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Optimizing Tof-SIMS Analysis for Isotope Exchange Depth Profiling and Imaging on Functional Oxides

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1. Introduction

Isotope exchange depth profiling (IEDP) enables the study of oxygen transport in functional oxides including diffusion in the bulk of the materials and along interfaces such as grain boundaries [1]. Subsequent time of flight-secondary ion mass spectrometry (ToF-SIMS) can be used to quantify the tracer diffusion profiles and to visualize oxygen exchange-active zones by determining the local oxygen isotopic fraction [2]. The main challenge of measuring isotopic fractions by ToF-SIMS is to achieve sufficient ion intensities for minority isotopes while preventing the highly intensive major isotope signal from saturating the ion detector [3]. This is far from trivial since SIMS analysis of oxides results in huge oxygen secondary ion (SI) intensities due to an enhanced oxygen ionization yield and high primary ion (PI) intensities in conventional ToF-SIMS operation modes. High SI intensities can lead to systematic errors in the determination of isotopic fractions. In this contribution we introduce a novel ToF-SIMS operation mode, the so-called "Collimated Burst Alignment" (CBA) mode, to enable a more accurate determination of oxygen isotopic fractions and simultaneously an improved lateral resolution [4,5].

2. Experiments

As an indication for an accurate measurement we analyzed the $^{18}$O natural abundance

$$f_{I_{O}} = \frac{I_{I_{O}} - I_{I_{O_{8}}} + I_{I_{O}} - I_{I_{O_{8}}}}{I_{I_{O}} - I_{I_{O_{8}}} + I_{I_{O}} - I_{I_{O_{8}}}} \tag{1}$$

of several technologically relevant functional oxides to compare it with the expected natural abundance value. Accordingly we discuss the accuracy in that part of the diffusion profile where the maximum majority isotope intensity ($I_{I_{O}}$) shows the highest impact on the error of the isotopic fraction.

3. Results and Discussion

Sputtering a samples surface with positive primary ions (PI) of suitable energy leads to interactions which cause the emission of secondary ions. Operating in conventional ToF-SIMS modes like "Burst Alignment" (BA) and "High Current Bunched" (HCBU) with $\text{Bi}_{5}^{+}$, $\text{Bi}_{3}^{+}$ or $\text{Bi}_{2}^{+}$ produces high PI and SI intensities. High intensities can cause collision-induced ion interactions and signal saturation, both leading to an underestimated value of the detected $^{18}$O ion intensity. Consequently, the calculated natural $^{18}$O abundance erroneously shifts to higher values, for example 0.258% ($\text{BA}, \text{Bi}_{5}^{+}$, 1μA emission current) in Fig. 1. However, even if highly intensive PI clusters ($\text{Bi}_{5}^{+}$) are used, analysis in the novel CBA mode results in an $^{18}$O level of 0.207%. The more accurate value is enabled by significantly decreasing the SI intensity by a specifically modified PI gun beam guidance. Since lower SI intensities reduce detector dead time effects and ion interactions, the $^{18}$O fraction in Fig. 1 indicates an increasing error with increasing majority isotope intensity $I_{I_{O}}$. Many additional measurements are presented dealing with the importance of an accurate isotopic fraction for quantifying oxide ion diffusion and detailed information about the beam guidance in CBA mode is given.

4. Conclusions

Oxygen isotope fractions measured in established ToF-SIMS operation modes only allow medium accuracy and sub-micron lateral resolution. The novel CBA mode provides an accurate determination of the oxygen isotopic fraction in addition to an optimized lateral resolution below 90nm.

References