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A comparison between micro-Raman spectroscopy and SIMS of beveled surfaces for isotope depth profiling

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ABSTRACT

The diffusion in fast oxygen ion conductors is typically analyzed by isotope exchange experiments followed by secondary ion mass spectrometry (SIMS). This study demonstrates confocal Raman spectroscopy in combination with beveling of the specimen's surface as an interesting non-UHV alternative to SIMS. This simple and comparably inexpensive approach is shown to result in practically the same values for the diffusion properties as the SIMS technique. Thereby, the limitations of both techniques are compared for an easy understanding under which conditions they are applicable.

1. Introduction

Secondary ion mass spectrometry (SIMS) is widely used to analyze the diffusion processes in solids [1,2]. The diffusion properties of oxygen in oxygen ion conductors are typically determined by isotope exchange experiments followed by SIMS depth profiling [3–5]. In the case of fast oxygen ion conductors deep diffusion profiles (>5 μm) are commonly obtained, i.e. the depth profiling technique cannot be employed due to the low sputtering rate by ion bombardment, requiring alternative approaches. Most frequently a linescan SIMS analysis on a cross-section of the isotope exchanged sample is applied in this regime (5 μm to <2 mm) [6–8] covering a range of diffusion constants D^* of ca. 2×10^{-3}–1×10^{-5} cm^2 s^{-1}. However, this technique requires a sufficient lateral resolution of the focused primary ion beam, e.g. provided by Cs^+ or Ga^+ sources [9], which are rather expensive compared to the standard Ar-ion sources.

It has been shown that for a maximum error of 10% in the determination of D^* and the surface exchange coefficient k the condition

$$\frac{\mathrm{FWHM}}{L_D} \leq 0.1 \tag{1}$$

with FWHM as the full width at half maximum of the primary ion beam and L_D the length of the diffusion profile needs to be fulfilled [8]. Beveling provides a strategy to overcome this limitation as the depth scale is translated to a magnified lateral scale. In this case the depth profile can be acquired by a lateral linescan of the ion beam across the beveled surface.

In this work we demonstrate how the beveling technique can be used to determine isotope depth profiles in the case of a fast ion conductor, i.e. yttria stabilized zirconia (YSZ) despite a large ion beam. In addition to the SIMS technique, which serves as the reference measurement, micro-Raman spectroscopy was used to show its capabilities for isotope depth profiling with the advantages of non-destructiveness and a comparably simple measurement set-up. To the best knowledge of the authors, this is the first time that Raman spectroscopy is applied in combination with the beveling approach for obtaining diffusion properties.

2. Experimental

9.5 mol% yttria stabilized zirconia single crystalline substrates (Crystec GmbH) were used for the exchange experiments. This ensures a simple evaluation of the measured diffusion profiles as only one diffusion process (e.g. through the bulk material) has to be considered [10]. The isotope exchange experiments were conducted in a custom built setup comprised of a sealed tubular furnace connected to a gas distribution system that allows to adjust the partial pressures of research grade $^{16}O_2$ (99.995% chemical purity) and $^{18}O_2$ (97.9%, balance: $^{16}O_2$) individually after previous evacuation of the system. A coupled mass spectrometer allows determining the exact gas phase composition. The samples were heated to the targeted temperature of the exchange with a rate of 5 K/min and cooled after the specified dwell time with the same rate. An effective duration of the exchange, which takes into account the finite heating and cooling rate, was calculated using the method described by Killoran [11].

The long term (100 h) annealed YSZ samples (in either gas mixture described above) attained the isotope equilibrium, i.e. the ^{18}O isotope fraction in the solid is constant and corresponds to the gas phase. These specimens served as reference standards whereas diffusion

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depth profiles were measured for the short term annealed YSZ samples. The SIMS measurements were conducted in a UHV chamber with a base pressure of ~9^{-10} mbar using a 5 keV Ar^+ primary ion beam, which was focused (ion beam diameter: ~100 μm) on the sample surface at an incident angle of 45°. Co-bombardment by low energy (~300 eV) electrons prevented specimen charging. The sputtered secondary ions were detected with an electrostatic quadrupole SIMS (EQS, Hiden Analytical Ltd.) analyzer, which was positioned in a 30 mm distance to the sample in the direction of the surface normal. The instrument was adjusted for optimum transmission and detection efficiency of monoatomic negatively charged oxygen species. A positive extractor voltage was set for analyzing the negative secondary ions.

To obtain a ^{18}O diffusion profile, the YSZ specimen was isotope exchanged for 5 h at 600 °C. Subsequently, it was mechanically beveled using a tripod polisher (Model 590, South Bay Technology Inc.) in combination with diamond coated plastic foils (grain size: 15–0.25 μm) for dry polishing. As shown in Fig. 1, this procedure enables the precise preparation of shallow bevels with a constant slope and a smooth surface.

The bevel translates the vertical diffusion profile (*z*-direction) to the lateral bevel axis (*x*-direction) with a magnification, M, given by

$$\mathrm{M} = \frac{x}{z} = \tan^{-1}\alpha, \tag{2}$$

e.g. a factor of 27 for the bevel angle a of 2.11° ± 0.01°in the case of the YSZ sample. Each distance on the beveled surface in *x*-direction to the edge of the original surface ($x = 0$) corresponds to a certain depth *z* in the initial exchanged sample. A SIMS depth profile was thus obtained by a point-to-point linescan across the sample in *x*-direction. The specimen was mounted to a manipulator and then moved in incremental steps of 100 μm with respect to the stationary ion beam and SIMS spectra were acquired for 45 s each to obtain stable steady-state signals.

Micro Raman spectra were measured on the isotope exchanged YSZ samples utilizing a LabRAM Series Raman Microscope (Horiba Jobin Yvon) with a He–Ne excitation laser (λ: 632.8 nm, output power: ~10 mW), which was focused to probe a volume of ~1 μm^3 (determined by measuring several Raman spectra across an edge of a sample).

The diffusion profiles were analyzed in terms of the relative isotope concentration:

$$c'(z,t) = \frac{c(z,t) - c_{bg}}{c_g - c_{bg}} \cdot \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}. \tag{3}$$

Herein, *z* is the depth coordinate, *t* is the exchange time, c_g is the isotope fraction in the exchange gas, and c_{bg} is the isotope fraction in the specimen at the beginning of the exchange (generally the natural abundance of the according isotope). The diffusion constant D^* and surface exchange coefficient *k* were determined by least-squares fitting of the depth profiles to an equation given in [12] describing the given conditions of a semi-infinite medium containing initially the natural abundance of oxygen isotopes in contact with a gas phase of constant arbitrary oxygen isotope composition:

$$c'(z,t) = \operatorname{erfc}\left(\frac{z}{2\sqrt{D^* t}}\right) - \exp\left(\frac{k}{D^*}z - \frac{k^2}{D^*}t\right) \cdot \operatorname{erfc}\left[\left(\frac{z}{2\sqrt{D^* t}}\right) + \left(\frac{k}{D^*}\sqrt{D^* t}\right)\right], \tag{4}$$

where erfc is the complementary error function.

3. Results and discussion

3.1. SIMS

The normalized ^{18}O diffusion profile $c'(z)$ measured on the beveled 9.5YSZ sample, with an isotope exchanged at 600 °C for 5 h are shown in Fig. 2. At a bevel magnification of ~27 times the boundary condition of Eq. (1) is clearly fulfilled. The diffusion profile can reliably be fitted by Crank's equation (Eq. (4)) yielding a diffusion and surface exchange coefficient of $(3.2 \pm 0.4) \times 10^{-9}\ cm^2\ s^{-1}$ and $(1.1 \pm 0.2) \times 10^{-7}\ cm\ s^{-1}$, respectively. Manning et al. [13] reported a similar D^* value of ~$3 \times 10^{-9}\ cm^2\ s^{-1}$ for a 9.5YSZ single crystal at 600 °C, but a significantly smaller *k* value of ~$5 \times 10^{-10}\ cm\ s^{-1}$. De Souza et al. [14] reported a comparable tracer diffusion and surface exchange coefficient of ~$1 \times 10^{-9}\ cm^2\ s^{-1}$ and ~$8 \times 10^{-10}\ cm\ s^{-1}$ (600 °C), respectively, for dense nanocrystalline samples of 8YSZ, showing no evidence for an enhancement of oxygen transport by nanocrystalline microstructures. The surface exchange coefficient is very sensitive to the surface state [6] and may e.g. be affected by the segregation of impurities or dopants [15] or remaining water in the exchange set-up [16], which could account for the observed differences of the *k* values.

Magnifications by a factor of up to 800 are feasible by the beveling approach [17,18], which yields according to Eq. (1) a lower limit for the diffusion profile depth of ~1 μm for a meaningful linescan SIMS

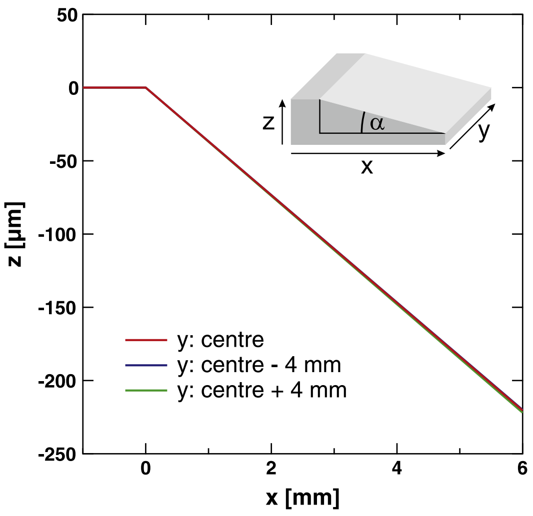

Fig. 1. Profilometric linescans on a mechanically beveled 9.5YSZ(100) single crystal ($10 \times 10 \times 0.5\ mm^3$). The geometry including the bevel angle α, which was determined from the slope to 2.11° ± 0.01° is shown in the inset.

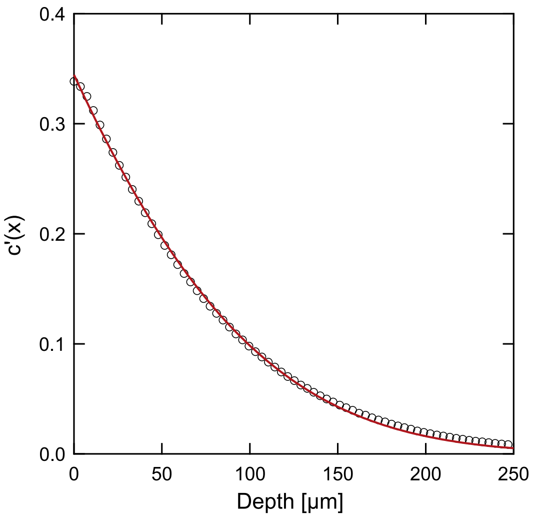

Fig. 2. Depth profile of the normalized ^{18}O isotope fraction measured with SIMS by a linescan along the bevel direction of the mechanically beveled 9.5YSZ(100) sample exchanged at 600 °C for 5 h. The solid line represents a least square fit according to Eq. (4).