

## Secondary Ion Mass Spectrometry and its Application to Diffusion in Oxides

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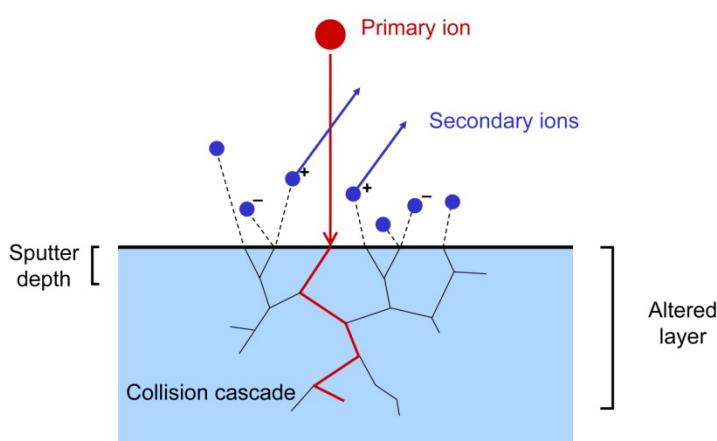
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In this paper we give an introduction to Secondary Ion Mass Spectrometry (SIMS). At first, we focus on the fundamentals and on the principles of operation. Secondly, we show that SIMS is a powerful technique to analyze elemental distributions and mass transport processes over various length scales ranging from some nanometres to several hundred micrometers. For this purpose, we have used stable, enriched isotopes to investigate oxygen diffusion and cation diffusion in oxides. By combining different modes of SIMS analysis – depth profiling, line scanning and imaging – it was possible to measure diffusion coefficients from about  $10^{-22} \text{ cm}^2 \text{s}^{-1}$  to  $10^{-6} \text{ cm}^2 \text{s}^{-1}$  and to determine surface exchange coefficients as well. In addition, high resolution SIMS makes it possible to investigate diffusion through space charge layers at surfaces and to distinguish between bulk and grain boundary diffusion in polycrystalline materials.

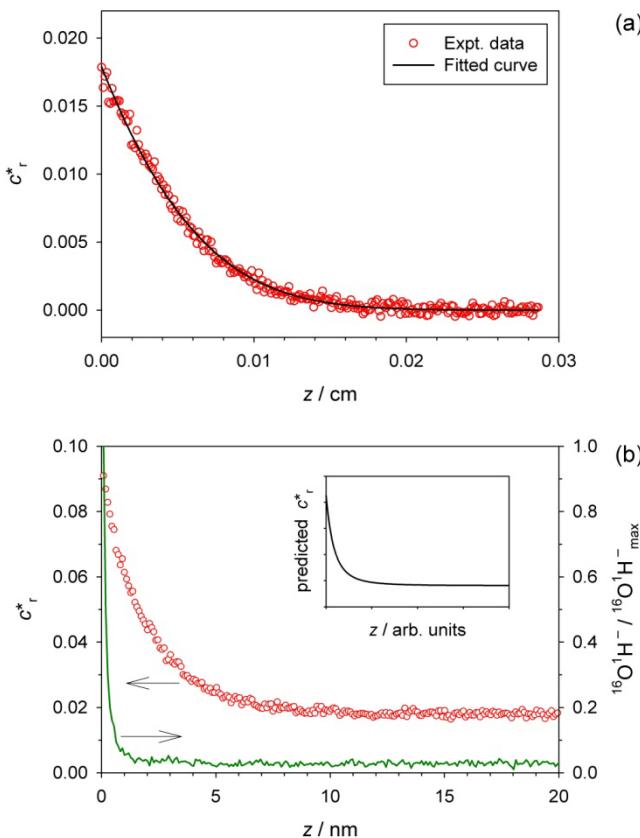
The SIMS process is illustrated schematically in Fig. 1. Primary ions with an energy between 0.25 and 30 keV are fired at a solid; in common use as primary ions in SIMS are  $\text{Cs}^+$ ,  $\text{O}_2^+$ ,  $\text{Ar}^+$ ,  $\text{Xe}^+$  and



**Fig. 1** Schematic illustration of the principle of SIMS.

$\text{Ga}^+$ , with the recent developments of Bi and Au cluster ions ( $\text{Au}_n^{z+}$ ,  $\text{Bi}_n^{z+}$ ) and even  $\text{C}_{60}$ . Upon entering the solid, the primary ions transfer their energy in binary collisions to the atoms of the target. Collision cascades that reach the surface may cause target material to be ejected from the top two to three monolayers in the form of atomic and molecular moieties if sufficient energy and momentum are imparted to surface species to overcome binding energies. Most of these sputtered particles are neutral, but some are charged: these secondary ions can be collected by means of a suitable electrical potential and sorted in a mass spectrometer according to their mass to charge ratio ( $m/z$ ).

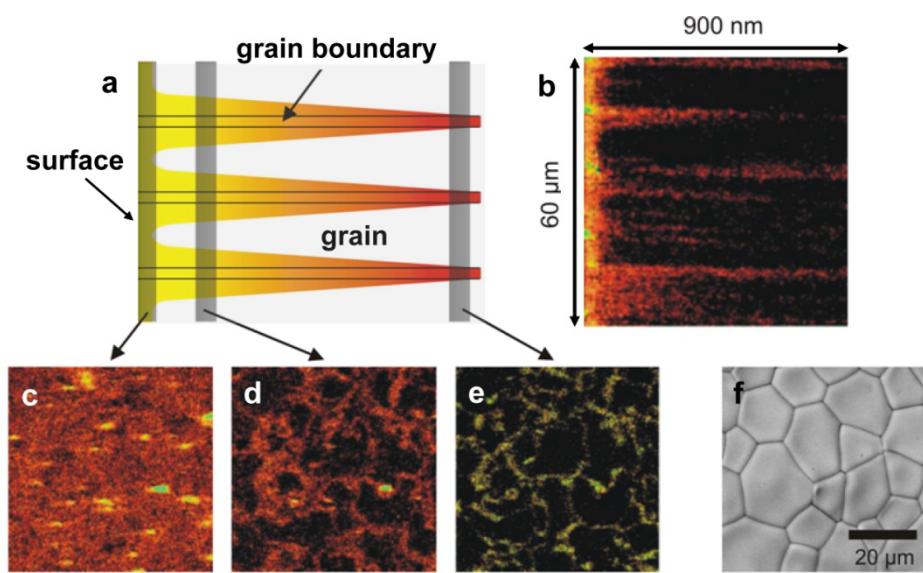
As SIMS is capable of detecting different isotopes, a standard application is the oxygen isotope exchange technique from which oxygen diffusion coefficients  $D_O^*$  and surface exchange coefficients  $k_O^*$  can be obtained by depth profiling, line scanning and imaging [1]. In Fig. 2 we show results obtained for Fe-doped  $\text{SrTiO}_3$ . SIMS imaging was used to detect the overall profile with a length of around 220  $\mu\text{m}$  (Fig. 2a); yielding the parameters  $D_O^* = (3.7 \pm 0.9) \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  and  $k_O^* = (1.05 \pm 0.07) \times 10^{-9} \text{ cm s}^{-1}$ . A very short depth profile of the original surface was carried out in addition (Fig. 2b). It corresponds to the first 20 nm of the 220  $\mu\text{m}$  oxygen diffusion profile. We attributed this additional profile to  $D_O^*$  being lower in the surface region on account of a space-charge layer depleted of oxygen vacancies being present [2]. It is well documented that grain boundaries in Fe-doped  $\text{SrTiO}_3$



**Fig. 2** Normalized oxygen isotope fraction,  $c_r^*$ , in a Fe-doped  $\text{SrTiO}_3$  single crystal ( $T = 973 \text{ K}$ ,  $p(\text{O}_2) = 500 \text{ mbar}$ ,  $t = 86300 \text{ s}$ ). (a) Imaging analysis of exposed cross-section. (b) Depth profile of the original surface.

have space-charge layers in the adjacent bulk regions; this result indicates that the (001) surface of acceptor-doped  $\text{SrTiO}_3$  does too.

In oxygen ion conductors such as YSZ or LSGM cation diffusion is one source of long-term degradation although it is orders of magnitude slower than oxygen diffusion. Fig. 3 shows schematic concentration contours for diffusion in the bulk and along grain boundaries (Harrison type B regime) together with experimental contours of Fe in polycrystalline  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$  [3]. Quantitative analysis of the corresponding diffusion profiles shows that iron diffusion along the grain boundaries is more than 4 orders faster than diffusion in the bulk.



**Fig. 3** (a) Schematic concentration contour for diffusion from the surface of a polycrystalline material into the bulk and along grain boundaries. (b) Experimental concentration contour for Fe diffusion into polycrystalline LSGM as obtained by SIMS imaging. (c) - (e) Fe distribution in cross sections parallel to the sample surface and at different depths. (f) micrograph of the sample surface as obtained by SEM [3].

## References

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- [3] O. Schulz, M. Martin, C. Argirius, G. Borchardt, Phys. Chem. Chem. Phys. 5 (2003) 2308.