D-SIMS Analysis of Electrochemical Sensors

Investigating ion diffusion and performance of ITO-modified YSZ oxygen sensors

In response to the challenges associated with the bulky size and high-temperature operation of Yttria-stabilized zirconia (YSZ)-based electrochemical sensors, scientists investigate the potential of indium tin oxide (ITO) as an electrode material to enable lower temperature operation. They examine the performance of a thin film-based multilayered YSZ oxygen sensor, configured as (RE)Pt|Cu,Cu_2O|YSZ|O_2,ITO(WE), with Cu-Cu_2O serving as the reference electrode (RE) and ITO as the working electrode (WE) on a (100) $SrTiO_3$ substrate. This sensor demonstrates sensitivity to oxygen levels ranging from 10 to 824 ppm in inert streams, even when operating at temperatures as low as 623 K, without encountering any baseline drifts.

To investigate the interdiffusion of Indium and Tin ions between ITO and YSZ, researchers from the Indira Gandhi Centre For Atomic Research, India, employ Dynamic Secondary Ion Mass Spectrometry (D-SIMS), a technique renowned for its high depth resolution and excellent detection limits. Their D-SIMS results reveal a significant change in concentration, with approximately 90% variation occurring within a 20 nm thickness for both ^{115}In and ^{120}Sn ions. This depth measurement indicates similar diffusion characteristics between the ions, likely due to their close mass and ionic size (Fig. 1). Furthermore, the examination of ^{89}Y and ^{90}Zr ion diffusion from YSZ into ITO across the interface suggests that over 90% of the concentration change occurs within the same 20 nm depth profile, signifying a sharp interface.

The narrowness of the interface, even under the deposition temperature of 998 K and an overall growth duration of nearly 90 minutes, is depicted by the width of the boundary revealed in the SIMS depth profiles (Fig. 2). Additionally, the ITO/YSZ sharp interface exhibits a high exchange current density of 10^{-3} A cm^{-2} at 973 K, which decreases by an order of 10^{-4} A cm^{-2} at 523 K for a 450 K drop in temperature.

D-SIMS proves to be an indispensable tool for quantifying changes in ion concentration in depth profiles measuring hundreds of nanometers. Its unparalleled depth resolution, high sensitivity and excellent detection limits make it the ideal choice for measuring sharp interfaces deep within a sample, thereby providing critical insights that drive the optimization of sensor materials.

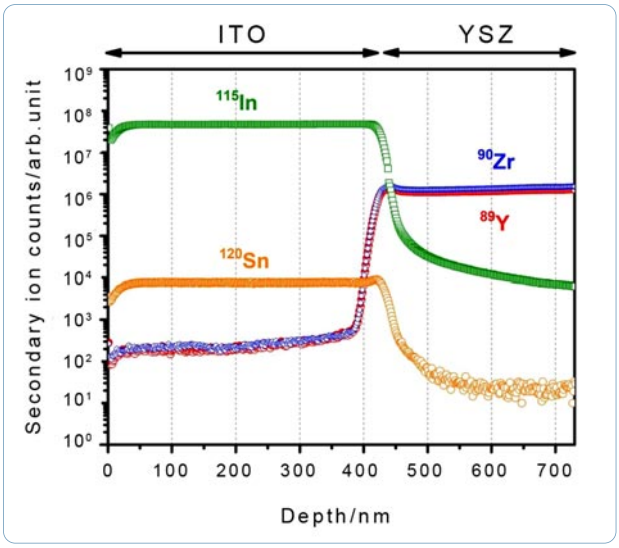


Figure 1: SIMS depth profiles showing the diffusion of ^{120}Sn, ^{115}In, ^{89}Y and ^{90}Zr across an ITO/YSZ interface.

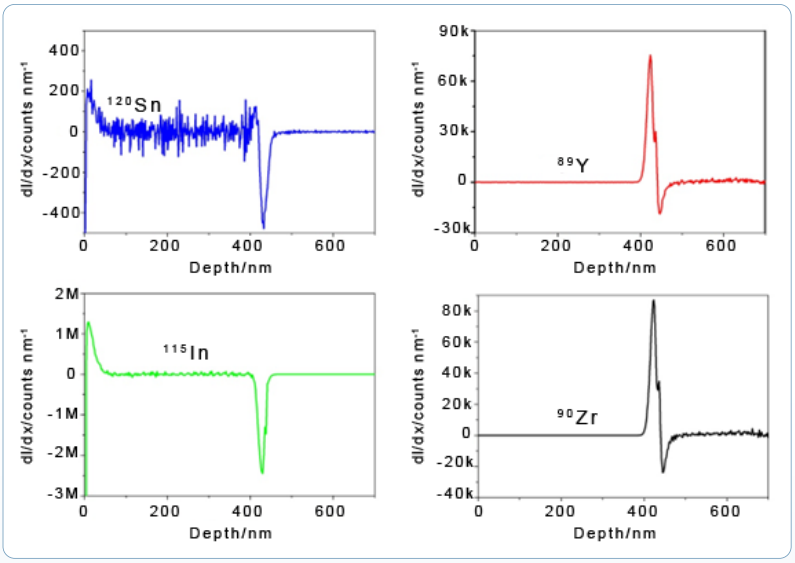
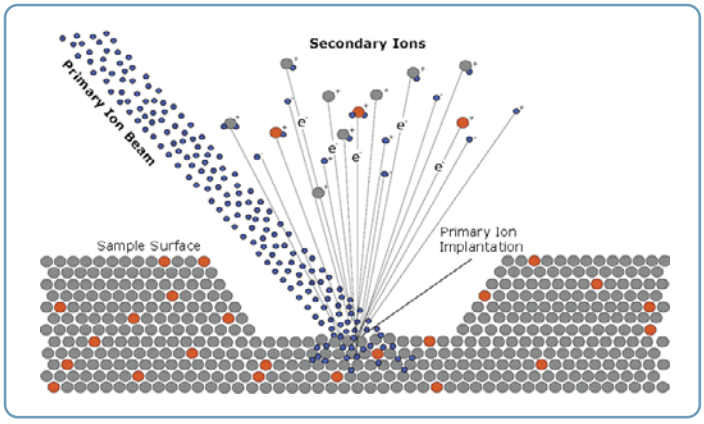


Figure 2: SIMS depth profiles showing the diffusion of ^{120}Sn, ^{115}In, ^{89}Y and ^{90}Zr across the ITO/YSZ interface of a STO|YSZ|ITO multilayer.

SIMS data obtained on a CAMECA IMS series Secondary Ion Mass Spectrometer at the Indira Gandhi Centre For Atomic Research, India.

Adapted from: N.A. Ravindranath et al. A low-temperature thin film-based multilayered YSZ electrochemical oxygen sensor with ITO as working electrode. Electrochim. Acta Vol 467 (2023).

The Technique Behind

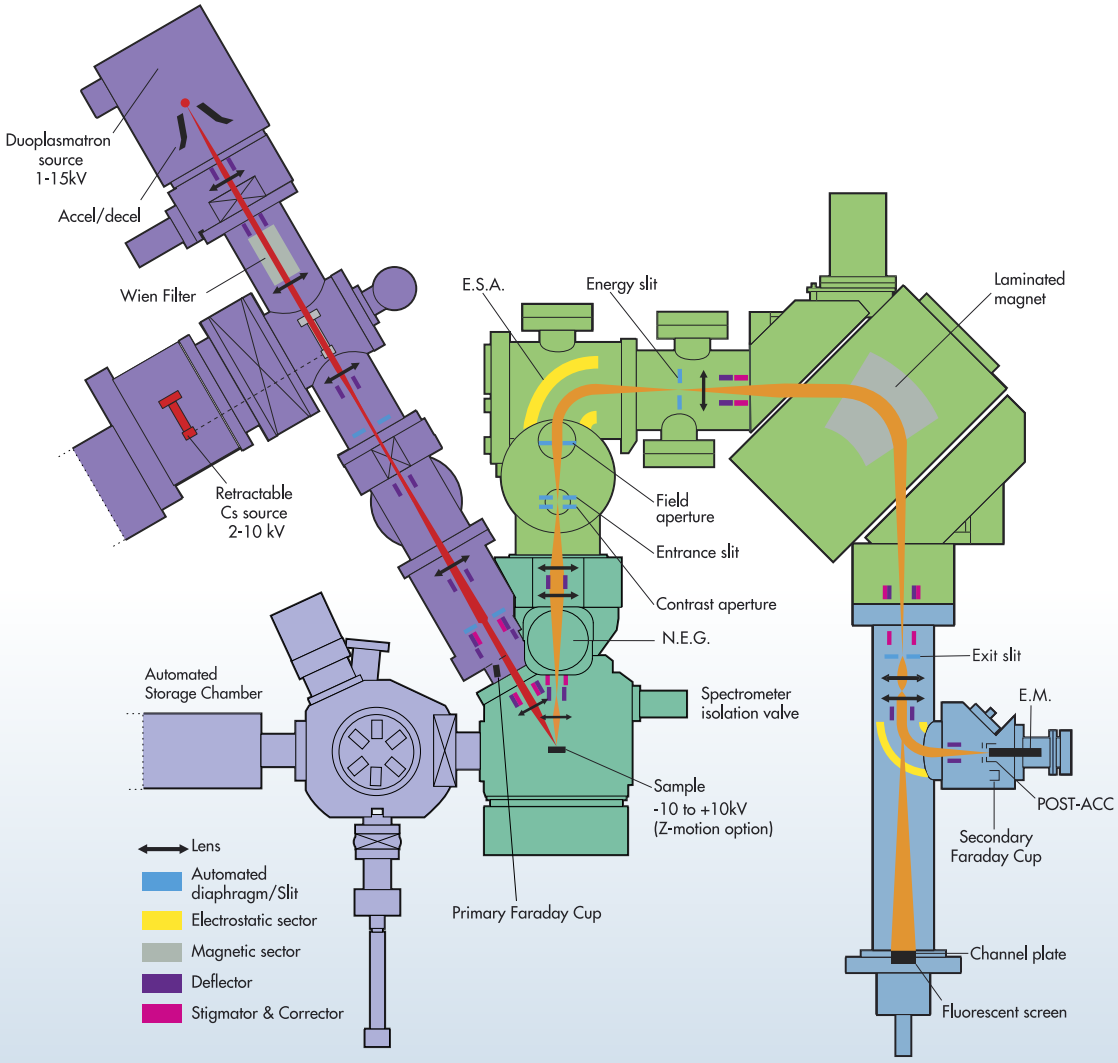


Dynamic SIMS

When a solid sample is sputtered by primary ions of few keV energy, a fraction of the particles emitted from the target is ionized. Secondary Ion Mass Spectrometry consists of analyzing these secondary ions with a mass spectrometer.

The SIMS technique is "destructive" by its nature (sputtering of material). It can be applied to any type of flat, solid material that can be kept under vacuum.

In dynamic SIMS, bulk composition and in-depth distribution of trace elements are investigated with a depth resolution ranging from sub-nm to tens of nm. SIMS is recognized as the most sensitive elemental and isotopic surface analysis technique.



CAMECA IMS 7f-Auto

The IMS 7f-Auto is a versatile SIMS tool offering reference detection sensitivity with high throughput and full automation. Its motorized storage chamber and sample transfer allows the analysis of multiple samples in chained or remote mode.

For more information please visit www.cameca.com/products/sims/ims7f-auto

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