Enhanced displacement of sodium ions in a glass network studied by ion-induced photon emission

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Abstract. The influence of thermal and electric fields on the behaviour of Na^+ ions in the near-surface zone of compound silicate glass is presented. The in-depth profiling of the Na concentration was performed by means of ion-induced photon emission. It was found that, apart from the field effect caused by the implanted primary ions, there is also the influence of an external electric field that generates a strong maximum in the sodium distribution in glass. The mechanism of formation of this maximum is explained as a result of glass electrophoresis and can be described by a transport equation.

1. Introduction

The mechanism of interaction between energetic charged particles and the surface of compound oxide glasses strongly depends on mobile framework modifiers included in the glass structure. In a commercial soda–lime–silica glass irradiated by an electron beam, displacement of mobile Na^+ ions along the field produced by the introduced particles was observed [1, 2]. A similar effect was recorded when protons were introduced into the same type of glass [1, 2]. In the case of Ar^+ bombardment of glass, the creation of a zone with varied sodium concentration in the near-surface layer was observed [2–5]. This phenomenon results from preferential sputtering and preferential dislocation of sodium atoms in the rigid SiO_2 network. A drift of Na^+ ions towards the deeper layers of the target is also possible owing to the positive space charge created by the primary ions implanted in the near-surface layer, which did not undergo neutralisation. In order to analyse the field effect in more detail, the influence of an external electric field on the behaviour of mobile Na^+ ions in the near-surface zone of the glass was studied. This problem has not been investigated experimentally so far. In-depth profiling of the sodium concentration was performed by means of ion-induced photon emission.

2. Experimental procedure

In the present experiment a target of compound silicate glass was used. The composition of the samples is presented in table 1. The samples which are of cylindrical form, 1.5 mm high and 8 mm in diameter, were bombarded perpendicular to the polished surface by

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Table 1. Composition of the samples.

Oxide	SiO_2	Na_2O	K_2O	CaO	MgO	BaO	Al_2O_3	B_2O_3	Other
Amount (wt%)	68.00	11.42	3.00	8.22	1.99	0.60	4.46	1.52	0.79
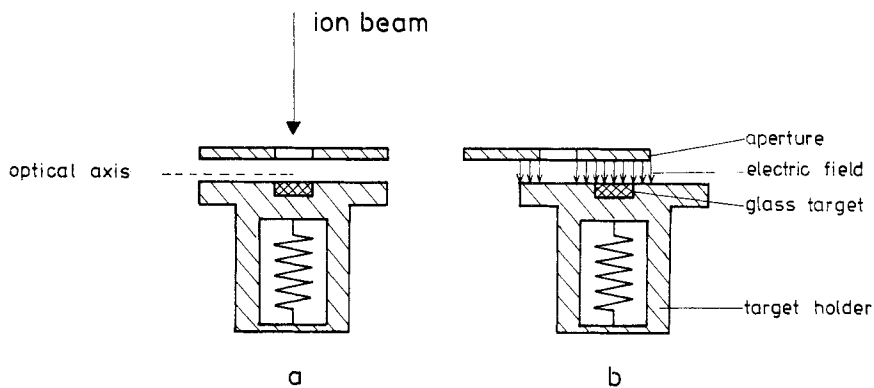
Figure 1. Target set-up and geometry of the experiment: (*a*) ion beam action; (*b*) electric field action.

a focused Ar^+ ion beam with an energy of 2.5 keV. The Ar^+ beam was produced by a duoplasmatron ion source, which was described in an earlier paper [6]. Before the measurements, the target was specially prepared in order to minimise the electric charge on the surface under action of the ion beam. For this purpose, a carbon mask was deposited on the sample face with the exception of the bombarded spot. The sample was mounted on a special holder which was connected with a manipulator provided for application of an external electric field under vacuum conditions. The field was directed perpendicular to the bombarded surface. It was possible under the same experimental conditions to record the resonance D-line intensity of sodium as a function of bombardment time. The geometry of the experiment together with the target set-up are presented schematically in figure 1. Figure 1(*a*) shows the position of the target during recording of the light intensity, whereas figure 1(*b*) corresponds to the configuration of the target set-up under the operation of an electric field. The intensity of the sodium D line was measured by means of a photorecording system consisting of a narrow-band 589 nm interference filter, photomultiplier and an electronic system for signal processing and recording. In the transmission band of the filter (half-width, 7.5 nm) no spectral lines of other elements were found. The glass samples were heated at the proper temperature by a tungsten filament mounted inside the target holder and supplied with stabilised current. The actual temperature of the target was measured by means of a (Ni–Cr)–Ni thermocouple with an accuracy of ±3 K. The target chamber had a base pressure of the order of 10^{-6} mbar.

The resonance D-line intensity of sodium as a function of bombardment time was a measure of the in-depth profile of sodium concentration [5].

The relation between bombardment-induced light emission and sodium concentration was tested experimentally. The test was performed under identical conditions that were applied in former measurements described in the paper. Glass samples which had a composition similar to that presented in table 1 were used. They were different only in the concentration of Na_2O (within the range 7–20 at.%) which was compensated by the change in SiO_2 concentration. Within the limits of experimental error a linear dependence of the D-line intensity on sodium concentration was obtained.

In order to convert bombardment time into depth, knowledge of the sputtering yield of the glass surface was needed. This quantity was obtained from a theoretical calculation of the total sputtering yield, which was gained on the basis of Sigmund's [7] theory of sputtering assuming glass to be a collection of averaged atoms. The surface binding energy of the averaged atom was approximated by the heat of atomisation of SiO_2 equal to 6.4 eV/atom, as this is the dominant component of the glass [8]. This results in a sputtering yield of 0.78 atoms for 2.5 keV Ar$^+$ ions. In order to check the correctness of the theoretical evaluation and to compare it with available experimental data, the sputtering yield for 5 keV Ar$^+$ ions was also calculated. The calculated value of 0.88 is in good agreement with an experimental value of 0.96 obtained for a sodium silicate glass [9]. Consequently, in our experiment the sputter removal rate equals 5 Å min^{-1}. Taking into account the parameters of the applied ion beam, we find the theoretical value comparable with that found experimentally for a sodium silicate glass [3].

3. Results and discussion

### 3.1. Variation in the sodium concentration in glass induced by thermal processing of the sample

Prior to the study of the influence of the electric field on mobile Na$^+$ ions, we decided to carry out an investigation on the in-depth sodium concentration as a function of temperature and duration of thermal processing, in order to obtain comparative experimental data for the analysis of the field effect. At an initial stage of the experiment the sample surface was submitted to Ar$^+$ ion bombardment at an energy of 2.5 keV and current density of 30 μA cm^{-2} until a constant photon emission was achieved. This introductory procedure was dictated by the need for a well defined state of the surface as a basis for the proper interpretation of the experimental results, as it is known that the structure of the glass surface is strongly perturbed by the action of atmospheric agents and differs from the bulk structure [10]. After the introductory beam processing, the sample was heated at a constant temperature of 505 K. After 1 h an analysing ion beam was turned on while keeping the target at 505 K. The analysing beam had the same parameters as previously. The dependence of the sodium D-line intensity on bombardment time is indicated in figure 2 (curve a). This curve shows that the photon emission disappears after 3 min of bombardment. This effect can be due to recoil interaction between incident argon ions and the mobile sodium ions as well as due to the action of the electric field by the positive spatial charge in the near-surface layer from non-neutralised Ar$^+$ ions. The observed process is very effective with respect to the increased mobility of sodium ions at higher temperatures.

On the other hand, if the target was cooled to room temperature, before the analysing beam is switched on we obtain a dependence of the sodium D-line intensity on bombardment time as shown in figure 2 (curve b). The increase of the sodium concentration in the near-surface layer due to migration of this element from the bulk to the surface can be explained as a result of weathering process of glass [11].

Preliminary experiments showed that the in-depth profiling of sodium concentration in a hot target is strongly perturbed by the ion beam itself. In order to obtain a result close to the real sodium distribution, one has to perform the measurements at room temperature, when the sodium mobility is small enough. In this case the influence of the ion beam on the sodium distribution can be neglected. However, it should be taken into account in the precise quantitative analysis.
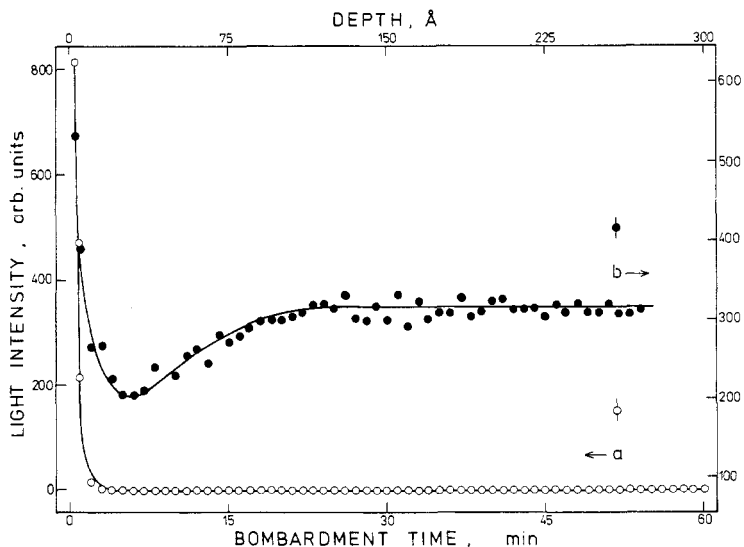
Figure 2. Sodium in-depth profile: curve a, hot target (left-hand scale); curve b, cold target (right-hand scale).
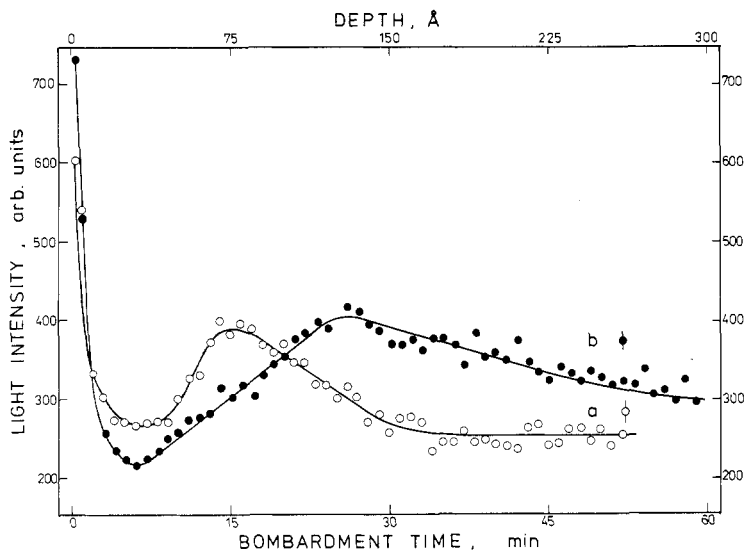
Figure 3. Sodium in-depth profile after positive electric field action: curve a, 2.5×10^5 V m^{-1}; curve b, 1.75×10^6 V m^{-1}.

3.2. Displacement of sodium in near-surface layers of glass induced by external electric field

In the next experiment we applied the same procedure as before (figure 2, curve b), but in addition an external electric field was applied during heating of the target and its cooling to room temperature. An electric field of intensity 2.5×10^5 or 1.75×10^6 V m^{-1} and positive polarisation with respect to the bombarded surface were applied. The sodium concentration profiles affected by the field processing are presented in figure 3. Curves a and b correspond to weak and strong field intensities, respectively. Both the
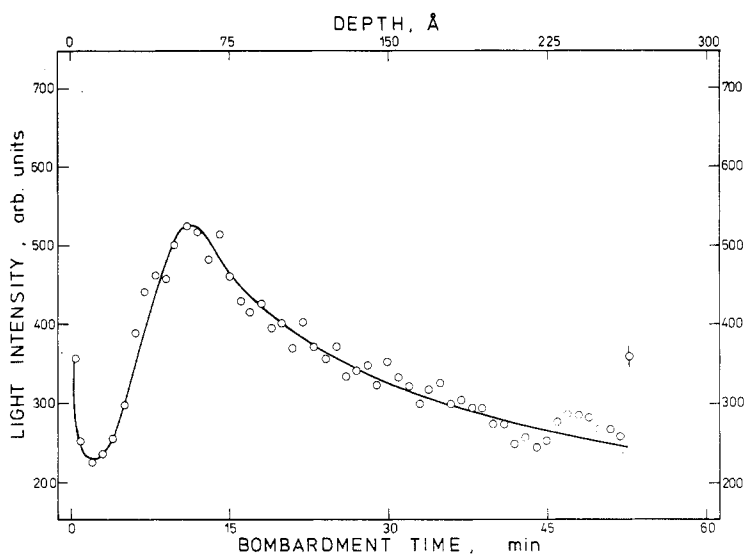
Figure 4. Sodium in-depth profile after negative electric field action (1.75×10^6 V m^{-1}).

curves have a similar character, but for the stronger field a shift of the maximum of sodium concentration towards the interior of the sample is observed. The maxima are situated at 75 and 128 Å below the surface. Enrichment in sodium in the near-surface layer observed for both profiles can be explained in a similar way as for profile b in figure 2. This enrichment exists in spite of the application of an external positive field due to stronger (compared with the bulk) binding of sodium ions on the surface due to weathering process. The mechanism of creation of the sodium concentration maximum inside the bulk can be explained as a result of electrophoresis in the glass. At first, the electric field shifts the mobile modifying ions, e.g. Na$^+$, towards the interior of the glass. Simultaneously, in the area partially depleted of these ions the oxygen anions are bound with a single valency to the Si atoms. In this way a double layer between positive electrode and negatively charged surface layer is produced. Thus a continuous distribution of the electric field along the direction of the action is created. The increased value of electric field in the near-surface layer compared with the field intensity in the bulk is the origin of the sodium concentration maximum.

The ion migration process affected by the temperature and electric field can be described with the following transport equation:

$$D\, \partial^2 n/\partial x^2 - \mu\, \partial(nE)/\partial x = \partial n/\partial t \tag{1}$$

where n stands for sodium concentration as a function of time t and depth coordinate x; E is the electric field intensity; D and μ are the coefficients of diffusion and mobility, respectively. The numerical solution of this equation under initial and boundary conditions revealed a maximum at definite value of x [12]. Taking into account that in the present experiment similar initial and boundary conditions are fulfilled, the transport equation describes the maximum observed in the bulk except for the near-surface maximum which is due to the other, previously mentioned, process.

For comparison, an additional experiment was conducted with a negative external electric field, i.e. opposite to the field in the former experiment. The in-depth profile of the sodium concentration for a negative field of intensity 1.75×10^6 V m^{-1} is presented in figure 4. It shows the shift of the bulk maximum towards the surface and diminution

of the surface maximum in comparison with that previously observed. The bulk maximum does not reach the surface owing to the surface barrier created by the weathering process. The existence of such a barrier was reported in [10, 11]. The diminution of the surface maximum can be explained by enhanced sodium evaporation under the action of a negatively polarised electric field.

4. Conclusions

From the present study the following conclusions can be drawn.

(i) The sodium distribution in glass is strongly perturbed by the incident ion beam if the target temperature is high enough. After a few minutes of ion bombardment the disappearance of sodium in the analysed volume is observed.

(ii) The in-depth profiling of glass by means of secondary-ion–photon emission is possible after cooling the target to room temperature.

(iii) Sufficiently strong external electric fields can generate remarkable variations in the sodium distribution in glass containing this element. An evident maximum of sodium concentration appears at a depth that depends on the intensity and polarisation of the field.

(iv) The mechanism that is responsible for the Na peak is electrophoresis according to the cited transport equation.

Acknowledgment

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