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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 ≡SiO^- (Mg^{2+} or Ca^{2+})$^-$OSi≡ and ≡Si· (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.

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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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