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Potassium-silicate glass exposed to low energy H^+ beam

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ABSTRACT

Pristine surface of binary potassium silicate glass $85SiO_2{\cdot}15K_2O$ was prepared in vacuum and irradiated with a 5 keV proton beam within the range of 0.6–103 C/m^2. The response of glass surface was monitored by XPS and the evolution of atomic concentrations divided it into two stages. During the first one, amounts of both potassium and non-bridging oxygen (NBO) increase in the surface layer and are governed by surface relaxation. The second stage is characterised by a continuous decrease of NBO and K. Comparison of K and NBO concentrations yielded a constant surplus of K proving the existence of potassium elemental state on the glass surface. Ratio of bridging oxygen (BO) and silicon is conserved during proton bombardment. The extrapolation of the glass response to the enhanced irradiation predicts a formation of substoichiometric SiO_x with some elemental K on the topmost surface.

1. Introduction

Silicate glass is one of the mostly used non-crystalline material in industry. Despite of its wide usage the prediction of glass properties is problematic due to the unknown glass structure. Although Zachariasen model of silicate glass known as Continuous random network (CRN) [1] or its modification to Modified random network (MRN) [2] are wildly accepted in glass science community and both of them prescribe only the basic short-range connectivity of atoms with their nearest neighbours. In recent years property tailoring or surface improving attract an increasing focus. Although it is accepted, glass surface can be very different from its bulk. Only little information about structure and properties of glass surface is known. Bulk glass is assumed to be built up from the basic structural units formed by the tetrahedron $(SiO_4)^{4-}$, i.e. silicon is surrounded with four oxygen atoms, in glass slightly deformed. Silicon tetrahedrons are interconnected among themselves via covalently bonded oxygen, called bridging oxygen (BO). The interconnected silica network forming CRN is then taken as a basic network into which alkali ions, in our case potassium ones, enter. Potassium breaks Si—O—Si bond and creates ionic O—K bond according the following scheme

$$2(\equiv Si{-}O{-}Si\equiv) + K_2O \rightarrow 2(\equiv Si{-}O^-K^+)$$

where each horizontal line marks a covalent bond and O^-K^+ indicates ionic bond between O and K. Oxygen atom contributing to O^-K^+ bond, i.e. not forming Si—O—Si bond, is called non-bridging oxygen (NBO). It is assumed that the ideal glass is perfectly bonded, i.e. no dangling bond, over- or under-coordination is present. From such structural picture comes out the following theoretical atomic concentrations (in %) of $85SiO_2{\cdot}15K_2O$ glass (valid for bulk): $c_{Si} = 28.3$, $c_O = 61.7$ ($c_{BO} = 51.7$, $c_{NBO} = 10.0$), $c_K = 10.0$.

Even though real glass is far from ideally bonded its irradiation with particles is able to change its composition [3,4], surface roughness [5], density [6,7], and finally its structure. The incoming particles inject into glass energy, momentum, charge (if charged), and new atoms (in case of ion bombardment). Direct interaction with particle beam may break bonds and create additional point defects [8] connected with the breaking of bonds. The defects may then serve as traps for electrons and macroscopic electric field is established inside glass [9]. Phase separation [10] or gas accumulation [11] are also reported as examples of many modifications found in the irradiated glasses. In this connection many authors suggested the nature of radiation induced defects is independent on the particular characteristic of the source [8,12,13]. However, a correct comparison of various irradiation experiments should not be based only on the irradiation doses but it must take into consideration the used energy fluxes. Especially some of the older works utilised high fluxes what resulted in a substantial increase of temperature influencing so life time and mobility of defects.

Vitreous silica serves as a natural background system for silicate glasses. Silica glasses with various history and different amount of magnetically active impurities were studied by EPR [14,15]. Independent studies both confirmed increasing number of point defects with irradiation dose (up to 5 GGy) and unveiled the correlation of the amount of defects with an original concentration of impurities in unirradiated glass. Nevertheless, as pointed out in [16] the number of defect centres reaches only few hundreds of ppm in silica glass. Number of paramagnetic centres seems to achieve saturation at about hundreds of ppm [17] for doses exceeding 10 GGy but other

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results indicate that the found saturation could be only temporary [14].

Replacing vitreous silica with alkali-silicate glass one introduces NBO, number of which exceeds the number of point defects by a few orders. The NBO are natural precursors of the new point NBOHC defects due to the reaction

$$\equiv Si—O—K + \text{energy} \rightarrow \equiv Si—O\bullet + K^+$$

where • depicts an unpaired spin located on oxygen. It is therefore remarkable that in alkali-silica glass is observed the saturation of paramagnetic centres at significantly lower doses [18] and at a few orders lower values in comparison with silica glass. However, the doses used in high-energy beam experiments are still limited to 10 GGy due to the relatively low powers. On the other hand low- and medium-energy electron beams are able to achieve doses up to ~8 TGy [19]. In general doses used within this energy region often start at orders of a few GGy. Much work was carried out for medium-energy and high-dose electron irradiated alkali silicate glasses by means of electron probe microanalysis (EPMA) [20–22] and for low-energy and high-dose electron irradiation by AES [23,24], and XPS [24–26]. Mostly, the electron beam irradiation resulted in the diffusion of alkali element(s) towards bulk in contrary to high-energy electron irradiation where no change in composition was observed [27]. As a consequence, a considerable part of the analysed volume beneath the surface was alkali depleted after some time of irradiation. Glass surface irradiated with electrons was initially enriched with both NBO and alkali atoms and after further irradiation the depletion from alkali atoms started. Escape of alkali atoms was also accompanied with an increase of BO and decrease of NBO [28]. Similarly, the structural changes during high-energy electron irradiation were correlated with alkali mobility in glass [29].

The present paper enhances the study of electron irradiated glasses to the study of the surface response of glass to proton bombardment. Simple binary glass is chosen as a prototype of the mixed covalent-ionic bonded glass. Energy chosen for the beam injects hydrogen ions much deeper than the studied thickness of the surface layer. The surface is here investigated by X-ray photoelectron spectroscopy (XPS). The focus is placed on the behaviour of both BO and NBO and their relation to Si and K.

2. Method

Glass was prepared by melting a high purity batch and then annealed for 16 h. The glass compositional homogeneity was confirmed by electron probe microanalysis (EPMA). Theoretical composition of the glass is as follows: 61.7 ± 0.6 at.% of O, 28.3 ± 0.3 at.% of Si, and 10.0 ± 0.2 at.% of K. All values refer to glass bulk that can significantly differ from the surface.

The glass surface was bombarded with H^+ beam generated by means of a commercial ion source (VG Scientific, UK) that has used spectrally pure hydrogen. Ion beam energy was set to 5 keV and the current density was 1 μA/cm^2. The penetration depth of ions is estimated to be around 75 nm [30], significantly larger than the information depth of XPS analysis. Ion doses used were ranged from 0.6 to 103 C/m^2 (0.02–3.4 GGy). It corresponds to irradiation times from 1 to 173 min.

The pristine glass surface (4 × 4 mm^2) was prepared by *in situ* fracturing the glass rod in the UHV chamber of the photoelectron spectrometer ADES-400 (VG Scientific, UK) equipped with a twin anode X-ray source and with the high-energy resolution hemispherical analyser. The photoelectron spectra were recorded using MgKα radiation source operating at 200 W and at an angle of incidence 70° measured from the surface normal. The emission angle was set along the surface normal. Electron energy analyser operated in a constant pass energy mode at 100 eV. No electron flooding was used during spectra acquisition. As a result, the measured glass surface was positively charged. All the binding energies referred here are normalised to Si 2p binding energy at 103.5 eV [31]. The whole experiment was performed as continuous within the scheme "Fracture–Analysis–Proton bombardment–Analysis – ··· – Analysis". The first analysis started instantly after the glass fracturing (5–10 min) and lasted for 30 min. The time of recording of spectra was also kept constant for all other analyses. As no charge compensation was used spectrum shifts were observed: 3.7 eV at the pristine surface, decreasing to 2.5 eV after the first proton bombardment, and continuously increasing with proton dose up to 3.3 eV for the highest dose used. Hence, the charging more or less followed the course of potassium concentration.

Atomic concentrations of elements found in the analysed volume were determined from the O 1s, Si 2p, and K 2p peak areas following the Shirley's inelastic background subtraction method assuming a simple model of a homogeneous semi-infinite solid. The peak areas were corrected for the measured transmission function of the spectrometer, which comprises all instrumental factors influencing the measured quantity [32], for the photoelectric cross-sections [33], and for the inelastic mean free paths of photoelectrons in SiO_2 [34]. Experimental uncertainties accompanied with XPS quantitative analysis were estimated to be below 7%. The value covers overall uncertainties of the method that are mostly introduced by the background subtraction and the correction procedure used for the calculation of concentrations from the intensities of spectral lines.

3. Results

Directly after fracturing the glass rod and creating the pristine surface evident changes can be identified in both atomic concentrations and bonding. Table 1 shows a significant decrease of oxygen (by 15%) on the surface in comparison with the bulk value. Nevertheless, decomposing oxygen O 1s peak into BO 1s and NBO 1s peaks one can deduce that the overall decrease of oxygen is given only by the decrease of BO while the amount of NBO increased. The example of the decomposition procedure is given in Fig. 1 for both the pristine surface and the surface irradiated with

Table 1
Atomic concentrations of the elements present in glass as a result of H^+ bombardment. Oxygen is also distinguished into NBO and BO. The zero irradiation time corresponds to values obtained by XPS from the pristine glass after fracture.

Irradiation time (min)	O	NBO	BO	Si	K
0	56.5	12.6	43.9	30.4	13.2
1	55.2	14.0	41.2	28.2	16.6
2	54.1	15.0	39.1	27.3	18.6
3	53.1	15.9	37.2	26.8	20.1
4	52.6	16.9	35.7	26.4	21.0
5	52.9	16.5	36.4	26.3	20.8
6	53.7	17.0	36.7	25.3	21.0
7	53.4	16.3	37.1	26.2	20.4
8	53.8	16.9	36.9	26.1	20.1
9	53.2	15.6	37.6	26.5	20.3
10	54.0	17.1	36.9	25.9	20.1
15	54.5	12.6	41.9	27.7	17.8
20	54.8	13.0	41.8	27.7	17.5
30	55.0	11.4	43.6	30.0	15.0
40	55.7	10.5	45.2	31.3	13.1
50	56.3	9.8	46.5	31.4	12.4
60	56.5	7.7	48.8	33.1	10.4
70	56.8	7.0	49.8	32.6	10.6
80	57.2	6.4	50.8	32.5	10.3
90	57.3	6.7	50.6	33.0	9.7
110	57.8	5.8	52.0	33.9	8.3
130	58.3	5.0	53.3	34.1	7.6
173	57.9	3.5	54.4	35.8	6.3