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Complete List of Authors:	Zhang, Jiandong; Lanzhou University, Lanzhou, Gansu 730000, PR China, School of Nuclear Science and Technology, ; Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory Zhang, Yanyan; Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory; Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China, Beijing National Laboratory for Molecular Sciences, National Centre for Mass Spectrometry in Beijing, COLLIN, Marie; CEA, DEN, DE2D, SEVT, F-30207 Bagnols-sur-Ceze, , DEN, DE2D, SEVT Gin, Stéphane; CEA, DEN, DE2D, SEVT, F-30207 Bagnols-sur-Ceze, , DEN, DE2D, SEVT Neeway, James; Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory Wang, Tieshan; Lanzhou university, School of nuclear science and technology Zhu, Zihua; Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory
Keywords:	Hydrogen imaging, glass corrosion, H/Na interface, ToF-SIMS imaging, alteration layer, ISG glass

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Nanoscale Imaging of Hydrogen and Sodium in Alteration Layers of Corroded Glass using ToF-SIMS: Is an Auxiliary Sputtering Ion Beam Necessary?

Jiandong Zhang[1, 2], Yanyan Zhang[2], Marie Collin[3], Stephane Gin[3], James Neeway[4], Tieshan Wang[1*], Zihua Zhu[2*]

1. School of Nuclear Science and Technology, Lanzhou University, Lanzhou, Gansu 730000, PR China,

2. W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354 USA

3. CEA, DEN, DE2D, SEVT, F-30207 Bagnols-sur-Ceze, France

4. Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA

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* Corresponding authors: zihua.zhu@pnnl.gov; tswang@lzu.edu.cn;

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Abstract: The hydrogen (H)/sodium (Na) interface is of great interest in glass corrosion research. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is one of the few techniques that can provide nanoscale H and Na imaging simultaneously. However, the optimized condition for ToF-SIMS imaging of H in glass is still unclear. In H depth profiling using ToF-SIMS, H background control is a key, in which an analysis ion beam and a sputtering ion beam work together in an interlaced mode to minimize it. Therefore, it is of great interest to determine if an auxiliary sputtering ion beam is also necessary to control H background in ToF-SIMS imaging of H. In this study, a Bi^+ primary ion beam with different auxiliary sputtering beams (Cs^+, O_2^+ and Ar_n^+) were compared on a corroded International Simple Glass (ISG). It was surprising that the H/Na interface could be directly imaged using positive ion imaging without any auxiliary sputtering ion beam under a vacuum of 2-3 × 10^{-8} mbar. The H^+ background was about 5% atomic percent on the pristine ISG glass, which was significantly lower than the H concentration in the alteration layer (~15%). Moreover, positive ion imaging could show distributions of other interesting species simultaneously, providing more comprehensive information of the glass corrosion. The H^+ background could be reduced with an auxiliary O_2^+ sputtering ion beam; however, significant loss of signal intensities was observed. In addition, a higher H background in ToF-SIMS imaging than that in the depth profiling was observed.

Key words: Hydrogen imaging, glass corrosion, H/Na interface, ToF-SIMS imaging, alteration layer, ISG glass

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Introduction

Nanoscale elemental imaging has been of great importance in glass corrosion research[1-4]. Compared to depth profiling, imaging provides a direct view of the elemental distribution on the corroded glass surface and altered glass/pristine glass interfaces, which is very valuable to understand the complex mechanisms involved in glass corrosion. Corrosion can lead to inhomogeneous alteration layers, rough surfaces and interfaces, which are difficult to distinguish by depth profiling[2,5]. Moreover, some glass particle samples have been used to increase glass surface area and perform accurate rate measurement, and imaging may be the best way to characterize the alteration layers on particle surfaces[6,7].

Hydrogen (H) and sodium (Na) are both ions of interest in glass corrosion research. H^+ and Na^+ not only diffuse as exchanged ions (interdiffusion) in the early stage of glass corrosion but also affect pH values (hydrolysis) of the solutions during glass corrosion[8-11]. The thickness of alteration layers is usually from tens of nanometers to several micrometers. Therefore, nanoscale spatial resolution is required for accurate imaging of alteration layers. However, very few techniques can perform hydrogen imaging on the nanoscale. For example, transmission electron microscope (TEM) is a widely used imaging tool and can reach a resolution of ~0.1 nm (or better)[8], but hydrogen information can't be directly provided. Scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDX) is also widely used for elemental imaging, but is not efficient for light elements (e.g., H, Li, and B). Atom probe tomography (APT) is a novel method for nanoscale imaging of the alteration layers with 1-3 nm spatial resolution; however, it has a limited field-of-view and sample preparation is complex[12-14]. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is sensitive to most elements (except noble gases) and has been used for depth profiling of H/Na in previous studies[2,10,15]. Moreover, ToF-SIMS can provide elemental distribution with decent spatial resolution (~100

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nm)[16,17] and has been successfully used in imaging of alternation layers[7,13]. However, there are some tricks in hydrogen analysis using ToF-SIMS [18,19] and, to our knowledge, hydrogen imaging of alteration layers using ToF-SIMS has not been reported.

Signal intensity is key in SIMS analysis, especially imaging analysis. A challenge for H analysis using SIMS is that both H^- and H^+ are only moderately sensitive[20]. Because the sensitivity of H^- is higher than that of H^+, negative ion mode is recommended for H depth profiling using ToF-SIMS[18,19]. However, Na^- signal is very low in negative ion mode, so imaging of Na^- is unpractical. Considering that the sensitivity of H^+ is only one order of magnitude less than that of H^-[20], it may be a promising idea to use positive ion mode to image Na^+ and H^+ simultaneously. In addition, the residual gases in the SIMS analysis chamber may lead to significant interference during H analysis. Therefore, the pressure in the SIMS analysis chamber should be kept as low as possible and an interlaced dual beam analysis mode is recommended for H depth profiling [18,19]. For H imaging analysis, the above experimental condition may be still needed. Moreover, current ToF-SIMS instruments normally have two possible sputter beams for positive ion analysis, i.e., the traditional O_2^+ beam and the newly developed argon cluster (Ar_n^+) ion beam. Our previous work[21] suggests that during dual beam depth profiling analysis, the Ar_n^+ sputtering beam leads to less charging and better signal intensity in glass depth profiling analysis. Therefore, it is of interest to investigate which beam is better for H imaging analysis.

The International Simple Glass (ISG) has been a widely used model glass for reaching a common understanding among different glass corrosion experiments[22]. In this work, a corroded ISG coupon sample was fixed with a supporting glass for imaging of the H/Na interfaces using ToF-SIMS. Results obtained using different sputtering beams including 500 eV O_2^+, 1 keV O_2^+,

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2 keV O_2^+, 10 keV Ar_n^+, 20 keV Ar_n^+ and 2 keV Cs^+ were compared, and the optimized H/Na imaging settings using ToF-SIMS were determined.

Experimental Section

The nominal composition (mol %) of ISG glass is: Si (18.0), B (9.6), Na (7.5), Al (2.3), Ca (1.7) and Zr (0.5) and O (60.3). The glass was elaborated by MoSci Corporation (Rolla, MO, USA) and then cut into small coupons. A polished coupon of this glass (5.0 × 5.0 × 3.0 mm^3) was altered for 25 days at 90 °C in static conditions, in a solution initially saturated with respect to amorphous silica and at a fixed $pH_{90°C}$ of 7. These conditions enable the formation of a dense, B and Na-free gel layer (i.e., alteration later) of approximately 2.8 μm in thickness on the glass surface. More details could be found in the previous report[23].

As a commonly used method, the corroded ISG coupon was attached with a supporting ISG glass and then mounted by EpoThin™ 2 epoxy resin. The details are: (1) Attached slides were fixed using a plastic clip and then mounted in the center of a silicone gel mold. (2) Approximately 18 g of the well-mixed epoxy (2:1 in weight for epoxy resin and epoxy hardener) was poured in the mold. The epoxy was then kept in the fume hood overnight and then transferred into a 50˚C oven for 3 hours for a further cure. (3) The cured bulk was cut by a diamond saw to expose the cross section. (4) The cutting surface was polished by an ECOMET 6 grinder-polisher. A schematic of the prepared ISG sample was shown in Figure 1. The sample was gold-coated on the back prior to further ToF-SIMS analysis to reduce charging effects.

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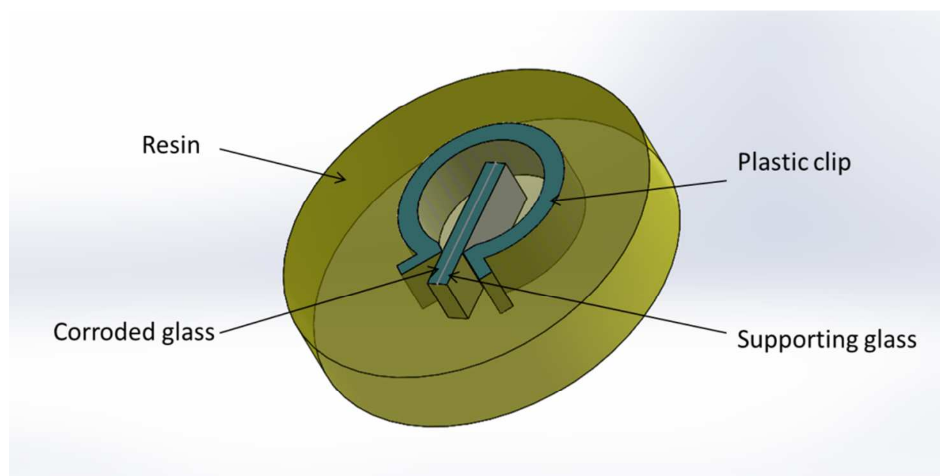

Figure 1. Schematic of the prepared ISG sample

The ToF-SIMS analysis was performed using a TOF.SIMS 5 spectrometer (IONTOF GmbH, Müster, Germany), which was equipped with a 25 keV bismuth (Bi) cluster ion source, a 20 keV Ar_n^+ and a 2 keV Cs^+/O_2^+ sputtering ion sources. Conditions of sputtering beams including 500 eV O_2^+, 1 keV O_2^+, 2 keV O_2^+, 10 keV Ar_n^+ and 20 keV Ar_n^+ with different currents were used as summarized in Table 1. Monatomic bismuth ions (Bi^+) were used as the analysis beam during the experiments[19]. A flood gun was used during all the processes to compensate charging effects. The base pressure of the ToF-SIMS analysis chamber was about 5×10^{-9} mbar. Overnight pumping in the introduction chamber was applied before a sample was introduced into the analysis chamber. During depth profiling analysis, a piece of ISG glass without resin fixation was introduced into the analysis chamber and the pressure slightly increased to about 6-7 $\times 10^{-9}$ mbar. With Cs^+ or Ar_n^+ sputtering, the pressure increased to about 1×10^{-8} mbar. When using O_2^+ for sputtering, the pressure increased to about 5×10^{-8} mbar arising from the O_2 gas from the O_2^+ sputtering source. For the resin-fixed sample used in imaging analysis, the vacuum pressure of the analysis chamber was about 2-3 $\times 10^{-8}$ mbar and did not change during single Bi^+ beam imaging analysis. However, the pressure was about 7-8 $\times 10^{-8}$ mbar during O_2^+ beam-auxiliary imaging analysis.

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Table 1 O_2^+ and Ar_n^+ sources as sputtering beams with different currents.

Sputter beam	500 eV O_2^+ beam		1 keV O_2^+ beam		2 keV O_2^+ beam		10 keV Ar_n^+ beam		20 keV Ar_n^+ beam	
Current ratio	Current (nA)	Current density (A/m^2)	Current (nA)	Current density (A/m^2)	Current (nA)	Current density (A/m^2)	Current (nA)	Current density (A/m^2)	Current (nA)	Current density (A/m^2)
100%	79.6	0.884	173.8	1.931	434.1	4.823	6.75	0.169	8.15	0.204
50%	39.6	0.44	87.1	0.967	217.1	2.412	3.33	0.083	4.09	0.102
20%	15.7	0.174	34.8	0.387	86.7	0.963	1.36	0.034	1.62	0.041
10%	7.8	0.086	17.4	0.193	43.3	0.481	0.67	0.017	0.81	0.02
5%	3.9	0.044	8.7	0.097	21.6	0.24	0.34	0.009	0.4	0.01
2%	1.6	0.018	3.5	0.039	8.6	0.096	0.14	0.004	0.17	0.004
1%	0.7	0.008	1.7	0.019	4.5	0.05	0.07	0.002	0.08	0.002
0%	0	0	0	0	0	0	0	0	0	0

Depth profiling was used to investigate the efficiency of secondary ion yields on a blank ISG coupon. The raster sizes were 300×300 μm^2 for Cs^+/O_2^+ and 200×200 μm^2 for Ar_n^+ sputtering beams. A 25 keV Bi^+ beam was used as the analysis beam at 10 kHz frequency. The analysis area was 100×100 μm^2 or 50×50 μm^2 in the center of the sputtering craters by Cs^+/O_2^+ and Ar_n^+, respectively. The current of Bi^+ was around 1.0 pA. The crater depths were measured by a stylus profilometer and a constant sputtering rate was assumed for each crater. For imaging, the sputter beam setting was almost the same as that in the depth profiling analysis (but with various currents). The analysis beam (pulsed Bi^+ beam) was rastered over a 30 × 30 μm^2 area in the center of sputtering area at a 25 kHz frequency. The beam size was tuned to be ~200 nm in diameter (using a 1000 mesh Cu grid reference sample) with a current of 0.5 pA. All ion images were 256 × 256 pixels with a collection time of about 1000 s. The imaging locations were selected on the interfaces between the corroded glass and the supporting glass. An un-corroded (blank) ISG glass was also analyzed for comparison.

The 2 keV Cs^+ depth profiling data was used to estimate the H concentration in the alteration layer based on the normalized $H^-/^{30}Si^-$ intensity and related RSF (relative sensitivity factor)

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values obtained from the reference[18]. The average H concentration in the alteration layer was found to be 15% (atomic ratio).

Results and discussion

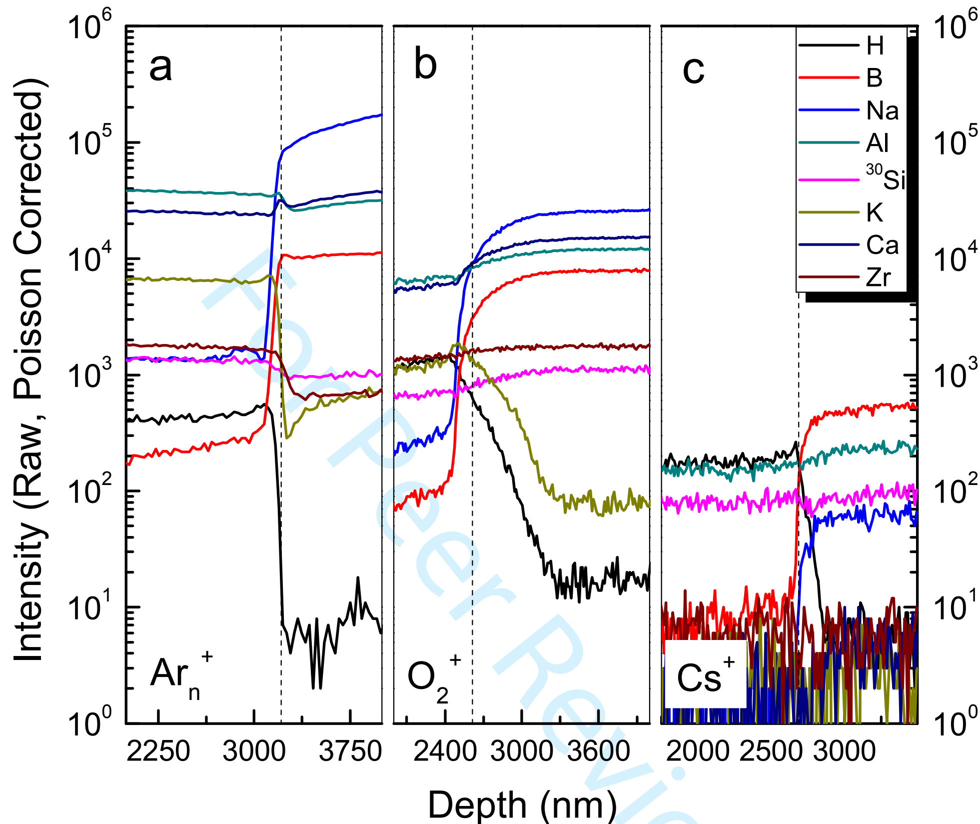

Figure 2. Depth profiles of several ion species of interest on corroded ISG glass in positive (with Ar_n^+, O_2^+ sputtering) and negative (with Cs^+ sputtering) ion modes: sputtering beams were 20 keV Ar_n^+ (a), 2 keV O_2^+ (b) and 2 keV Cs^+ (c) with the current ratio of 100%; analysis beam was 25 keV Bi^+. The dashed lines refer to the alteration layer-pristine glass interface. Common settings with reasonable sputtering rate and depth resolution in ToF-SIMS analysis were used. The ion intensities were all Poisson-corrected for dead-time correction during the analysis. The measured depths of the alteration front varied from 2700 nm to 3200 nm in different analysis areas, possibly due to an inhomogeneous thickness of the altered layers as depth profiling analysis using the above sputtering beams were conducted at different locations of the same sample.

Signal intensity is the key factor for image quality. Generally, the higher the signal intensity, the better the image quality is. As mentioned before, residual gases result in some background for SIMS analysis of H, so a dual beam depth profiling strategy with an interlaced analysis mode

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is recommended to reduce it. Figure 2 shows the depth profiles of several species of interest with Ar_n^+, O_2^+ and Cs^+ as sputtering beams. It should be noted that the thickness of ISG coupon was about 3.0 mm and this situation resulted in very serious charging effects when using Cs^+ sputtering beam and, thus, the effective signal intensity was low. We can see the H^- signal with Cs^+ sputtering was much lower than the H^+ signal from either Ar_n^+ sputtering or O_2^+ sputtering. More seriously, the signal intensities of metal ions when using Cs^+ sputtering, such as Na^-, K^-, Ca^- and Zr^-, were much weaker than the corresponding Na^+, K^+, Ca^+ and Zr^+ signals when using Ar_n^+ or O_2^+ beam. The above observations suggest that O_2^+ and Ar_n^+ sputtering instead of Cs^+ sputtering should be recommended for H/Na imaging analysis.

Our 2 keV Cs^+ depth profiling data suggest that the H concentration in the alteration layer is about 15%. This result is less than that from the bulk analysis (~27.6%)[23]. A possible reason is that SIMS is a high vacuum technique, and some less stable water molecules can escape from the sample before or during SIMS analysis.

It should be noted that the requirement of imaging mode is different from that in depth profiling mode. Generally speaking, in depth profiling, we hope the total analysis time can be as short as possible so we use high sputtering current values to obtain fast sputtering rate. However, for imaging analysis in this work, the sputtering beam is applied only to reduce the H background, so we hope the currents can be as low as possible. Therefore, we varied the current density of O_2^+ or Ar_n^+ beam at the sputtering interface, and monitored the detected H background signal on an un-corroded (blank) ISG sample in an interlaced mode of depth profiling. The results are shown in Figure 3.

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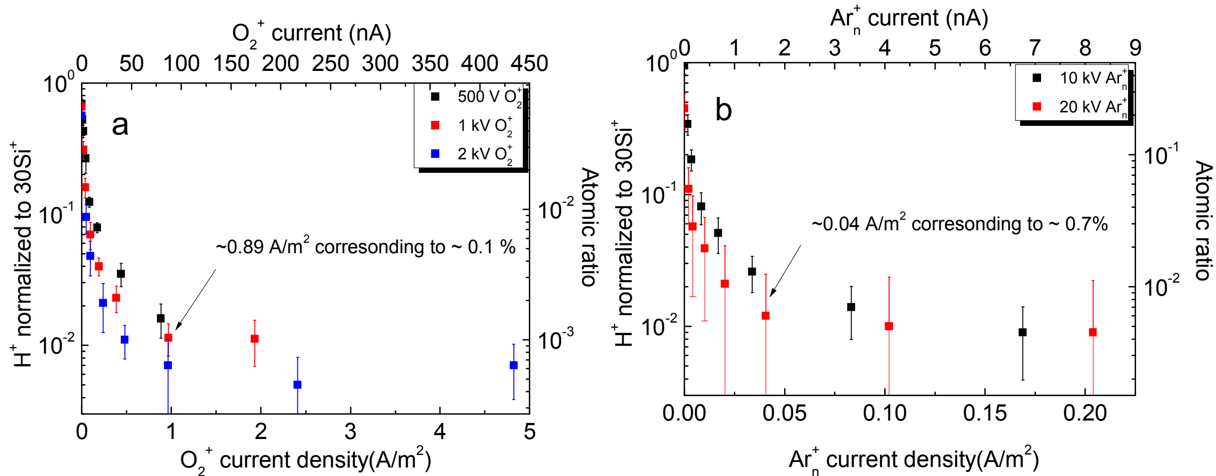

Figure 3. Normalized background H^+ noise intensities and corresponding H concentrations as a function of the current density of O_2^+ (a) and Ar_n^+ (b) in an interlaced mode of depth profiling. Left Y-axis represents the normalized H^+ intensity and right Y-axis represents the corresponding H concentration. The lowest H noise level with O_2^+ sputtering is about ~7×10^{-4} (atomic ratio), and the lowest H noise level with Ar_n^+ sputtering is about 1×10^{-3} (atomic ratio). The estimated concentrations of H were calculated based on the normalized $H^+/^{30}Si^+$ intensity here and the corresponding normalized $H^+/^{30}Si^+$ intensity in the alteration layer where 15% atomic H was determined.

As shown in Figure 3a, the H^+ noise level with O_2^+ is ~ 0.1 % (atomic ratio), and the noise level seems relatively stable if the sputtering current density is larger than ~ 0.89 A/m^2. As a comparison, the background noise level for Ar_n^+ sputtering is around 1.0 % (atomic ratio) and it becomes relatively stable when the beam current density is higher than ~0.04 A/m^2. Because we hope the sputter current is as low as possible, a 0.89 A/m^2 for O_2^+ beam or 0.04 A/m^2 for Ar_n^+ beam is recommended for H imaging analysis.

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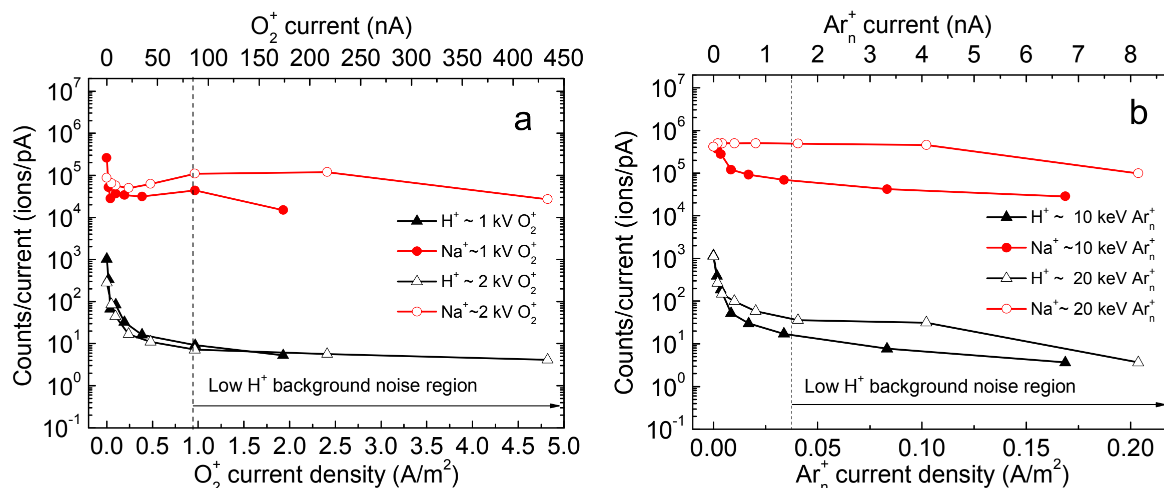

Figure 4. Secondary ion yields of H^+ and Na^+ ions on the blank ISG as a function of the current and current density in an interlaced mode depth profiling. Analysis beam was Bi^+ and the sputtering beams were O_2^+ (a) and Ar_n^+ (b).

Simultaneously imaging of H/Na is the key in this work. Therefore, Na^+ signal intensity is also of great interest. The relationship between the Na^+ signal intensity and the sputtering current density of O_2^+ beam is shown in Figure 4a. We observed a significant decrease in Na^+ signal intensity with a slight increase of current density and the signal rapidly reached a relatively stable value with further increasing of the beam current density. Therefore, we can only focus on H^+ signal when choosing the optimal sputtering current for H/Na imaging. The secondary ion yields of H^+ and Na^+ using Ar_n^+ are also shown in Figure 4b. Compared to the Ar_n^+ beam, the O_2^+ sputtering beam provided less but still very high yield of Na^+. Considering the background of H^+ signal with Ar_n^+ beam was considerably higher (as shown in Figure 3), 1 keV O_2^+ beam with a current density of 0.89 A/m^2 (~ 80 nA over 300×300 μm^2) is the best choice for imaging.

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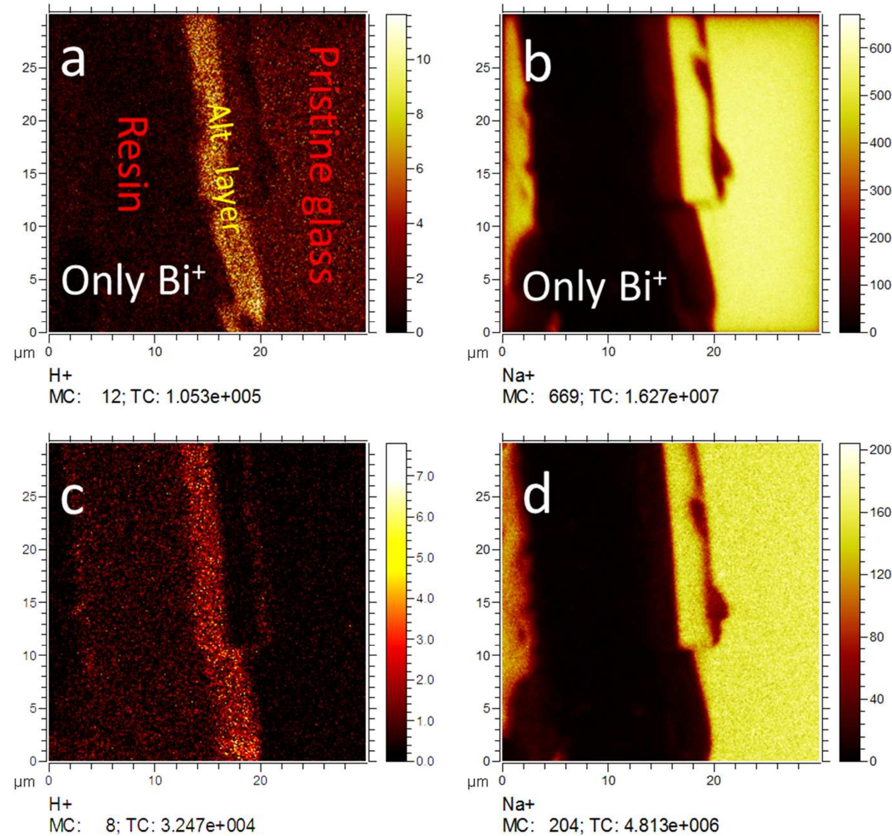

Figure 5. ToF-SIMS imaging of H^+ and Na^+ ions using only Bi^+ (a, b) and using Bi^+ with 1 keV O_2^+ beam at a current density of 0.89 A/m^2, interlaced mode (c, d). The locations of resin, pristine glass and alteration layer were indicated in a. Part of the attached glass was also shown on the left edge of the images. Note that the glass surface is broken beneath the alteration layer; this phenomenon usually occurs during the sample preparation.

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ToF-SIMS imaging of H/Na using Bi^+ without (Figures 5a and 5b) and with (Figures 5c and 5d) O_2^+ beams are compared. With only Bi^+, H^+ in the alteration layer was presented with a good intensity (Figure 5a). However, H^+ distribution was also obviously observed in the pristine glass. The ratio of H^+ in the alteration layer to the pristine glass was ~ 3:1, indicating a ~5 % (atomic ratio) H background in the pristine glass. The results using Bi^+ with a 1.0 keV O_2^+ sputtering beam are shown in Figure 5c and 5d. It is not surprising that the H^+ intensities decreased (Figure 5c) as compared to that with only Bi^+ (Figure 5a), but the H background in the pristine glass was controlled to a much lower level. The ratio of H^+ in the alteration layer to the pristine glass was ~

8:1, indicating a lower H background of ~1.9 % (atomic ratio) in the pristine glass. However, this is still significantly higher than the value (~0.1%) in the corresponding depth profiling analysis (Figure 3a). This observation may be attributed to two possible reasons. Firstly, the sample fixed in resin used in imaging analysis degassed in the vacuum to degrade vacuum quality (as shown in the Experiment session), leading to increasing of H background. Secondly, less H^+ signal can be collected from the interesting alteration layer (in depth profiling mode, 100% of the analysis area is interesting location; as a comparison, only a small amount of area is the alteration layer in imaging mode).

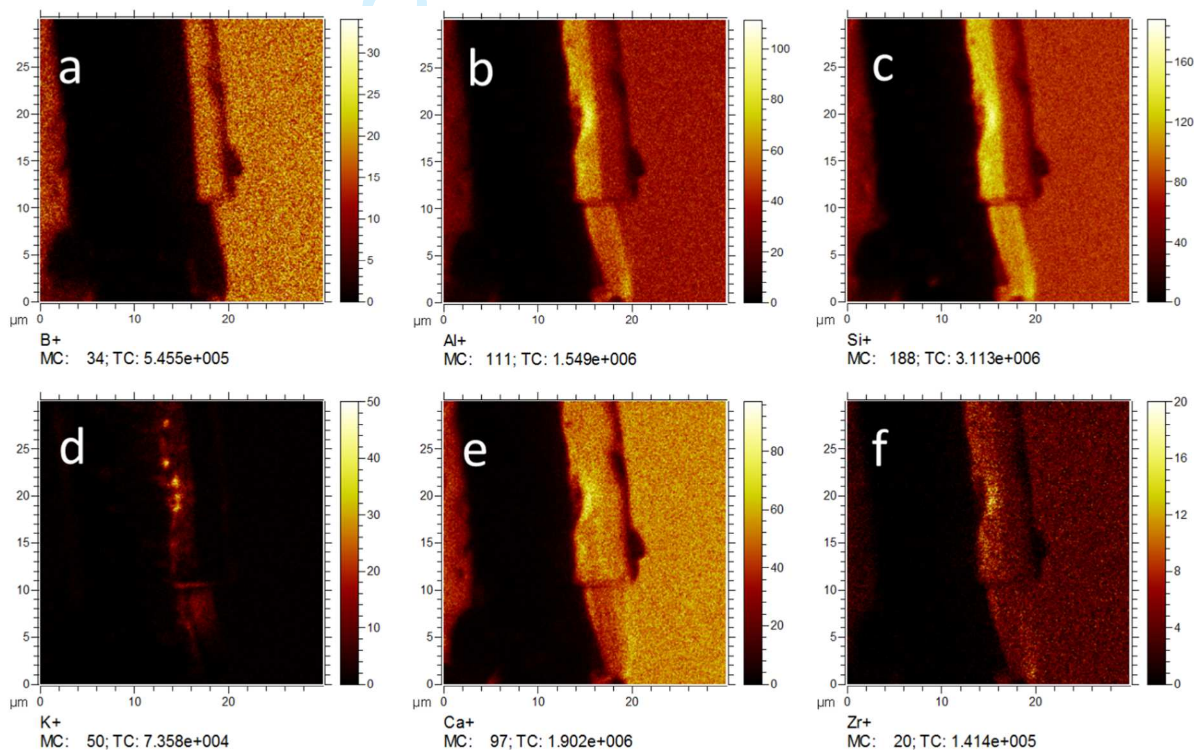

Figure 6. ToF-SIMS images of (a) B^+, (b) Al^+, (c) Si^+, (d) K^+, (e) Ca^+ and (f) Zr^+ ions. These images were collected simultaneously with those in Figures 5c and 5d using a 1 keV O_2^+ auxiliary sputtering beam at a current density of 0.89 A/m^2.

A unique advantage of ToF-SIMS is that full mass spectrum can be collected and other interesting ion images can be obtained simultaneously. For example, in the positive ion mode, not only H^+ and Na^+ but also other interesting ions (B^+, Al^+, Si^+, K^+, Ca^+ and Zr^+) can be

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simultaneously detected. Figure 6 shows the varied behavior of different elements during glass corrosion. For example, Al, Si, Ca and Zr stay in alteration layer; however, B is almost totally dissolved. K, an exogenous element, was supplied to the leaching solution by the pH-electrode, which was used to monitor the pH and then adjust it to the target value. These behaviors are consistent with the observations in depth profiling analysis, as well as in solution analysis reported previously[23].

It should be noted almost all signal intensities decreased after using an auxiliary O_2^+ sputtering beam. For example, the Na^+ intensity was decreased to ~1/3 (Figure 5b) compared to that without O_2^+ (Figure 5d). However, because sensitivities of all other ions of interest are much higher than that of H^+, such a signal decrease has limited effects on the overall image quality.

In Figures 5 and 6, the alteration layer was observed partly detached from the sample surface. Such a structure can be easily characterized using ToF-SIMS imaging, but it is unachievable to be reflected by SIMS depth profiling. It has been well known that the formation of alteration layers can change the stress force in the alteration layer and at the alteration layer-pristine glass interface, leading to detachment of sample surface, usually during the sample preparation [2]. However, the depth at which the sample detaches is not the alteration layer-pristine glass interface, but a few microns deeper, suggesting the alteration layer-pristine glass interface may not be mechanically weak.

Our previous work showed that the H background during SIMS depth profiling is roughly proportional to the vacuum of the analysis chamber [18]. Therefore, it is possible to further reduce H background in ToF-SIMS imaging of H by improving the vacuum. In this work, because the glass sample was immobilized in a resin block, the pressure in the analysis chamber was about 2-3 × 10^{-8} mbar. As a comparison, the pressure was about 6-7 × 10^{-9} mbar when only ISG glass

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sample was used. Therefore, it might be possible to reduce the volume of resin in the sample to improve vacuum. For example, using a wire saw to cut a thin piece (e.g., 0.3 mm) of the sample and attaching it to a silicon substrate may be a feasible way. In addition, baking the analysis chamber before analysis might also help reduce the base pressure, and 7×10^{-10} mbar was achievable in our previous work[18]. If so, H background could be reduced by at least one order of magnitude, and less than 0.5% H background can be expected in ToF-SIMS positive ion imaging of glass samples using a single analysis ion beam.

Conclusion

In this work, nanoscale H/Na imaging of ISG glass alteration layers was realized by ToF-SIMS. It is surprising to observe that nanoscale H/Na imaging can be done using only a 25 keV Bi^+ analysis beam without any auxiliary sputtering ion beam, because the H background on the pristine glass was found to be only ~5% atomic percent under a vacuum of 2-3 $\times 10^{-8}$ mbar, which is much lower than the H concentration in the alteration layer of about 15% atomic percent. Besides, if using an auxiliary 1 keV O_2^+ sputtering beam with a current density of ~0.89 A/m^2 in imaging, the H background noise was observed to be reduced on pristine ISG glass. However, the H background in imaging was significantly higher than that in the depth profiling mode with the same sputtering beam (e.g., ~1.9% H background in imaging mode versus ~0.1% in depth profiling mode with a 1 keV 0.89 A/m^2 O_2^+ sputtering beam), possibly due to relatively low signal intensity in the imaging mode. Moreover, it has been known that the H background is roughly proportional to the vacuum of the analysis chamber during SIMS analysis[18]. Therefore, it is possible to further reduce H background by improving vacuum. With proper sample preparation (e.g., reducing amount of resin as less as possible) and baking of vacuum chamber,

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better than 0.5% H background in ToF-SIMS positive ion imaging of glass samples using a single analysis ion beam can be expected.

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