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Lead-silicate glass surface sputtered by an argon cluster ion beam investigated by XPS

J. Zemek^{a,*}, P. Jiricek^a, J. Houdkova^a, K. Jurek^a, O. Gedeon^b^a Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, 162 53 Prague 6, Czech Republic^b University of Chemistry and Technology, Technicka 5, 166 28 Prague, Czech Republic

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ABSTRACT

The conventional ion beam sputter-cleaning technique is frequently used for removing surface adsorbates and carbon contamination from air-exposed glass surfaces. Due to the ion-surface interaction, however, an altered near-surface layer is formed with a modified composition and modified bonding. In the present work, we first examine changes in surface composition and bonding due to X-ray and electron irradiation for both air-exposed and sputter-cleaned surfaces. Then we apply argon cluster ion beam sputtering, known as a very gentle technique with respect to the changes in surface chemistry, to air-exposed lead-silicate glass surfaces analyzed by high-energy resolved core-level photoelectron spectroscopy. It was found that (i) the surface contamination present on air-exposed lead-silicate glass surfaces has a qualitative influence on the results of an XPS analysis, and (ii) Ar cluster ion beam sputter-cleaning with mean energy per Ar atom in clusters of a few eV was successfully used to remove surface contamination from air-exposed lead-silicate glass with no substantial violation of the glass surface structure. This made it easier to reveal their intrinsic surface properties.

1. Introduction

Ion beam techniques are currently used in surface science for surface cleaning and for concentration depth profiling. The interaction between conventional (monoatomic) ion beams and solid glass surfaces is a rather complex process [1]. It includes the formation of an altered surface layer with a modified composition and modified bonding, structural damage, and high gradients of mechanical stresses. The composition changes originate mainly from preferential sputtering, radiation enhanced diffusion, internal electric field formation and ion implantation of primary ion beam species.

For example, the outermost surface regions of a sodium-silicate glass, $30\text{Na}_2\text{O}\cdot 70\text{SiO}_2$, studied by XPS [2], was found to be dealcalized by a 2.5 keV Ar ion beam and, simultaneously, the percentage of oxygen and silicon on the surface increased with sputtering time. Consequently, the amount of non-bridging oxygen (NBO) dropped and the amount of bridging oxygen (BO) increased with the ion dose. In sodium phosphate glass $30\text{Na}_2\text{O}\cdot 70\text{P}_2\text{O}_5$, an increasing content of Na and a drop in O and P with the ion dose was found [2]. Soda-lime-silica glass sputter-cleaned by a 900 eV Ar ion beam and analyzed by XPS resulted in sodium surface enrichment [3]. Potassium-silicate glass surfaces exposed to a 5 keV proton beam and monitored by XPS revealed a rather complex evolution of atomic concentrations at the

glass surface. The initial response of the glass surface to the proton beam resulted in an increase in K and NBO - and reached a maximum followed by a gradual decrease in K and NBO at higher proton doses [4]. Similar results were obtained earlier on soda-lime-silica glass surfaces irradiated by proton beams of energies 30, 100, and 600 keV and for an Na depth concentration profile measured with the $^{23}\text{Na}(p,\alpha)^{20}\text{Ne}$ resonant nuclear reaction [5].

From the studies mentioned above one can conclude that ion bombarded glass surfaces can be enriched or depleted by network modifier element(s). The NBO concentration behaves accordingly. The resulting surface composition and bonding depends on the dominating mechanism, which can depend on the glass composition, bonding, experimental geometry, and/or ion beam parameters. Sputter-induced artefacts therefore often obscure the real surface-related properties of the investigated glasses particularly their natural surface composition and bonding.

Much efforts have been devoted to suppressing the formation of altered surface layers. The most promising method seems to be the application of multi-atomic or molecular ion beams consisting of large aggregates of atoms or molecules, known as clusters. The first example was when Yamamoto and Yamamoto [6] compared concentration depth profiles deduced from photoelectron core level spectra of soda-lime-silica glass using monoatomic Ar and buckminsterfullerene (C_{60})

* Corresponding author.

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ion beam sputtering. When the classical Ar ion beam was applied, the glass surface was found to be sodium depleted, but when the C₆₀ ion beam was used the sodium concentration appeared to be constant, dose-independent, and close to the value expected for bulk glass composition. Unfortunately, the authors provided no information about chemical bonding at the analyzed surfaces, which can be more sensitive than compositional changes to ion beam-glass surface interactions [6].

Gas cluster ion beams can be generated by an adiabatic expansion of the working gas in a nozzle passing from the high-pressure side to a vacuum chamber [7,8]. Here the atoms or molecules are cooled and merged to clusters of various dimensions [9]. They are then ionized, separated, accelerated and formed by ion optics into a well-defined ion beam. Collisions of multi atomic or molecular ion clusters with solid surfaces result in impact effects differing from those induced by conventional ion beams. For example, the dependence of cluster stopping on momentum was found to be completely different than for monoatomic projectiles, where the dependence is linearly scaled with energy [10]. For a large number of atoms in clusters the energy per atom may be rather low, even in the range of a few eV. Because the constituent atoms in clusters are mutually weakly bonded, the clusters disintegrate during impact upon a solid target and do not penetrate deeply beneath the surface [11], though they can be still used for surface cleaning and for shallow concentration depth profiling.

Argon is one of the most frequently used working gases for generating cluster ion beams, because it does not react with atoms on solid surfaces and practically no Ar atoms are left on the surface [8,9,11,12]. Ar cluster ion beam bombardment is characterized with respect to conventional Ar ion beams by a high sputtering yield per one cluster ion, enhanced lateral sputtering effects, low-level surface roughness, and by substantially suppressed surface structure damage [13–18]. Moreover, Ar clusters can be used for molecular depth profiling of soft materials as crosslinking polymers and, generally, reveal low-level or almost non-degrading bonding of atoms at bombarded surfaces [12,19].

In this paper, we investigate lead-silicate glass surfaces with the use of high-energy resolved X-ray induced photoelectron spectroscopy before and after argon cluster ion beam sputtering. Emphasis is laid on possible changes in surface composition and in chemical bonding. Before starting our experiment, the possible influence of X-rays and low-energy electrons on the measured quantities was carefully tested and discussed [20–21].

2. Materials and methods

Lead-silicate glasses were melted from 18.3 g PbO, 2.14 g PbO₂ and 2.78 g SiO₂ at 780 °C, using a high purity batch in a Pt crucible, and were cast on a metal plate to prevent crystallization. Subsequently, the glass was annealed at 400 °C for a few hours. The glass was transparent and contained no bubbles or cords. A composition close to the orthosilicate was used for the present analysis. Fragments of the glass were analyzed by electron probe micro-analysis (EPMA) in order to check their homogeneity and bulk composition. Glass surfaces were prepared by fracturing a glass plate in air and were immediately inserted into the UHV measuring chamber for XPS analysis.

High-energy resolution XPS spectra were measured in UHV with the AXIS-Supra photoelectron spectrometer (Kratos Analytical Ltd., UK), using monochromatized AlK α radiation (1486.6 eV, 150 W, analyzed area 0.7 × 0.3 mm²), and were collected in constant analyser energy mode with pass energy of 10 eV and a step of 0.05 eV, resulting in overall energy resolution of 0.45 eV, measured on the Ag 3d^{5/2} line width. The X-ray incidence angle was 54.4° and the photoelectron emission angle was 0° with respect to the surface normal. The Kratos magnetic confinement charge compensation system was used during the analysis in order to obtain the narrowest possible spectral line widths. The shift in energy due to the surface charging effect, even after it had been compensated, was calibrated to the binding energy of C 1s

(285.0 eV). The atomic concentrations of lead, silicon, oxygen and carbon were determined from the corresponding photoelectron peak areas after standard Shirley inelastic background subtraction using the ESCAPE data system and the relative sensitivity factor method. The carbon present at the air-fracturing glass surfaces reached from 15 to 40 at.% in dependence on time of air exposition. The Pb 4f and O 1s high-energy resolution spectra were analyzed by peak fitting using Gaussian – Lorentzian sum functions to differentiate bonding states and possible changes to them due to X-ray and argon cluster ion beam irradiation. The experiments were organized as follows.

First, the survey and core level spectra of the Pb 4f, Si 2p, O 1s, and C 1s were recorded continuously from the as-received glass surface. The surface of the sample was thus irradiated by AlK α radiation (and by low-energy electrons from a flood gun) for an extended period of time in order to map possible changes in composition and chemical bonding during photoelectron spectra acquisition [20–21]. The measurements were repeated with the sputter-cleaned surface, as described in greater detail below. The typical acquisition time for recording the survey and core level spectra was from 10 to 20 min.

Second, the survey and core level spectra of the Pb 4f, Si 2p, O 1s, and C 1s were recorded from the as-received glass surface. The virgin sample surface was sputtered and analyzed step-by-step by an argon cluster ion beam (Minibeam 6, Kratos, UK) and by XPS. The ion beam was focused beam diameter of 0.2 mm and scanned over impact area 2 × 2 mm² at an incident angle of 50° from the surface normal. The ion beam was stabilized for 30 min before starting the experiment. The ion beam energy and the average number of Ar atoms were varied in order to find optimum sputtering conditions leading to minimal bonding degradation. Finally, the following sputtering conditions were adjusted and used in the present work: 5 keV ion beam energy, 7 nA ion beam current, and the average number of Ar atoms in the clusters was set to 2000. This means that the average energy per Ar atom was as-low-as 2.5 eV.

3. Results and discussion

3.1. Surface composition and the position of the core level peaks

Analytic and batch compositions of the analyzed glass expressed in at.% are summarized in Table 1. The EPMA and batch values are in good mutual agreement, while the XPS values indicate a slight surface enrichment by lead. Modest but systematic surface enrichment by lead was found for binary lead-silicate glass surfaces [21]. Surface enrichment was also observed for alkali network modifier atoms in as-fractured surfaces of silicate glasses analyzed by ISS [22] and by XPS [4,23–25]. This suggests that crack propagations may occur preferentially along regions rich in network modifiers.

The core level peak positions and FWHM values (in brackets) were found to be consistent with the published data [21,26,27]: Pb²⁺ 4f_{7/2}–138.6 eV (1.33 eV), Pb²⁺ 4f_{5/2}–143.5 eV (1.33 eV), Pb⁰ 4f_{7/2}

Table 1

Surface and bulk composition of analyzed lead-silicate glass. Analyses of two different sputter-cleaned surfaces were inserted to show the repeatability of the results.

Mol. frac. at batch	Method	Pb (at. %)	Si (at.%)	O (at.%)	Pb/Si
0.598 PbO + 0.065 PbO ₂	XPS as-received	28.8	12.3	59.0	2.3
	XPS as-received, C ignored	30.1	14.8	55.1	2.0
	Sputter-cleaned (10 min), 1st fracture	29.6	15.4	55.0	1.9
	Sputter-cleaned (10 min), 2nd fracture	31.9	16.1	52.0	2.0
	Sputtered (80 min)	27.3	16.7	56.0	1.6
	EPMA	27.1	15.2	57.6	1.8
	Batch composition	27.6	14.0	58.4	2.0

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