Ca and O increased with the total charge. The Na deficient layer is thicker than those of other elements (Mg, Ca, O), whereas the thickness of O deficient layer is similar with those of Mg and Ca.

Fig. 5 shows the ESR spectra at room temperature in the magnetic field around $g = 4.0$ for the soda-lime silicate glasses before and after the electrical poling. The microwave power and the magnetic field modulation were respectively 4 mW and 150 ± 50 mT. The signal located at $g = 4.3$ is assignable to the Fe^{3+} contained in the glass as an impurity [26]. The signal intensity decreased by 20% after the electrical poling. No intensity change caused only after the heat treatment at 450 °C.

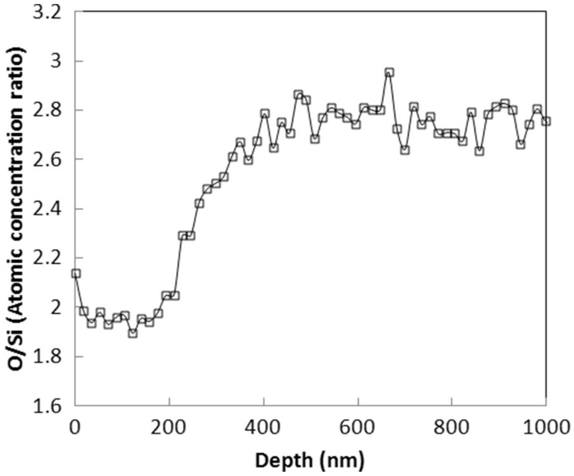

Fig. 3. Depth profile of O_{1s}/Si_{2p} ratio in the surface layer of soda-lime silicate glass after electrical poling at 450 °C, 400 V under the press of 3 MPa.