Acquisition of artifact free alkali metal distributions in SiO$_2$ by ToF-SIMS Cs$^+$ depth profiling at low temperatures

Michael Leitzenberger$^1$ | Peter Kuegler$^1$ | Stefan Krivec$^2$ | Herbert Hutter$^1$

1Institute of Chemical Technologies and Analytics, TU Wien, Vienna, Austria
2Infineon Technologies Austria AG, Villach, Austria

Correspondence
Michael Leitzenberger, Institute of Chemical Technologies and Analytics, TU Wien, Getreidemarkt 9, Vienna, 1060, Austria. Email: michael.leitzenberger@tuwien.ac.at

Artifact-free depth profiles of alkali ions in SiO$_2$ were obtained using a time-of-flight secondary ion mass spectrometer (ToF-SIMS) equipped with a Cs$^+$ beam as sputter gun. Samples were set to low temperature ($\sim-100^\circ$C) using a heating/cooling sample holder. The effects of temperature on the depth profiles was determined with multiple measurements at different temperatures. To validate the described method, obtained depth profiles of alkali metal implanted SiO$_2$ samples were compared with simulated depth profiles. Evidence for artifact-free depth profiles is given for potassium, sodium, and lithium, three prominent examples of fast diffusing ions in various materials. This described approach enables more laboratories to acquire depth profiles of alkali metals in non-conducting samples without time-consuming sample preparation. It offers artifact-free depth profiling of alkali metals using a classic ToF-SIMS without advanced extensions, which are not available in many laboratories.

KEYWORDS
alkali metals, depth profiling, heating cooling stage, ToF-SIMS

1 | INTRODUCTION

In semiconductor industry, mobile ions are unwelcome contaminants in dielectric layers that can lead to malfunction and chip failure due to altered threshold voltages. Such species are fast diffusors both directly after production and in actual use. These problems occur if mobile ions are present in the non-conductive gate oxide. As the trend in modern semiconductor devices goes towards smaller structures, the study of mobile ions in non-conductive layers will gain even more importance.$^1$

Over the last decades, ToF-SIMS has been established as a reliable tool for analysis of small structures. For analysis, a primary ion (e.g., bismuth) beam is focused on the sample surface generating secondary ions, which are analyzed using a time-of-flight mass analyzer. For depth profiling, a dual beam mode with an additional reactive sputter gun (e.g., O$_2^-$ or Cs$^-$) is used. ToF-SIMS can be used for surface analysis of elements and molecules and for getting in-depth sample information. It offers lateral imaging and depth profiling with a wide mass range, high lateral resolution, and good sensitivity. Almost all types of solid materials, even non-conductive ones, can be analyzed without elaborate sample preparation.$^2$

O$_2^-$ ions are often used in a reactive sputter beam for depth profiling of positive metal ions. Sputtering with oxygen ions leads to an increased positive ion yield. This is explained due to oxide formation and resulting positive partial charges on metal atoms.$^3$ For enhancement of the negative ion formation, a Cs$^+$ sputter beam can be used for depth profiling of negative ions.

For non-conductive samples, surface charge represents a major issue. As the ion beam collides with the atoms of the sample, charge transfer and emission of secondary electrons can occur, leading to accumulation of positive charges on the surface.$^4$ Especially the sputter gun contributes to the charging of the surface since the ion currents exceed those of the primary gun by orders of magnitude. A surface charging that leads to a potential difference as low as 1 V
between a 100-nm-thick sample layer and the conductive bulk material results in an electric field of 0.1 MV/cm. Such strong fields can cause migration of small ions, for example, of alkali metals. A consequence of this are artifacts in the alkali ion depth profiles, as these ions are displaced towards the conducting bulk material.3

There are several methods for charge compensation. One approach is the use of a high energy electron beam. It has been shown that the use of 2 keV electrons is suitable for optimum charge neutralization due to the emission of secondary electrons.5 Some reports stated that sample cooling can lead to suppressed ion migration.3,6

The latest approach for depth profiling of mobile ions is the use of polyatomic ion beams for the sputtering of the samples. It is described in literature that one can use C60- large O2 clusters or large Ar clusters. Although these methods are more sensitive than the one described in this paper, they all need a specially equipped ToF-SIMS. These instruments are expensive and rarely available in laboratories.7–9

Typically, many ToF-SIMS are equipped with a Dual Source sputter gun for Cs+ and O2+ reactive sputtering. Therefore, the following article describes depth profiling of alkali metals with these two sputter ion species.

2 | EXPERIMENTAL

All used wafers were manufactured by Infineon Technologies Austria AG in Villach, Austria, under ISO 4 clean room conditions. Thermally grown SiO2 was applied on a Sb-doped Si-Wafer ($\rho < 0.3 \, \Omega \cdot \text{m}$) using a vertical furnace at a temperature of 1000°C. O2 and HCl were used as reactive gases and N2 as inert gas. After the application of a backside metallization, the wafer was cut to 1 × 1 cm² pieces.

The alkali ion implantation was carried out by Helmholtz Zentrum Dresden (Rosendorf, Germany) with acceleration voltages of 7 keV for lithium, 25 keV for sodium, and 45 keV for potassium. The implantation dose of 10¹⁴ cm⁻² and a 7° beam tilt were identical for all three ions.

The depth profiles were obtained with a ToF-SIMS 5 (IONTOF GmbH, Germany), equipped with a Dual Source Column (Cs⁺ and O₂⁺ gun) for sample sputtering and a bismuth Liquid Metal Ion Gun (LMIG) as primary ion source. The measurements were carried out using dual beam mode and non-interlaced sputtering, alternately combining sample sputtering with the sputter gun and subsequent analysis of the sample with the LMIG. Each second of sputtering was followed by 1 s of pause time where the sample was flooded with low energy electrons for charge compensating.

**FIGURE 1** ToF-SIMS depth profile of (A) Li⁺ implanted SiO₂ layer, (B) Na⁺ implanted SiO₂ layer, and (C) K⁺ implanted SiO₂ layer using 1-keV O₂⁻ as sputter beam in positive mode with Bi⁺ at 25°C and −100°C compared with simulated depth profile using a Monte Carlo simulation method (dashed line)
The ion energies of the beams were set to 1 keV for the Cs\(^{+}\) gun and 25 keV for the Bi\(^{+}\) primary ions. The sputter crater size was 300 × 300 μm\(^2\) with a field of view of 100 × 100 μm\(^2\) at a resolution of 128 × 128 pixels. The extraction bias was adjusted to −15 V.

The surface charging was reduced using a low energy electron shower. For cooling the samples during measurements, the heating and cooling sample holder of the ToF-SIMS was utilized.

The sputter rate was determined by measuring the depth of the sputter crater with a DektakXT stylus profilometer (Bruker cooperation, Billerica). Quantification of ion signals was derived from the implantation dose using the quantification tool in SurfaceLab 7 (IONTOF GmbH, Münster).

To measure the roughness inside the crater, an atomic force microscope (AFM) was utilized. A Veeco MultiMode V (Veeco Instruments Inc., UK) was used in tapping mode with a Si-cantilever at a frequency of 300 kHz and an analysis area of 5 × 5 μm\(^2\).

For theoretical calculations of implantation profiles via Monte Carlo method simulation, the Stopping and Range of Ions in Matter (SRIM) software package was used.\(^{10}\) The density of silicon dioxide needed for the simulation was stated as 2.32 g/cm\(^3\).

All measured data were smoothed using a parabolic Savitzky-Golan filter with 10 cycles and a range of 25.\(^{11}\)

3 | RESULTS AND DISCUSSION

First, the migration behavior of alkali ions during a standard operating procedure for measuring depth profiles of positive ions was investigated. Measurement parameters were set as declared in the previous section but with O\(_2^{+}\) ions as sputter beam and at ambient temperature. Figure 1 clearly shows that all lithium and sodium migrate to the SiO\(_2\)/Si interface during the measurement at room temperature. Although the migration of potassium was lower compared with lithium and sodium, the measured depth profile differs significantly from the simulated profile. Therefore, it was shown that is not possible to get depth profiles of alkali metals in non-conductive samples with a ToF-SIMS with these measurement conditions. Additional cooling to −100°C did improve the quality of the depth profiles, but artifact free depth profiles could also not be recorded with these settings. This was due to migration effects caused by charging of the surface during the sputter process.

It was also shown in literature that it is not possible to achieve artifact-free depth profiles using these measurement conditions and that mobile ions accumulate in an atomic mixing zone at the sputter front.\(^3\)

Although sputtering with Cs\(^{+}\) ions leads to a reduced yield of positive ions, there have been successful recordings of sodium depth

![FIGURE 2](image)

**FIGURE 2** ToF-SIMS depth profile of (A) Li\(^{+}\) implanted SiO\(_2\) layer at −120°C, (B) Na\(^{+}\) implanted SiO\(_2\) layer at −100°C, and (C) K\(^{+}\) implanted SiO\(_2\) layer at −100°C using 1-keV Cs\(^{+}\) as sputter beam in positive, non-interlaced mode with Bi\(^{+}\) compared with simulated depth profiles using Monte Carlo simulation method (dashed line) for all profiles
profiles with dynamic SIMS by using Cs$^+$ as primary ions. As can be seen in Figure 3, it is not possible to archive artifact-free depth profiles with a ToF-SIMS in non-conductive samples just by sputtering with Cs$^+$ at room temperature. Also using oxygen flooding did not improve the quality of the depth profiles.

Nevertheless, in order to record reliable depth profiles with ToF-SIMS, ion migration must be further reduced. Krivec et al. showed in their previous work, that the sodium migration during ToF-SIMS measurements can be reduced by cooling the samples. Considering this, the samples were cooled down to $-100^\circ$C for sodium and potassium implanted samples and to $-120^\circ$C for lithium implanted samples utilizing the heating and cooling sample holder of the ToF-SIMS instrument.

Figure 2 shows the measured depth profiles of lithium, sodium, and potassium compared with the simulated depth profiles.

As can be seen in Figure 2, the measured depth profiles match the simulated data well. The detection limit of the described method is about 20 ppm by mass for both ions, which is three magnitudes higher than using large O$_2$ clusters as a sputter beam.

The influence of the temperature on the analysis of the alkali implanted sample is shown in Figure 3. The depth profiles show that a temperature lower than $-120^\circ$C is needed for depth profiling of lithium. For sodium, a temperature up to $-80^\circ$C is suitable to obtain artifact-free measurements. As the temperature increases, the maximum of the lithium and sodium concentration is shifted to the Si/SiO$_2$ interface and increasing amounts of these ions are detected at the interface. Measurement temperature does not have a significant influence on the depth profiles of potassium. Even at 20°C, the measured distribution matches the simulated data well. This observation coincides with previous work, which stated that the diffusion coefficients of lithium and sodium are bigger than the one of potassium.

The quality of all depth profiles mainly depends on the field assisted migration of ions, but also on sputter time and crater roughness. Since a shorter sputter time in non-interlaced mode did not improve the quality of the measurements at these conditions, it can be deduced that the roughness of the crater surface is of higher importance for artifact-free depth profiles.

The roughness of the crater is 4 nm, which is sufficiently small for measuring depth profiles (Figure 4). It is not yet fully clarified, why sputtering with Cs$^+$ suppresses the migration of small ions. As shown in this paper, only depth profiles with Cs$^+$ sputtering enables artifact free depth profiles with a ToF-SIMS. Measuring with low temperatures but with O$_2^+$ as sputter species did not show good results.

Sputtering with Cs$^+$ leads to implantation of Cs atoms. The Cs concentration inside the sputter crater was measured by Yamamoto et al. They found a concentration of only 4% inside the crater. It is

**FIGURE 3** ToF-SIMS depth profile of an (A) Li$^+$, (B) Na$^+$, and (C) K$^+$ implanted SiO$_2$ layer using 1-keV Cs$^+$ as sputter beam in positive, non-interlaced mode with Bi$^+$ at different temperatures compared with a depth profile simulated with Monte Carlo simulation method (dashed line)
not likely that the formation of a conductive layer is the reason for suppressed ion migration, but it is possible that Cs has an influence on the topmost region of the sample surface. Due to ion implantation, the composition and the structural properties are altered.

4 | CONCLUSION

We have developed a new method for ToF-SIMS depth profiling of alkali metals in non-conductive layers using the example of SiO2. The use of Cs⁺ as sputter beam in positive ion mode suppresses the field assisted migration of small ions. Only the combination of low temperatures and Cs⁺ as sputter beam is sufficient for obtaining artifact free depth profiles of sodium and lithium with ToF-SIMS.

For potassium, sputtering with Cs⁺ instead of O₂⁺ is enough for obtaining depth profiles that matches the simulated data. For sodium and lithium, the field assisted migration must be additionally decreased by cooling the samples to −120°C for lithium and to −80°C for sodium.

There is literature that describes the use of a ToF-SIMS with cesium sputtering at room temperature for measuring depth profiles of sodium, and only Kudriavtsev et al. are using a ToF-SIMS 5 like in this paper.12,14

Also, the use of low temperatures for reduced ion mobility is discussed in literature.5,6 Both authors showed that low temperatures lead to suppressed ion mobility during the measurements. But despite the reduced mobility of sodium, Krivec et al. was not able to record artifact free depth profiles with ToF-SIMS 5.

This paper is the first that describes the combination of the use of low temperatures and cesium sputtering to achieve artifact free depth profiles of alkali metals that match the simulated data. To this date, this is the only versatile method for obtaining accurate depth profiles of alkali metals with a with ToF-SIMS 5 that was verified with sodium implants and does not need careful charge compensation or advanced equipment like cluster sputter guns.

With the measurement conditions described in this paper, it is now possible to eliminate field assisted migration effects of small ions in non-conducting samples caused by sample charging.

Although the new method is less sensitive than measurements with a cluster sputter gun, one can get reliable depth profiling information of alkali metals. If the analysis of extremely small amounts of sodium is necessary, cluster sputter guns are still irreplaceable. For all other cases, the method described in this paper is an alternative to advanced and expensive ToF-SIMS extensions like gas cluster guns.8

ORCID

Michael Leitzenberger https://orcid.org/0000-0001-9584-625X
Peter Kuegler https://orcid.org/0000-0003-2372-0847
Stefan Krivec https://orcid.org/0000-0002-1181-6510
Herbert Hutter https://orcid.org/0000-0002-3007-0734

REFERENCES

1. Simon M, Sze KKN. Physics of Semiconductor Devices. 3rd ed. Wiley; 2006.
2. Benninghoven A. Chemical analysis of inorganic and organic surfaces and thin films by static time-of-flight secondary ion mass spectrometry (TOF-SIMS). Angewandte Chemie International Edition in English. 1994;33(10):1023-1043.
3. Krivec S, Detzel T, Buchmayr M, Hutter H. On the temperature dependence of Na migration in thin SiO2 films during ToF-SIMS O₂⁺ depth profiling. Appl Surf Sci. 2010;257(1):25-32.
4. Hagenhoff B, van Leyen D, Niehuis E, Benninghoven A. Time-of-flight secondary ion mass spectrometry of insulators with pulsed charge compensation by low-energy electrons. J Vac Sci Technol a. 1989;7(5): 3056-3064.
5. Magee CW, Harrington WL. Depth profiling of sodium in SiO2 films by secondary ion mass spectrometry. Appl Phys Lett. 1978;33(2): 193-196.
6. Vajo JJ. Effects of sample cooling on depth profiling of Na in SiO2 thin films. Surf Interface Anal. 1997;25(4):295-298.
7. Kobayashi D, Yamamoto Y, Yamamoto K, Funatsu S, Harada K, Nishii J. Mechanism of hologram formation on glass surface by recording technique with corona discharge. Journal of Surface Analysis. 2014;20(4):226-229.
8. Holzer S, Krivec S, Kayser S, Zakel J, Hutter H. Large O$_2$ cluster ions as sputter beam for ToF-SIMS depth profiling of alkali metals in thin SiO$_2$ films. *Anal Chem.* 2017;89(4):2377-2382.
9. Wang Z, Liu B, Zhao EW, et al. Argon cluster sputtering source for ToF-SIMS depth profiling of insulating materials: high sputter rate and accurate interfacial information. *J Am Soc Mass Spectrom.* 2015;26(8):1283-1290.
10. Ziegler JF. Srim-2003. *Nucl Instrum Methods Phys Res, Sect B.* 2004;219–220:1027-1036.
11. Savitzky A, Golay MJE. Smoothing and differentiation of data by simplified least squares procedures. *Anal Chem.* 1964;36(8):1627-1639.
12. Greeuw G, Verwey JF. The mobility of Na$^+$, Li$^+$, and K$^+$ ions in thermally grown SiO$_2$ films. *J Appl Phys.* 1984;56(8):2218-2224.
13. Kudriavtsev Y, Hernández AG, Asomoza R, Korol VM. Time-of-flight mass spectrometry depth profiling of sodium-implanted polyethylene terephthalate. *Surf Interface Anal.* 2017;49(10):1049-1052.
14. Yamamoto Y, Shimodaira N. SIMS depth profile analysis of sodium in silicon dioxide. *Appl Surf Sci.* 2008;255(4):860-862.

**How to cite this article:** Leitzenberger M, Kuegler P, Krivec S, Hutter H. Acquisition of artifact free alkali metal distributions in SiO$_2$ by ToF-SIMS Cs$^+$ depth profiling at low temperatures. *Surf Interface Anal.* 2021;53:675-680. https://doi.org/10.1002/sia.6956