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Aluminum-enhanced alkali diffusion from float glass to PVD-sputtered silica thin films

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Abstract

Interdiffusion processes between aluminum enriched PVD-sputtered silica thin films and industrial float soda-lime silicate glass substrates are quantitatively studied using SIMS analysis. Heat treatments are performed at temperatures close or above the glass transition temperature of the float glass. Aluminum doping of the film is shown to strongly increase the migration of alkali from the glass substrate to the silica thin film. In particular the final alkali content in the film exhibits a linear scaling with the aluminum concentration. An interdiffusion process is evidenced between bulk alkali ions and protons originating from a significant water content in the as-deposited silica film. Experimental measurements of sodium concentration are shown to be consistent with a simple thermodynamic model based on the equilibration of the activity of sodium between the film and the glass substrate.

Keywords: Silica thin film, Barrier layer, Alkali-ions migration, Interface diffusion

1. Introduction

Industrial glasses coated with thin films are often subjected to thermal treatments, in the framework of a forming process, or in order to enhance specific properties of the glazing, or to improve the mechanical properties of glass. At high temperature close or above the glass temperature of the substrate, several species diffuse from the substrate to the thin films. For soda-lime float glass, the diffusion of sodium or other alkali ions is the most significant effect. Alkali diffusion is beneficial for a minority of active layers, such as CuGaSe₂ thin film for solar cells, in which controlled diffusion of sodium and potassium has been shown [1] to enhance energy conversion. However, sodium alters the electrical properties of most active layers used in solar cells [2, 3, 4, 5], with dramatic effects such as electrical shunting caused by the widening of grain boundaries [6]. The diffusion of sodium also decreases the

mechanical or electrical properties of low-emissivity coatings [7, 8] used in the building and automotive industry, or of transparent conducting oxide layers used in displays [9].

In order to limit the diffusion of alkali from the glass substrate to the active layers, barrier layers are deposited on the glass surface [2]. Alkali diffusion through a barrier layer has been studied for a variety of compositions, such as silicon nitride [10], silica, alumina [11, 12] or ceria [13], and for different deposition processes such as chemical vapor deposition (CVD) [14, 15], physical vapor deposition (PVD) [7, 8], or sol-gel coating [16, 17]. One of the most common compositions of barrier layers is silica, which is usually doped with aluminum in PVD coaters in order to increase the deposition rate [18]. For non-doped silica thin films, Araujo et al. [19] showed that the chemical potential of sodium in the substrate could be used to predict whether sodium would diffuse from the substrate to the silica layer, or in the other direction in the case of alumina- or boron-rich substrate compositions.

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Table 1: Composition (in weight percent) of the soda-lime glass substrates.

| oxides | weight % |
|--------------------------------|----------|
| SiO ₂ | 73.0 |
| Na ₂ O | 13.5 |
| CaO | 10.0 |
| MgO | 2.5 |
| Al ₂ O ₃ | 0.5 |
| K ₂ O | 0.1 |
| Other elements | < 0.4 |

Little experimental data exist on the influence of aluminum on alkali diffusion in silica thin films. Nevertheless, the structure and transport properties of bulk aluminosilicate glasses and melts have been studied extensively in the geochemistry community [20, 21, 22, 23, 24]. In particular, the structural role of sodium changes progressively from network modifier to charge compensator of Al³⁺ when alumina is added to a silicate melt [25, 21, 26, 27, 28]. Therefore, adding aluminum to a sodium silicate melt with a fixed Na/Si ratio increases its viscosity, since less sodium is available to depolymerize the silica network [28, 29].

In this work, we study the influence of the aluminum content in silica thin layers on alkali migration at temperatures close to the glass transition of the glass substrate. In particular, our aim is to identify and characterize the diffusion mechanisms at play at the interface between the glass substrate and the PVD-sputtered silica thin films. Using Secondary Ion Mass Spectroscopy (SIMS), we study experimentally alkali migration at 650°C from soda-lime float glass to PVD-sputtered alumina-doped silica layers with different values of aluminum doping. Our experimental results are compared with thermodynamic predictions.

2. Materials and methods

2.1. Glass substrates

Commercial flat soda-lime glass (Saint-Gobain Planiclear[®]) with a thickness of 2 mm was used as substrate. Its composition is given in Table 1. Samples were prepared, cleaned with RBSTM detergent and rinsed with deionized water before thin film deposition.

2.2. Silica thin films deposition

Pure and aluminum-doped silica layers were deposited by Physical Vapor Deposition (PVD) by cathodic magnetron sputtering at room temperature. Si and Si:Al (8% in weight) targets were used for silica thin films deposition under reactive atmosphere at 2 μbar in Ar/O₂ plasma. Silica layers containing 0% and ~ 4% (in weight) of Al₂O₃ were obtained by using a single target and SiO₂ thin films with 0.2% to 1% (in weight) of Al₂O₃ were obtained by co-sputtering with the two targets. Therefore, various silica samples with Al₂O₃ concentrations between 0.0 and 4% in weight (corresponding to 0.0 to 2.4% in moles) have been elaborated for this study.

The thickness of the films was measured with surface profilometry (DektakXT, Bruker) or atomic force microscopy (Icon, Bruker). Results for silica layers with thicknesses between 100 nm to 250 nm are presented here. Several deposition chambers were used for this work depending on the size of the samples and the configuration needed (sputtering or co-sputtering).

2.3. Thermal treatments

After deposition on glass, silica thin films were annealed in air at 650°C in an electrical furnace. This temperature is in the range of temperatures used industrially for glass tempering or shaping. One should note that it is higher than the glass-transition temperature (T_g) of the substrate (~ 550°C). Annealing durations between 5 min and 16 hours were used at this temperature. Samples were directly placed in the furnace prepared at 650°C and quenched in air at the end of the thermal treatment.

2.4. Silica thin films characterization

Quantification of the silica layer was first performed by EPMA (Electron Probe MicroAnalysis) for one thick layer. The measurements were carried out on an SXFive apparatus (CAMECA, France), on samples coated with a thin carbon layer to reduce charging effects. The electrons energies were 5, 10, and 15 keV and the current was 15 nA in order to avoid any sodium diffusion during the acquisition applied on an area of 2 x 40 μm. The X-rays line selected were the following: Na Kα, Si Kα, Al Kα and O Kα. Due to the larger probed depth (> 1 μm) of the technique compared to layer thickness (250 nm), modeling was performed using Stratagem software (SAMX, France). The latter

Table 2: Concentrations (in weight %) of SiO_2 , Na_2O and Al_2O_3 in a 250 nm thick silica thin film deposited on glass after 1h at 650°C , measured on the same sample by SIMS (in the central zone), EPMA and XPS.

| (weight %) | SiO_2 | Na_2O | Al_2O_3 | Na/Al (atomic) |
|------------|----------------|-----------------------|-------------------------|----------------|
| SIMS | 92.4 | 3.7 | 3.9 | 1.6 |
| XPS | 90.8 | 4.5 | 4.7 | 1.6 |
| EPMA | 89.9 | 5.2 | 4.8 | 1.8 |

126 takes into account the in-depth distribution of the
 127 ionization function (called $\phi(\rho z)$) and based on
 128 the XPP model which is well adapted for stratified
 129 samples [30]. Quantification by EPMA is given in
 130 Table 2.

131 Furthermore, layer composition for the same
 132 sample was estimated by X-ray Photoelectron Spec-
 133 troscopy (XPS). The analyses were performed on
 134 a NOVA system (Kratos-GB) equipped with a
 135 monochromatic Al $K\alpha$ X-ray source, operating at
 136 225W. The collection angle was set at 0° (normal
 137 detection) in order to maximize the probe depth
 138 (to 5nm in case of such silica-rich material). Re-
 139 sults obtained are also given in Table 2.

140 Since EPMA results consider that the layer com-
 141 position is homogeneous and XPS only probes the
 142 layer surface, SIMS depth profiles were carried out
 143 for depth-resolved measurements of the composi-
 144 tion. Measurements on as-deposited and annealed
 145 silica layers were performed on a TOF.SIMS 5
 146 (ION-TOF GmbH, Münster, Germany). The pri-
 147 mary ions Bi^+ , accelerated at 30 kV were generated
 148 by a LMIG (Liquid Metal Ion Gun) operating in
 149 high-current bunched mode with a beam current of
 150 3 pA at 16 kHz. The scanned area of $50 \times 50 \mu\text{m}^2$
 151 was centered in the middle of the $200 \times 200 \mu\text{m}^2$
 152 sputter area performed by the DSC (Dual Source
 153 Column) source generating Cs^+ . The sputter beam
 154 energy was 2 keV and the applied current was 150
 155 nA. A usual methodology for non-conductive sam-
 156 ples was applied: an electron flood gun was used (E
 157 $\sim 21 \text{ eV}$) in order to reduce charging effects during
 158 the acquisition in non-interlaced mode (1s sputter-
 159 ing, 0.5s pause, 2.5s acquisition)[31].

160 An example of typical SIMS depth profile is given
 161 in Fig. 1. It is generated by the collection of the
 162 positive ions coming from the main isotopes ele-
 163 ments present within the glass substrate and the
 164 layer (i.e.: $^1\text{H}^+$, $^{30}\text{Si}^+$, $^{23}\text{Na}^+$, $^{40}\text{Ca}^+$, $^{24}\text{Mg}^+$,
 165 $^{39}\text{K}^+$, $^{27}\text{Al}^+$, $^{120}\text{Sn}^+$). Cs was selected as abra-

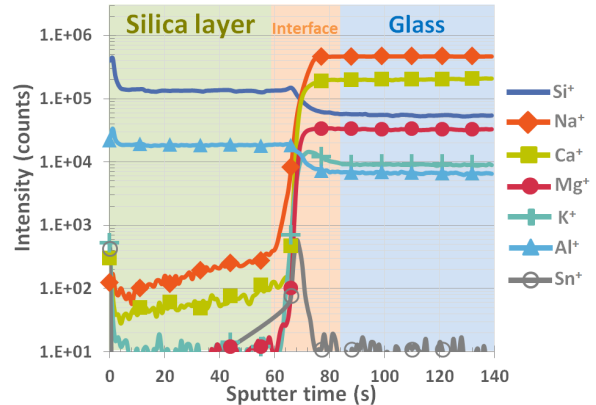


Figure 1: Example of a SIMS depth profile (before calibration) of a silica thin film doped with 0.9-wt% Al_2O_3 as-deposited on glass.

166 sive species because it induces less artifacts due to
 167 alkali-ions migration during depth profiling [32, 33].
 168 Only monoatomic ions (as opposed to polyatomic
 169 clusters) were followed to generate the composition
 170 depth profiles, in order to increase the sensitivity
 171 within the silica layer [34]. SIMS values at the ex-
 172 treme surface are affected by transitory effects and
 173 should not be interpreted [35].

174 Depth calibration was obtained from stylus pro-
 175 filometry (Dektak XT, Bruker) performed on two
 176 different SIMS craters. The first one stopped at the
 177 glass/layer interface determined by the maximum of
 178 $^{120}\text{Sn}^+$ signal. Indeed, tin condensates on the at-
 179 mospheric side of glass during the floating process
 180 (see Fig. 1). We assume that tin is totally oxidized
 181 after annealing into Sn^{4+} , which has a negligible
 182 mobility [36]. Typical values of the sputtering rate
 183 inside the silica layer were between 1.2 and 1.5 nm/s
 184 depending on (i) the amount of aluminum, (ii) the
 185 deposition conditions and (iii) the thermal treat-
 186 ment. The second crater was stopped deeper in the
 187 substrate in order to estimate the sputtering rate for
 188 the glass substrate (approximately 1.2 nm/s).

189 For quantitative depth profiling with SIMS (ex-
 190 cept for hydrogen), the use of relative sensitivity
 191 factors (RSF) is necessary for the conversion of
 192 intensities into concentrations [37, 14]. The sec-
 193 ondary ion yields of SIMS can be strongly depen-
 194 dent on the composition of the matrix. However,
 195 according to the author's experience, we made the
 196 assumption that matrix effects are comparable in
 197 the dense silica thin films and the soda-lime glass
 198 substrate. Therefore the determination of relative
 199 sensitivity factors has been made from the compo-

200 sition of the glass substrate measured by wet chem-
 201 istry (cf Table 1). Results of the average values
 202 of SiO_2 , Na_2O and Al_2O_3 content over a central
 203 zone (in order to avoid SIMS artifacts) are given
 204 in Table 2. Values obtained with these three tech-
 205 niques converge with differences less than $\pm 20\%$.
 206 Consequently, our assumption for SIMS quantifica-
 207 tion appears to be relevant.

208 Finally, hydrogen amount was evaluated by Elastic
 209 Recoil Detection Analysis (ERDA). The experi-
 210 ment was carried out on the 2.1MeV Van-der-Graff
 211 accelerator AIFIRA (CENBG-France). The $^4\text{He}^+$
 212 ions produced, impinged the sample surface at graz-
 213 ing incidence and the hydrogen atoms were collect-
 214 ed through a filter (in order to stop He ions).
 215 The spectra were processed using SIMRA software.
 216 SIMS and ERDA results concerning hydrogen will
 217 be discussed in Section 4.2.

218 3. Results

219 Typical quantified SIMS depth profiles inside sil-
 220 ica thin films deposited on glass are presented on
 221 Fig. 2, before and after thermal treatment.

222 As shown on Fig. 2a and 2c, deposition of silica
 223 thin film with our PVD protocol allows us to ob-
 224 tain pure and aluminum-doped silica layers without
 225 contamination by the various oxides contained in
 226 the glass substrate. Nevertheless, after annealing
 227 for one hour at 650°C pure or alumina-doped silica
 228 layers (Figs. 2b and 2d), we observe the migration
 229 of sodium and potassium from the glass substrate to
 230 the silica layer. On the other hand, alkaline-earth
 231 elements such as calcium and magnesium are not
 232 measured in significant amounts. Interestingly, the
 233 concentration of alkali oxides (both Na_2O and K_2O)
 234 after thermal treatment is substantially higher for
 235 an Al_2O_3 -doped silica layer (Fig. 2d) than for a pure
 236 silica layer (Fig 2b).

237 In order to study the relationship between alu-
 238 minium doping and alkali migration, we extracted
 239 the average value of the Na_2O and K_2O content (av-
 240 eraged over a central zone in order to avoid SIMS
 241 artifacts at interfaces) in doped and pure silica lay-
 242 ers. Na_2O and K_2O contents are plotted respec-
 243 tively in Fig. 3a and Fig. 3b as a function of Al_2O_3
 244 content, for different annealing durations at 650°C .
 245 We observe a clear affine relation between Al_2O_3
 246 and alkali oxides concentrations (mol %), with a
 247 best least-square fit given by:

$$248 \quad C_{\text{Na}_2\text{O}} = 1.47 C_{\text{Al}_2\text{O}_3} + 0.22 \quad (1)$$

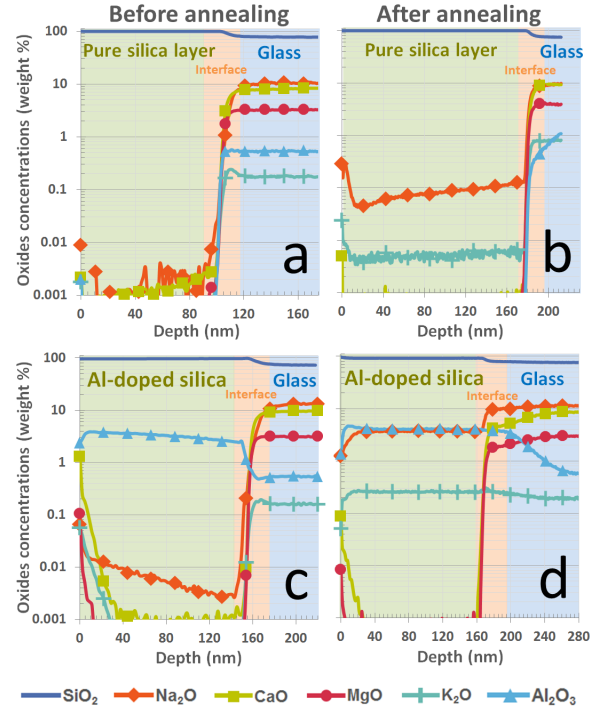
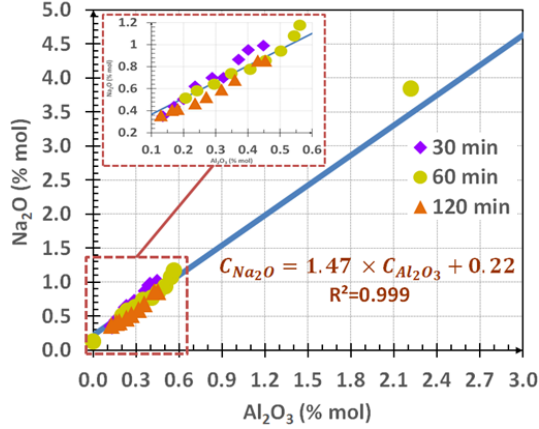
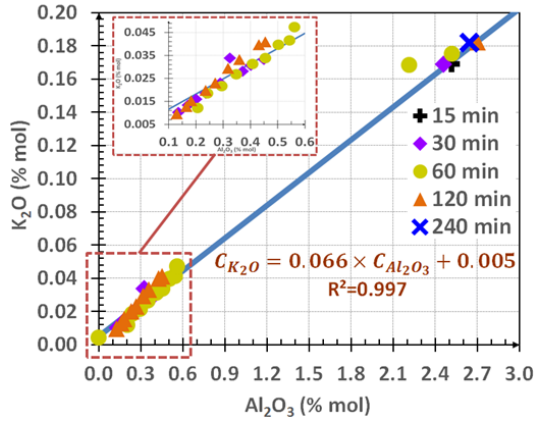


Figure 2: SIMS profiles of silica thin films deposited on glass: a- pure silica layer before annealing, b- pure silica layer after 1h-annealing at 650°C , c- 4-wt% Al_2O_3 -doped silica layer before annealing, d- 4-wt% Al_2O_3 -doped silica layer after 1h-annealing at 650°C .



(a)



(b)

Figure 3: Na₂O content (a) and K₂O content (b) in silica layers after annealing at 650°C for different Al₂O₃ contents and annealing durations.

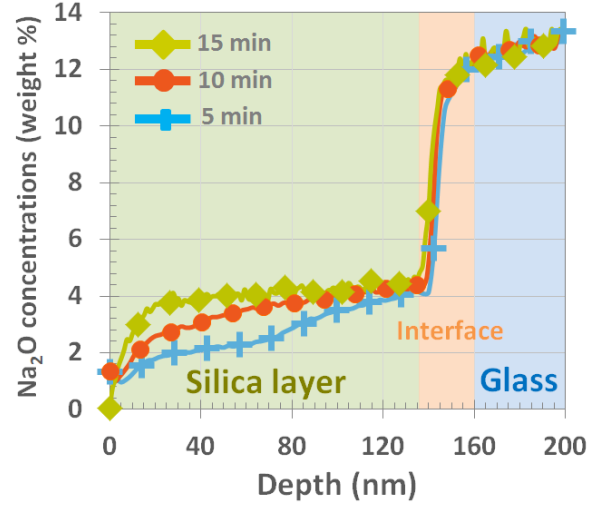


Figure 4: Na₂O SIMS profiles after diffusion in silica layers for short annealing durations at 650°C, for a 4-wt% Al₂O₃-doping of the silica layer.

$$C_{K_2O} = 0.066 C_{Al_2O_3} + 0.005 \quad (2)$$

The agreement between experimental data and the affine law is as good for both alkali species. However, the K₂O content is very low (always < 0.2 mol %), while the Na₂O content is larger than the Al₂O₃ content, with ~1.5 times more sodium atoms than aluminum atoms in silica after the thermal treatment at 650°C. Note that the atomic ratio between sodium and potassium is ~25, while it is 200 in the substrate.

Fig. 3 also shows that, for a given aluminum content, Na₂O and K₂O concentrations saturate after an annealing time of about 15 minutes. For shorter annealing durations, Fig. 4 shows that the sodium concentration increases gradually from the interface with glass to the interface with air. After 15 minutes at 650°C, a uniform sodium concentration profile is observed throughout the layer.

At longer times, the migration of alkali is followed by a dissolution of the silica layer into the substrate, as shown in Fig. 5, where silica profiles are plotted for annealing durations from 15 to 240 minutes. The interface between the silica layer and the glass is marked by a sharp drop of the silica content. The interface shifts gradually from its initial position (green dotted line, which is detected as the position of the Sn⁺ peak), toward the upper surface of the film. This shift denotes a dissolution of the silica layer, due to interdiffusion between the high-silica layer and the substrate with a lower sil-

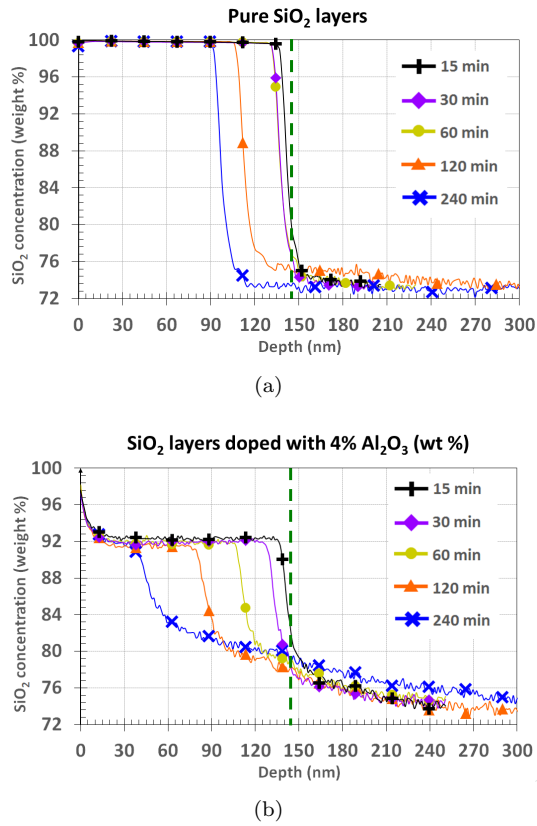


Figure 5: SiO₂ SIMS profiles of (a) a 150 nm pure silica thin film, and (b) a 150 nm Al₂O₃-doped silica thin film for various annealing durations at 650°C. Interface before annealing (vertical green dotted line) is followed by the maximal value of the Sn⁺ peak during SIMS analysis

279 ica content. For pure silica layers (with 0.2 mol
 280 % of Na₂O), the interface is simply translated (see
 281 Fig. 5b), as for the dissolution of a mineral. For
 282 the 4-wt% Al₂O₃-doped silica layer, the interface
 283 remains very sharp on the silica layer side, while it
 284 becomes broader on the substrate side, indicating a
 285 more pronounced interdiffusion between substrate
 286 and layer. Also note that the dissolution is faster
 287 for the doped layer than for the pure-silica layer,
 288 since the distance between the initial and the new
 289 interface grows approximatively twice faster for the
 290 Al-doped layer.

291 This slow process of dissolution of the silica thin
 292 film into the glass substrate and its dependence
 293 on the aluminum-doping of the layer will be ad-
 294 dressed in greater details elsewhere. In the follow-
 295 ing section, we focus the discussion on the effect
 296 of aluminum-doping on the migration of alkali ions
 297 from the glass substrate to the silica layer.

298 4. Discussion

299 4.1. Mechanism of alkali migration

300 Our experiments at 650°C demonstrate that al-
 301 kali ions such as Na⁺ and K⁺ diffuse from glass to
 302 silica thin films. As shown in Figs. 3 and 4, al-
 303 kali ions concentrations are already equilibrated in
 304 silica layers after a few minutes at 650°C indepen-
 305 dently of the Al₂O₃ content, so that the diffusion
 306 length is larger than the 150-nm-width of the sil-
 307 ica layer. Previous studies of sodium diffusion in
 308 bulk silica glass found diffusivities between 3.10⁻¹⁵
 309 and 3.10⁻¹¹ m².s⁻¹ [2, 38, 39, 40]. The discrepancy
 310 between diffusivity values in different experiments
 311 was attributed to the variable hydroxyl content of
 312 the silica glasses [39], depending on its elaboration
 313 process. The presence of H⁺ in silica was found
 314 to decrease the mobility of Na⁺, an illustration of
 315 the mixed-alkali effect [41]. Even the smallest diffu-
 316 sivity value obtained in previous studies (3.10⁻¹⁵)
 317 gives a diffusion distance of 1 micron in 10 minutes,
 318 that is a diffusion length greater than the width of
 319 the silica layer. Therefore, constant sodium pro-
 320 files after 15 minutes at 650°C are consistent with
 321 literature values for sodium diffusivity.

322 For bulk aluminosilicate glasses containing Na₂O
 323 and/or K₂O, interdiffusion between melts of differ-
 324 ing alkali concentrations is mostly governed by the
 325 exchange of alkali ions with SiO₂ [42, 43, 44, 45].
 326 Such exchanges, if present, would result in a vari-
 327 ation of the Si/Al ratio before and after sodium
 328 migration. However, during alkali-ions migration,
 329 we observe that the atomic ratio Si/Al in the sil-
 330 ica layer remains constant, as shown in the SiO₂-
 331 Al₂O₃-Na₂O phase diagram in Fig. 6 (red dotted
 332 arrows). Therefore, the migration of sodium and
 333 potassium corresponds to a dilution of the initial
 334 composition of the layer, and not to a counter flux
 335 of alkali and Si or Al.

336 Nevertheless, electro-neutrality requires a net
 337 flux of another charged species to compensate the
 338 charge of additional alkali. Previous studies in bar-
 339 rier layers [2, 19] suggested that a counter-flux of
 340 protons enables sodium migration into silica. The
 341 influence of water concentration on sodium migra-
 342 tion had also been studied in bulk silica [46, 39].
 343 The influence of water is discussed in more details
 344 in the next paragraphs.

345 4.2. Interdiffusion between protons and alkali ions

346 Water is one of the most common important im-
 347 purity found in PVD sputtered thin films. It's ori-

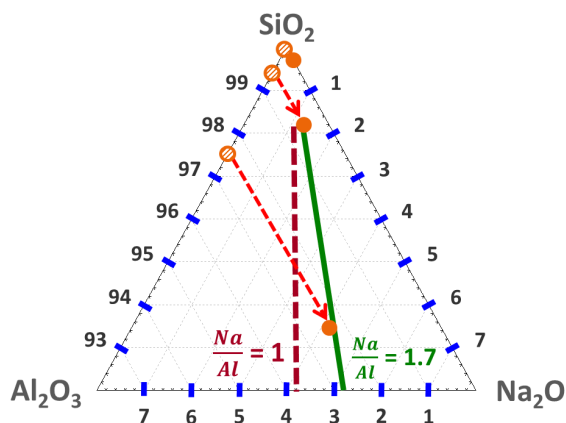


Figure 6: Zoom of the phase diagram in the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ between 92 and 100% SiO_2 in mol %. Empty circles correspond to silica thin films before annealing and filled circles to silica thin films after sodium migration. Red dotted arrows correspond to a constant Si/Al atomic ratio.

Table 3: Hydrogen content in silica films as measured by ERDA for a pure silica layer or a 2.4-mol% Al_2O_3 -doped silica layer. Analyses are performed on samples before and after thermal treatments 30 minutes at 650°C .

| H content (mol %) | Before annealing | After annealing |
|-------------------|---|-----------------|
| pure silica | 0.40 % ≈ 6000 ppm H_2O | < 0.1 % |
| Al-doped silica | 0.38 % ≈ 6000 ppm H_2O | < 0.1 % |

gin could be outgassing phenomenon of the deposition chamber walls during the process and surface adsorption during storage due to the porosity of the layers. Table 3 report ERDA measurements that could be performed on two samples (one pure-silica layer and one 2.4-mol% Al_2O_3 -doped layer) before and after thermal annealing. They first show that significant hydrogen contents (of the order of half percent) can be found in the deposited silica or aluminum-doped silica thin films. Interestingly, this hydrogen content shows a sharp decrease after thermal treatment.

The loss of H upon annealing is clearly consistent with a scenario of interdiffusion between hydrogens of the layer and alkali ions of the glass substrate. In order to test this hypothesis further we performed SIMS measurements on samples annealed at a lower temperature, $T=550^\circ\text{C}$. The slowing of the dynam-

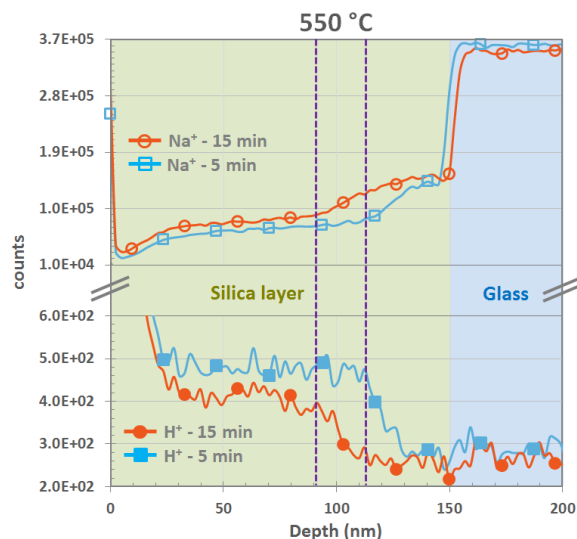


Figure 7: Na^+ and H^+ SIMS profiles after 5 and 15 minutes at 550°C , for a 4-wt% Al_2O_3 -doping of the silica layer.

ics thus allowed us to observe earlier steps of the diffusion process, i.e. before saturation of the alkali content in the film. We show in Fig. 7 SIMS profiles in a 4-wt% Al_2O_3 -doped silica thin film of H^+ and Na^+ ions after 5 min. and 15 min. of thermal treatment at 550°C , respectively. Although not quantitative, these profiles show a clear trend: an interdiffusion front of the two species moving from the glass substrate interface toward the surface of the thin film.

4.3. Equilibrium sodium concentration in silica layer

Since alkali concentration is constant after 15 minutes in the silica layers, alkali species are at thermodynamic equilibrium and should have a similar chemical potential in the substrate and in the silica layer. Using the software Factsage[®] with the FT oxides database and especially the FT oxid-SLAGA module (A-Slag-liq all oxides) developed for silicate systems ([47, 48, 49, 50, 51]), we computed the activity of sodium in the substrate and in the silica layer, for various aluminum and sodium concentrations. In order to stress the crucial effect of the water content in silica films on the alkali diffusion from the glass substrate, we present below results obtained in absence and in presence of water in the films.

The activity of sodium at 650°C as a function of sodium concentration in a dry silica layer is repre-

sented in Fig. 8a, for three different aluminum doping contents. We observe that increasing the aluminum content decreases the activity of sodium, a result that has been obtained experimentally in the literature [52] and that is explained by the smaller sodium content in network-modifying role. A sharp increase of sodium activity occurs when the molar concentration of sodium equates the one of aluminum. Qualitatively, this corresponds to the concentration at which sodium ions charge-compensate all aluminum tetrahedral units. Therefore, the activity of sodium in the layer depends strongly on the aluminum content. In Fig. 8a, the activity of sodium in the glass substrate is represented as a red dotted line.

We define the theoretical sodium equilibrium concentration as the concentration at which chemical potentials are the same in the substrate and the silica layer. The sodium equilibrium concentration is plotted in Fig. 8c (orange line) as a function of aluminum content of the silica layer. We observe an affine (almost linear) relation as in our experiments, but with a different Na/Al atomic ratio: thermodynamic calculations predict a ratio close to one (which amounts to compensating all aluminum tetrahedra), whereas a ratio of 1.5 is observed in our experiments. This means that (in experiments) 1/3 of sodium ions in the silica layer are not charge compensators of aluminum tetrahedra, but network modifiers bound to non-bridging oxygens.

However, it is known [53, 54, 55, 56] that the presence of water modifies the structure of aluminosilicate glasses and melts, hence the activity of sodium in these materials. This strong effect is illustrated in Fig. 8b, where we plotted the activity of sodium in a silica layer as in Fig. 8a, for a layer composition including both the aluminum doping and the presence of water (we arbitrarily chose 6000 ppm of water as measured by ERDA in a Al_2O_3 -doped silica layer - 2.4 mol % - cf Table 3, but we found that the value of sodium activity has a very weak dependence with water between 100 ppm to 20000 ppm). Calculations of sodium activities in presence of water are also performed using Factsage[®] with the FT oxides database but with the FT oxid-SLAGE module (E-Slag-liq with H₂O/OH) which can take into account interactions of water with the silicate network [57, 58]. Comparing Fig. 8a and Fig. 8b shows that: (i) for a pure silica layer, the activity of sodium does not change with or without water, (ii) but for an aluminum-doped silica layer, the

activity of sodium changes drastically when water is added. Indeed, the evolution of sodium activity is more gradual in the presence of water, suggesting that water-induced network depolymerization [53, 54] results in a greater diversity of sites for sodium. The sodium equilibrium concentration in the presence of water is plotted in Fig. 8c (violet line). We observe an affine scaling with aluminum content as in water-free layers, but with a greater slope. A least-square fit gives a value of 1.46 for the Na/Al ratio, which is very close to the experimental value (1.47) of Fig. 3a. Therefore, a quantitative prediction of sodium content in the layer can be obtained by balancing sodium activities in substrate and layer, if the presence of some water in the layer is taken into account.

5. Conclusions

In this work we have studied the diffusion processes occurring in silica-based thin films deposited on float glass during thermal treatments above the glass-transition temperature of the glass substrate. Using SIMS analysis, we have quantified the migration of sodium and potassium in silica thin films and shown that their concentration reaches a saturation value after only 15 minutes of annealing at 650°C. The aluminum doping of the silica film has been shown to strongly enhance (with a linear scaling) the diffusion of alkali ions from the glass substrate.

The presence of water in the as-deposited silica films (validated by ERDA measurements) has appeared to be a key element of understanding of this phenomenon. First we could identify an inter-diffusion process between the protons of the film and the sodium ions of the glass substrate. Then, taking water into account was shown to drastically modify the thermodynamic activity of sodium in the layer and thus its final equilibrium concentration.

In particular the latter exceeds the aluminum concentration of the thin film. The sodium ions in the aluminum-doped silica layer thus exist not only as charge compensators of the aluminum ions inserted in the silica network but also as network modifiers. As illustrated in Fig. 5, this depolymerization effect of aluminum on the silica network is likely to strongly affect the slower homogenization process (thin film dissolution) occurring at long times and will be addressed in more detailed in a future study.

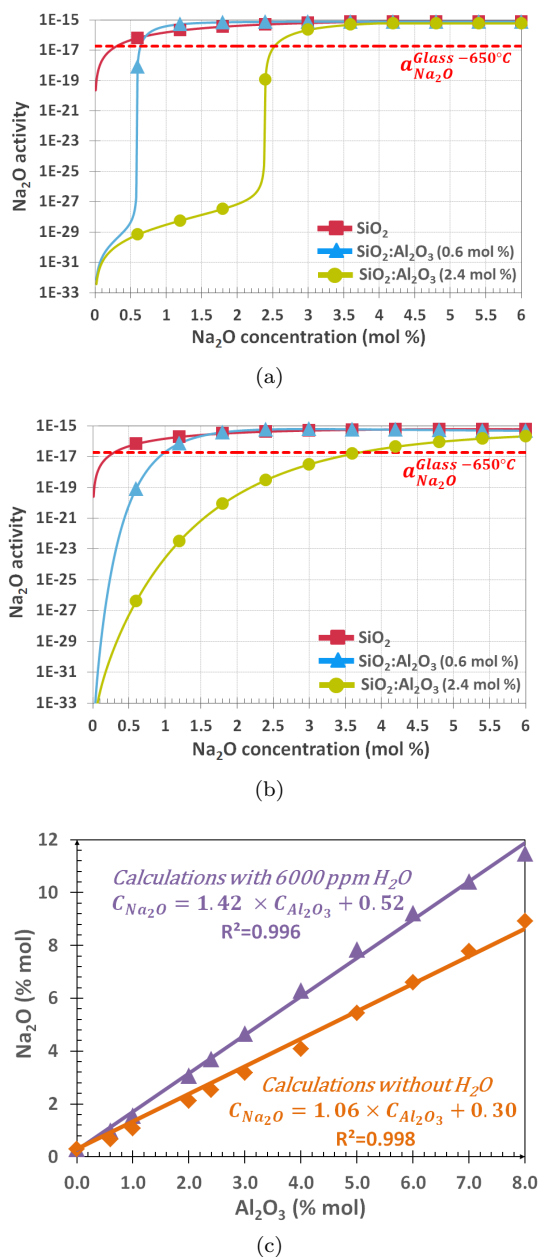


Figure 8: Energetics of sodium - (a) Na_2O activity in silica layer at 650°C as a function of Na_2O concentration, for different aluminum doping, and for free sodium atoms (i.e., network modifiers and not charge compensators). Calculations are made with Factsage[®] software, using the FT oxides database. The red dotted line marks the value of Na_2O activity at 650°C in the float glass substrate. (b) Same as (a), for silica layers containing 6000ppm of water. (c) Equilibrium sodium concentration in the silica layer as a function of aluminum doping, for dry layers (orange) and water-containing layers (violet).

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