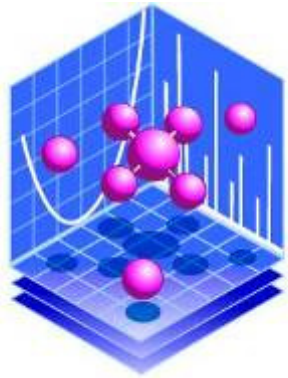

Isotopic depth profiles by GD spectroscopies: GD-OES and PP-TOFMS

Patrick Chapon, Sébastien Legendre, Agnès Tempez

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First … an ICPOES result !

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Validation of isotopic analysis of depleted, natural and enriched uranium using high resolution ICP-OES

Michael Krachler* and Paul Carbol

Received 22nd July 2010, Accepted 17th September 2010
DOI: 10.1039/c0ja00083c

Analytical procedures for the reliable determination of uranium isotopes employing a commercially available high resolution (HR)-ICP-OES installed in a glove box were developed and validated. To this end, nine commonly used U emission lines were tested for their potential to provide isotopic splitting of the U signal, thus providing isotopic information. Among all emission lines tested, the wavelength region around 424.4 nm offered the largest spread between individual U signals, *i.e.* ^{233}U, ^{235}U, ^{236}U, and ^{238}U. This study focused specifically on the reliable determination of the abundances of ^{235}U at 424.412 nm and ^{238}U at 424.437 nm in samples containing depleted, natural and slightly enriched U, but also included specimens with rather high (up to ~90%) ^{235}U enrichments. Appropriate selection of the spectral background and accurate positioning of the peaks proved essential for obtaining reproducible U isotope ratios. The accuracy of the developed methodology was confirmed by the analysis of eight certified isotopic reference materials as well as eight reference samples that have been characterised in an accredited laboratory in-house using TIMS. In addition, this study highlights the potential of the developed HR-ICP-OES procedure for identifying nuclear sources of various U specimens *via* the analysis of ^{233}U (424.398 nm) and ^{236}U (424.423 nm). In contrast to the commonly used techniques, the methodology applied in this study does neither require the separation of U from the matrix prior to analysis nor the regular analysis of a reference sample with a known isotopic composition to correct for bias effects as it is the case for more sophisticated and precise mass spectrometric measurements. Nevertheless, HR-ICP-OES provides fit for purpose U isotopic information with reasonable accuracy (typically <1.5%) and precision (~1%) within a few minutes. As such, HR-ICP-OES can be employed as a reliable, fast screening tool to identify the U isotopic composition and as such, complements the more laborious TIMS analysis routinely employed for this purpose.

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4 October 2010 on http://pubs.rsc.org | doi:10.1039/C0JA00083C

Findings

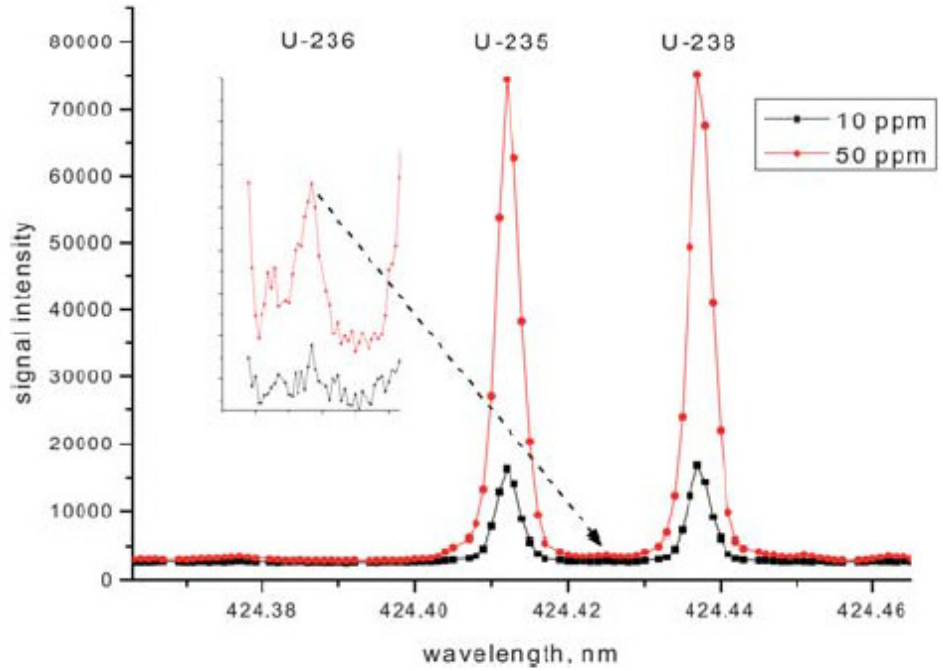

Fig. 1 High resolution ICP-OES spectrum of the analysis of the uranium isotopic reference material CRM U500 containing ^{235}U (abundance 49.696%, atom percent) and ^{238}U (49.711%) at comparable concentrations. Individual data are acquired for each picometre (pm) over a range of 100 pm. The total U concentration of each solution is 10 or 50 mg L^{-1}, *i.e.* ~5 or 25 mg L^{-1} of each ^{235}U and ^{238}U. The zoom-in highlights the well-resolved ^{236}U signal (0.0755%) at 424.425 nm between the intensive signals of ^{235}U and ^{238}U.

Some isotopes can be « resolved » with high resolution optics

2010 pubs.rsc.org | doi:10.1039/C0JA00083C

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G Model
FUSION-6243; No. of Pages 4

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Fusion Engineering and Design xxx (2012) xxx–xxx

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Fusion Engineering and Design

journal homepage: www.elsevier.com/locate/fusengdes

Measurement of deuterium and helium by glow-discharge optical emission spectroscopy for plasma–surface interaction studies

Yuji Hatano[a,*], Jie Shi[a], Naoaki Yoshida[b], Naoki Futagami[b], Yasuhisa Oya[c], Hirofumi Nakamura[d]

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[b] Research Institute for Applied Mechanics, Kyushu University, Kasuga, Fukuoka 816-8580, Japan
[c] Radioscience Research Laboratory, Faculty of Science, Shizuoka University, Shizuoka 422-8529, Japan
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ARTICLE INFO

Article history:
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Keywords:
Hydrogen isotopes
Helium
Surface analysis
Interface
Plasma–surface interactions

ABSTRACT

To examine the resolution of isotope analysis of hydrogen with glow-discharge optical emission spectroscopy (GDOES), depth profiles of hydrogen and deuterium in a H-containing Ta/D-containing Ti/Ni layered structure were measured. The depth profiles of deuterium could be measured with sufficient resolution in the presence of relatively large amounts of hydrogen and *vice versa*. In addition, measurements of depth profiles of He implanted in W at room temperature were also performed with Ne plasma. The intensity of the He emissions was sufficiently high at a fluence of 10^{20} He m^{-2} or higher. The depth profiles of He measured in this manner were in good agreement with the results of cross-sectional observations using a transmission electron microscope. Therefore, it was concluded that GDOES with Ne plasma is a promising technique for the depth profile analysis of plasma-facing materials and deposited layers formed on them.

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Measurement of D in OES

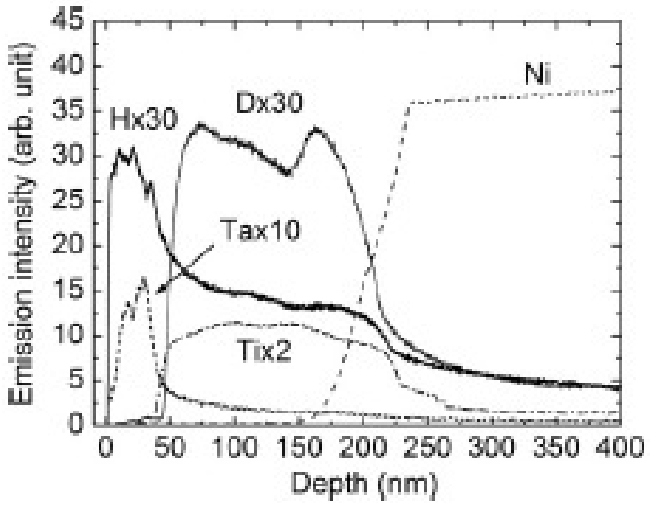
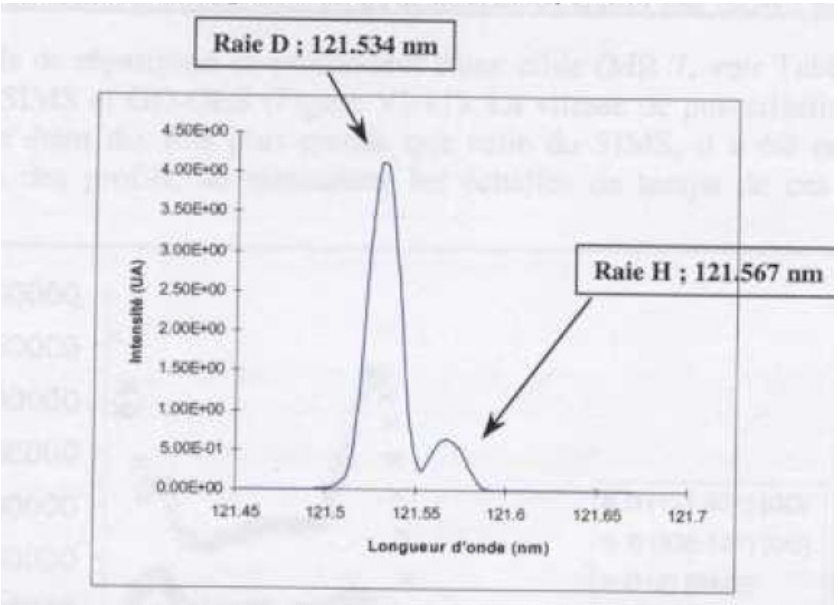


Fig. 3. Depth profiles of H, D, Ta, Ti and Ni in the Ta(H)/Ti(D)/Ni layered structure.

- D can be measured with GD OES



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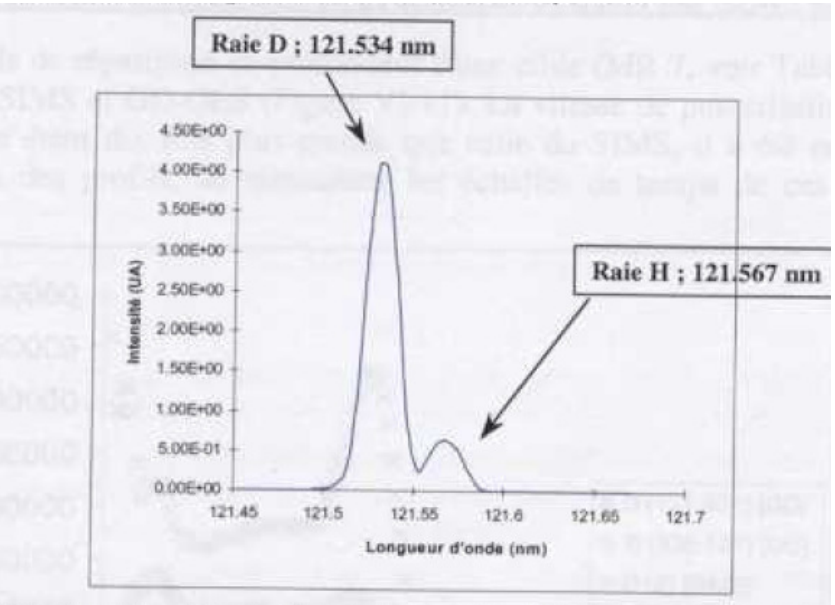
Measurement of D in OES

- Sequential (from H): Polyscan
- Simultaneous : Double order grating



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Principle of Polyscan

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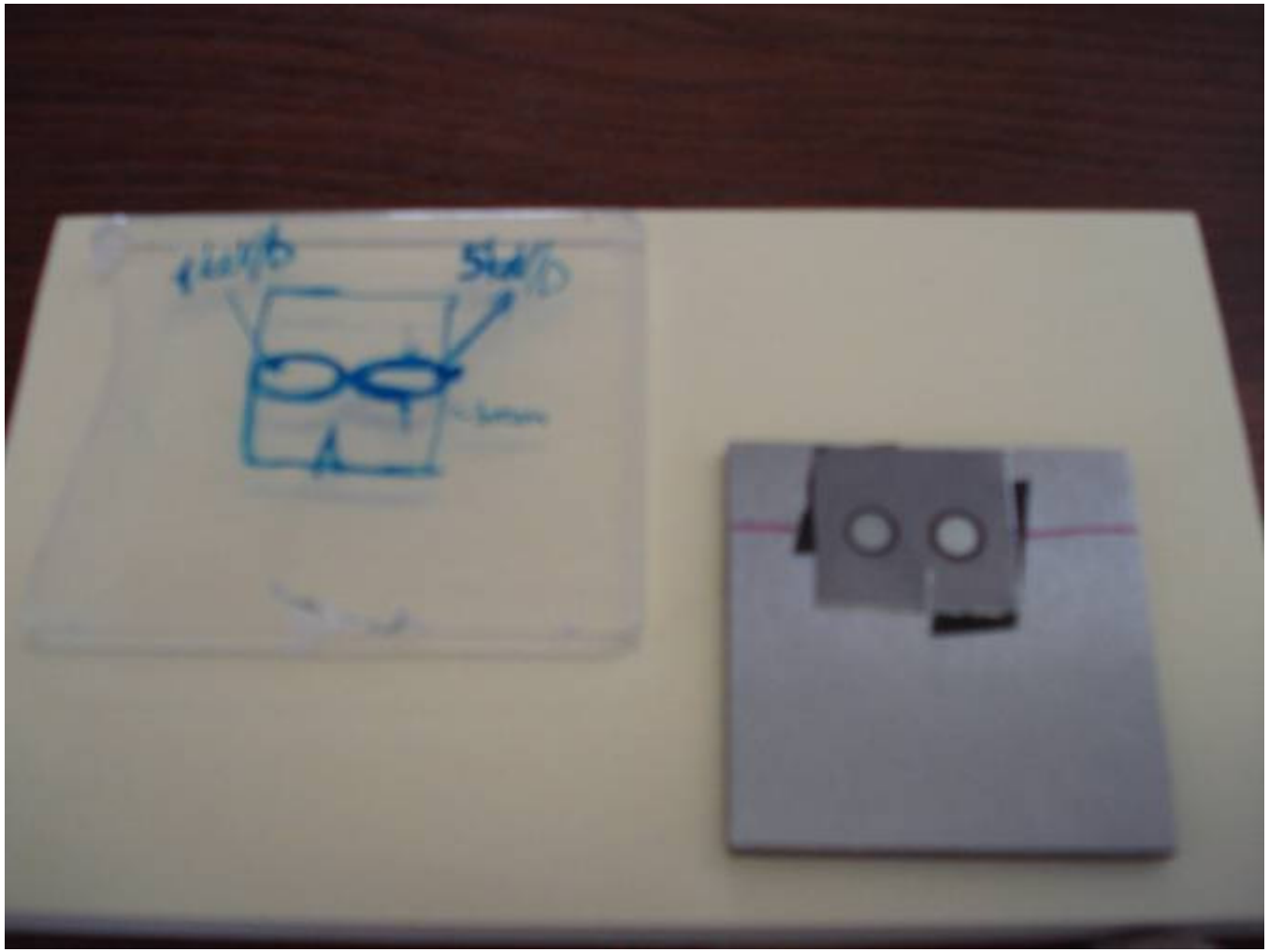
When simultaneous measurement matters …



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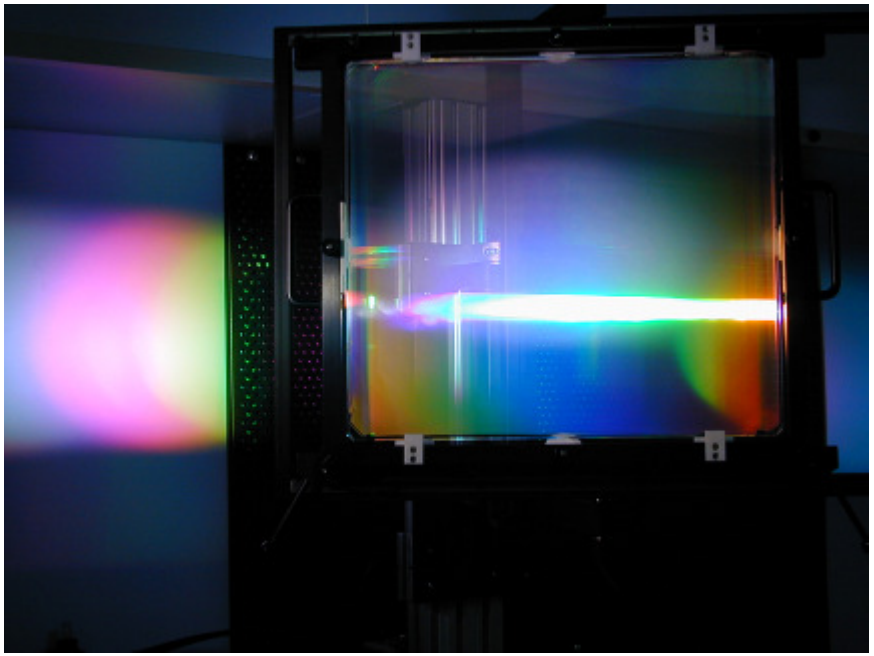
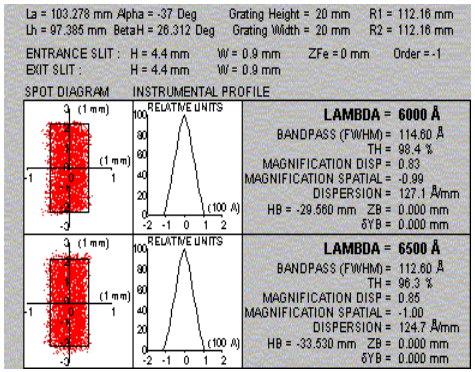
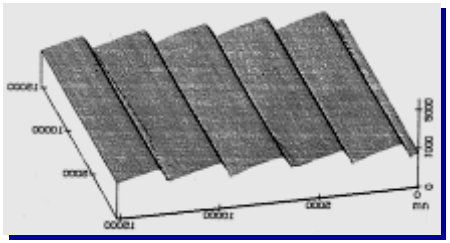
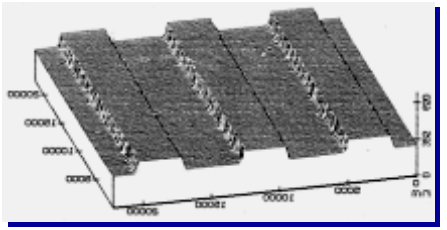
Optics : Diffraction gratings









Simultaneous measurement of
H/D - first/second order

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D interest : modeling of H

ELSEVIER

Thin Solid Films 387 (2001) 201–204

thin solid films

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Effects of D^+ implantation of CIGS thin films through a CdS layer

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[c]*Institute of Materials Technology, Tallinn Technical University, 19086 Tallinn, Estonia*
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[e]*Institut für Physikalische Elektronik, Universität Stuttgart, Stuttgart, Germany*

1. Introduction

$Cu(InGa)Se_2$ (CIGS)-based photovoltaic (PV) devices hold the world record efficiency for solar energy conversion (18.8%) for thin film solar cells [1]. One of the ways to improve the characteristics of semiconductor materials is to passivate electrically active defects using hydrogen. Hydrogen can be delivered through the CdS layer directly into the interface region. Excess energy is then absorbed by polycrystalline CdS. In this case implantation of hydrogen could be done using a conventional ion implanter. In addition, a CIGS layer coated with CdS will be protected against any possible detrimental effects of exposure to the atmosphere. A study of the effects of energetic ions in CdS/CIGS heterostructures may also help to understand the physics of radiation damage in CIGS and illuminate the origins of the remarkable high radiation hardness exhibited by CIGS-based photovoltaic (PV) devices. In this work, D^+ ions were used for modeling H behaviour because depth profiling of deuterium can be done with much higher accuracy.

2. Experimental details

$CuIn_xGa_{1-x}Se_2$ thin films were deposited on Mo-coated soda-lime glass substrates by the co-evaporation technique, and coated with 30 nm of CdS using a standard chemical bath deposition process at Stuttgart.

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D interest : (safe) modeling of T(tritium)

G Model
FUSION-6209; No. of Pages 5

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Deuterium behavior at the interface of oxidized metal under high temperature heavy water

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[b] Hydrogen Isotope Research Center, University of Toyama, Toyama 930-8555, Japan

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SS304
F82H
Nickel
Oxidation
Filtration

ABSTRACT

Deuterium behavior into the metals soaked in hot heavy water has been investigated in order to understand the oxidation initiated tritium infiltration in the fusion reactor. Disks of SS304, F82H and Ni and gold plated SS304 and F82H as the tritium permeation coating were soaked in an autoclave at 573 K. After the soaking, residual deuterium in the specimen was measured by the thermal desorption method and elemental depth distribution in the specimen was measured by a glow discharge optical elemental spectroscopy method. As the results, the oxide thickness has grown with the soaking time, and infiltrated deuterium amount also increases with oxidation time. Deuterium exists at the interface of the oxide and metals. Deuterium in the gold plated specimens was less than that in the bare SS304 about 1/5. Deuterium in nickel was less than that in the SS304 by one orders magnitude and oxide thickness was also thinner than SS304. Those results indicate that deuterium infiltration into the material would be initiated by the deuterium gas generated at the oxidation process of metal. Gold plating as the permeation reduction coating could be relatively effective to prevent deuterium infiltration into the metal in SS304.

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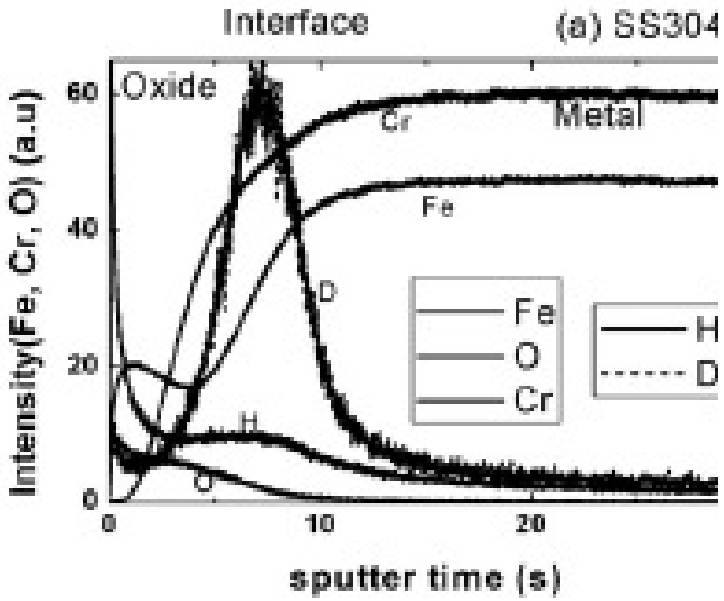
GD craters and depth profile



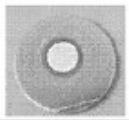
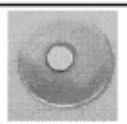
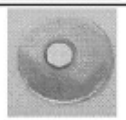
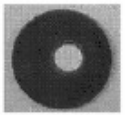
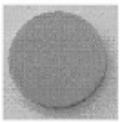
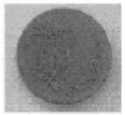
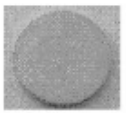
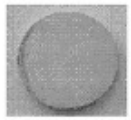
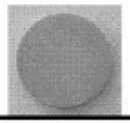
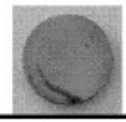
	Before Oxidation	After 81hrs Oxidation
SS304		
F82H		
Ni		
Au-SS304		
Au-F82H		

Fig. 1. Photographs of the samples before and after oxidation in D_2O.

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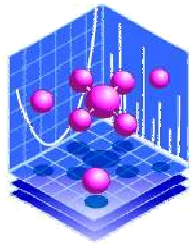
MS may be more adapted for isotopes…



New Instrument: Plasma Profiling TOFMS

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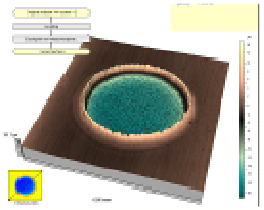
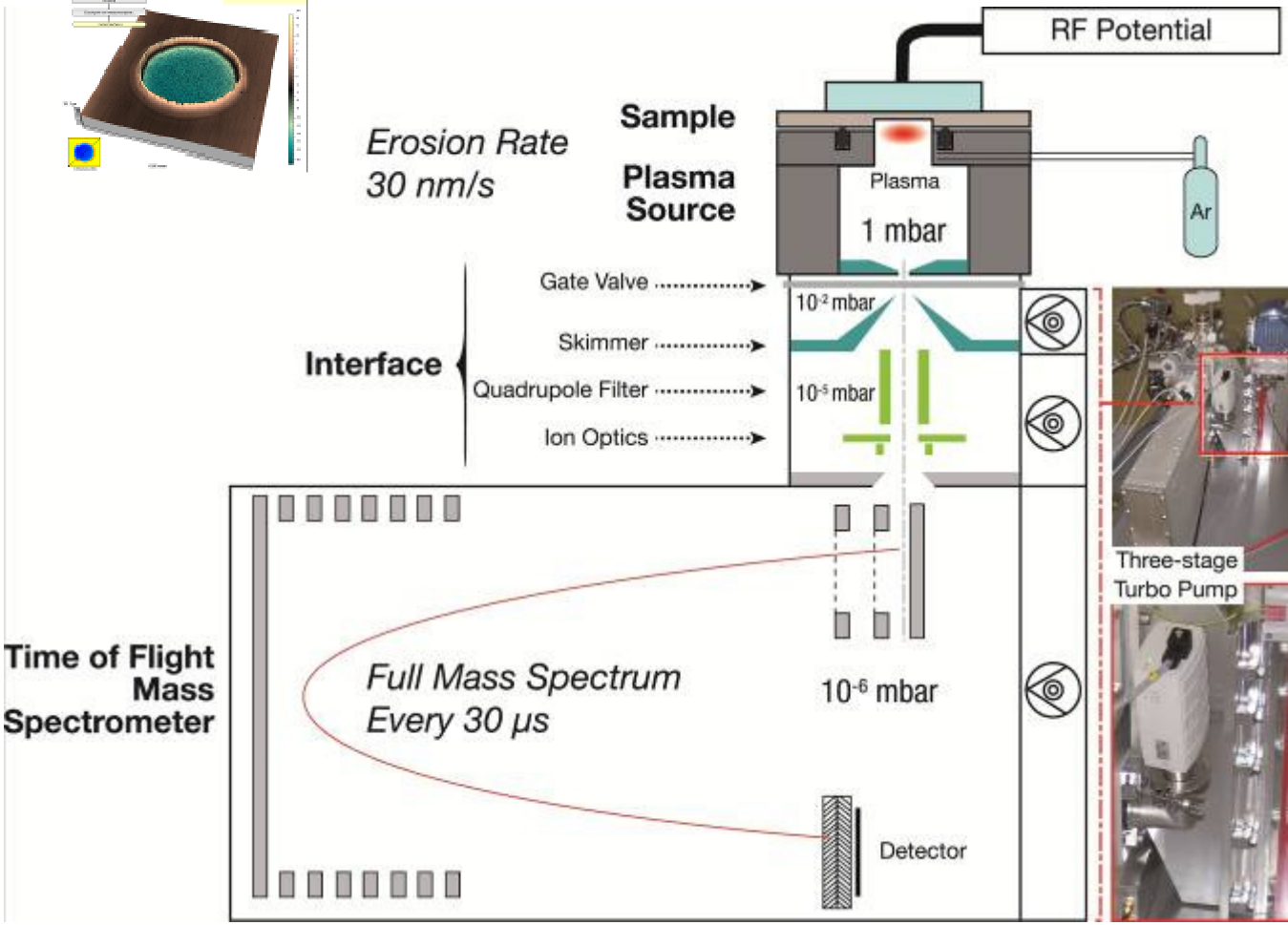
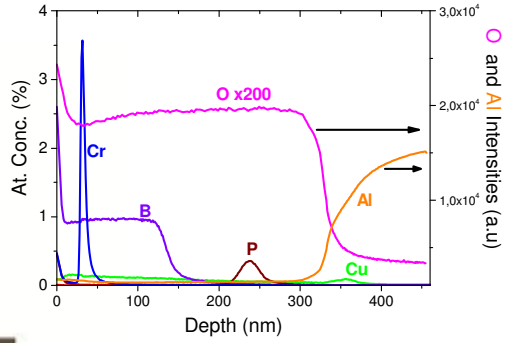
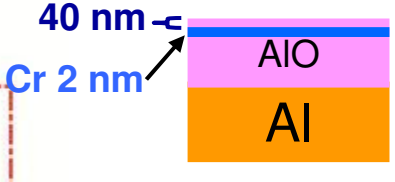
Technique









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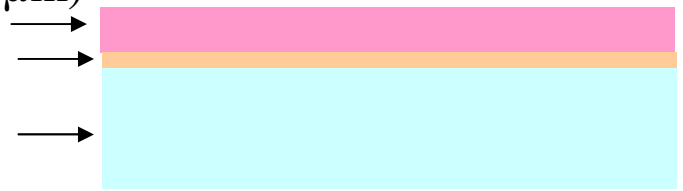
Example : organic PV

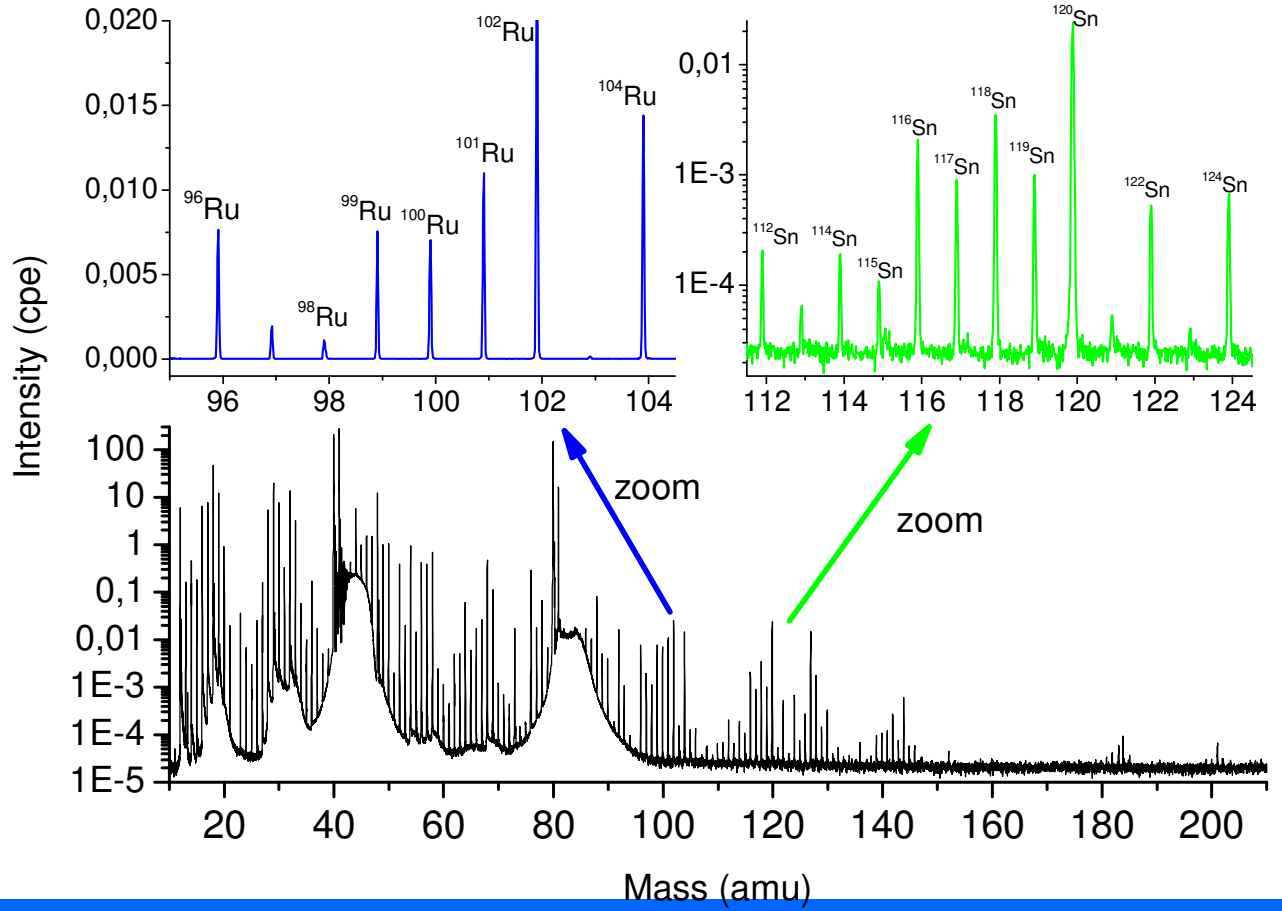
TiO_2 porous layer (4µm)

Transparent Oxide

Glass substrate



- Full mass spectrum at each depth
- All isotopes



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Research Article

SURFACE and INTERFACE ANALYSIS

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(www.interscience.wiley.com) DOI 10.1002/sia.3129

$^{18}O/^{16}O$ isotopic separation in anodic tantala films by glow discharge time-of-flight mass spectrometry

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Glow discharge mass spectrometry has been widely used for trace and ultra-trace element analysis of high-purity alloys. A novel pulsed radio frequency glow discharge time-of-flight mass spectrometer (rf GD TOFMS) has been developed that retains the pulsed radio frequency analytical ion source to provide ion signal enhancement due to processes involving Penning ionisation. A time-resolved detection mode has been implemented to sample the afterglow regime of the pulse profile, corresponding to the highest ion signal intensities. Here, the performance of rf GD TOFMS in isotope differentiation is discussed. Anodic tantala films, comprising ^{18}O-rich layers of controlled thicknesses and locations, were formed by appropriate combination of anodising of tantalum in electrolytes enriched with ^{18}O isotopes and of natural O isotopic abundance. Transmission electron microscopy (TEM) and radio frequency glow discharge optical emission spectrometry (rf GD OES) analyses were performed to examine the morphology and elemental distributions of the specimens, while the content of ^{18}O in the ^{18}O-rich layers was determined by elastic recoil detection analysis(ERDA). In pulsed rf GD TOFMS analysis, characteristic ionic species formed in the glow discharge allows differentiation of ^{18}O-rich layers. Particularly, the location of ^{18}O-rich layers was determined from the $^{16}O^{18}O$ and $Ta^{18}O$ ion signals at masses *m/z* 34 and 199, respectively. The locations of ^{18}O-rich layers in anodic films, controlled by the selected anodising conditions, were probed precisely. The ^{18}O profiles in anodic tantala were directly compared with those obtained by dual beam time-of-flight SIMS. **Copyright © 2009 John Wiley & Sons, Ltd.**

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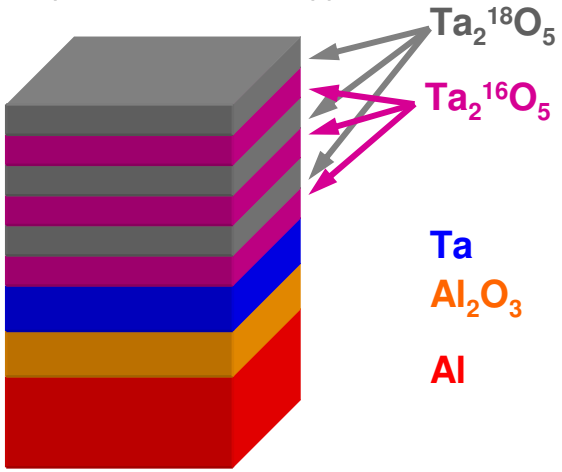
Illustration : ^{18}O enriched thin tantalum oxide bilayers

- Context:

  Control the growth of anodic Tantalum films on aluminium

- Recipe: (Courtesy of Corrosion and Protection Centre, School of Materials, The University of Manchester)

  1. Anodising Aluminium
  2. Sputter-deposition of Tantalum (99.9% purity Tantalum)
  3. Sequential anodising by sputtering in 0.1 M sodium Tungstate solution (Tungstate electrolytes prepared using deionised water (^{16}O solution) and enriched deionised water (^{18}O solution)).



Ref: A. Tempez et al, Surface and Interface Analysis, 41, 966 (2009)

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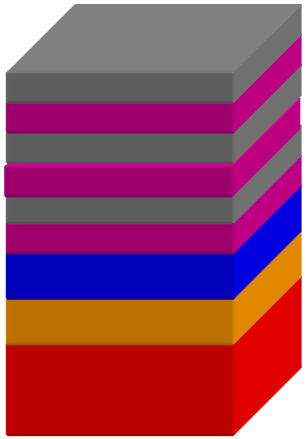
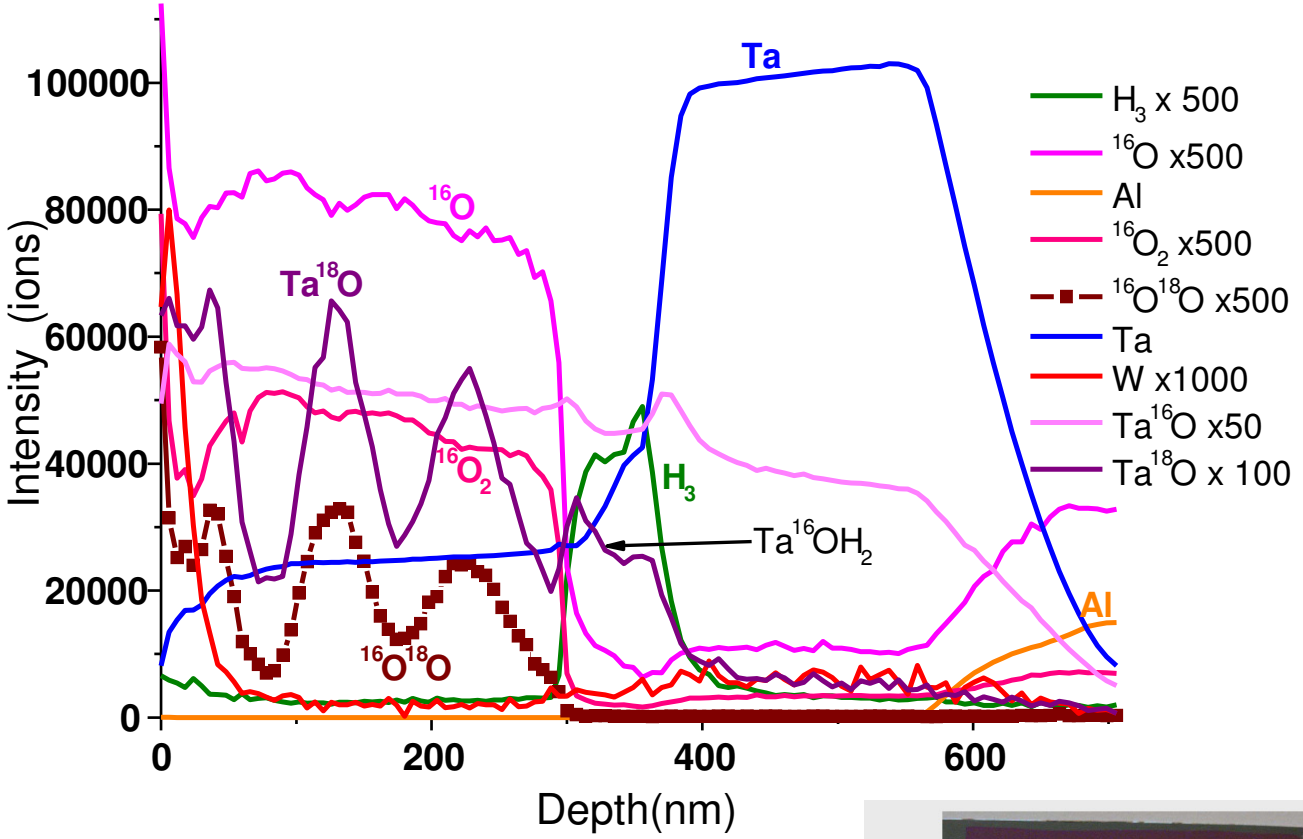
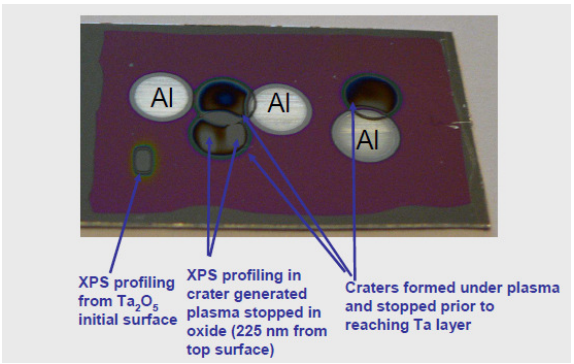
^{18}O enriched thin tantalum oxide bilayers

Analysis Conditions
Plasma 600 Pa, 45 W
Pulsed Mode 0.8 ms /4 ms





- *Resolution of isopically labeled layers ^{18}O (looking at $^{16}O^{18}O$ et $Ta^{18}O$) with 40 nm thickness*
- *Work in progress: cross studies with XPS*



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Quantitative depth profile analysis of boron implanted silicon by pulsed radiofrequency glow discharge time-of-flight mass spectrometry

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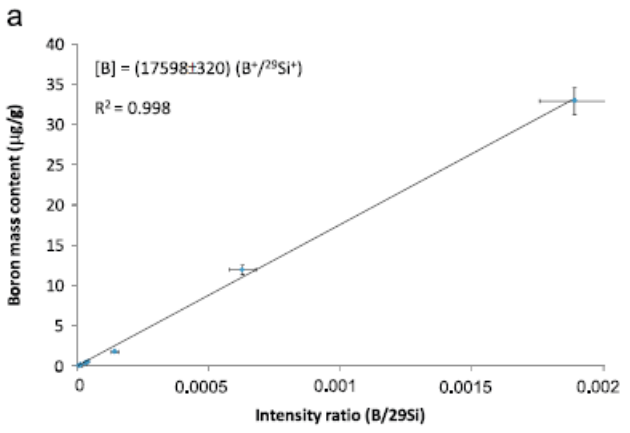

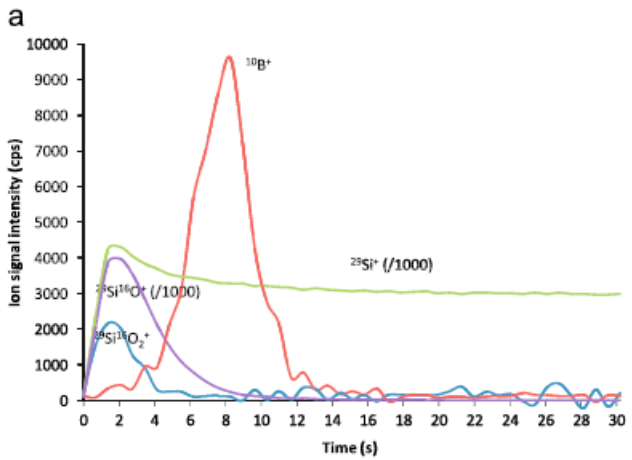

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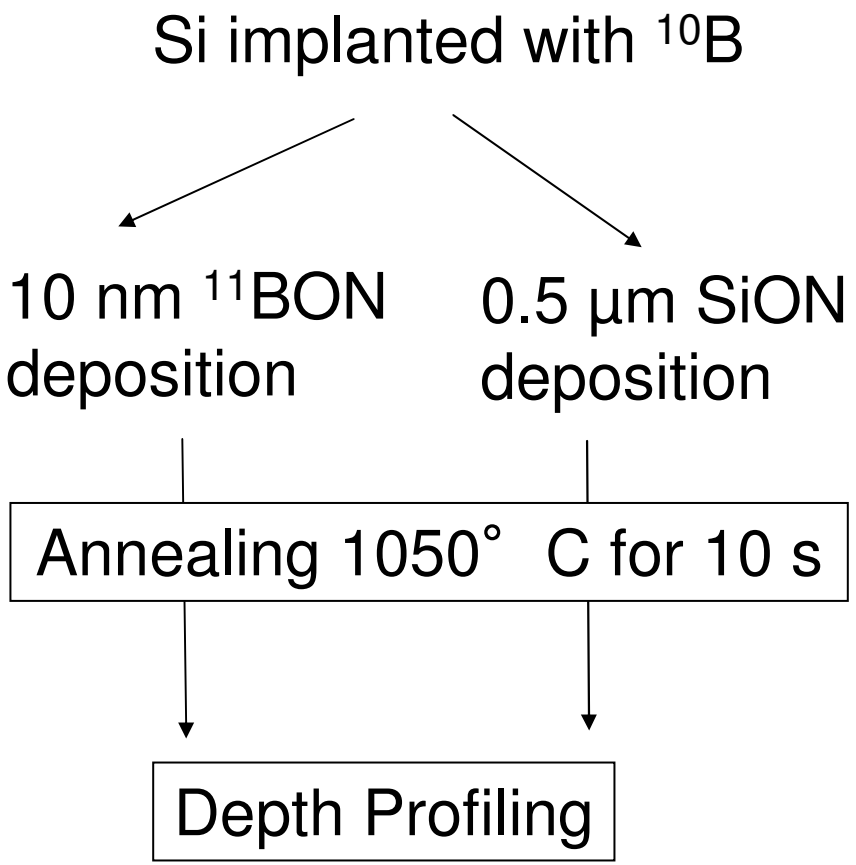
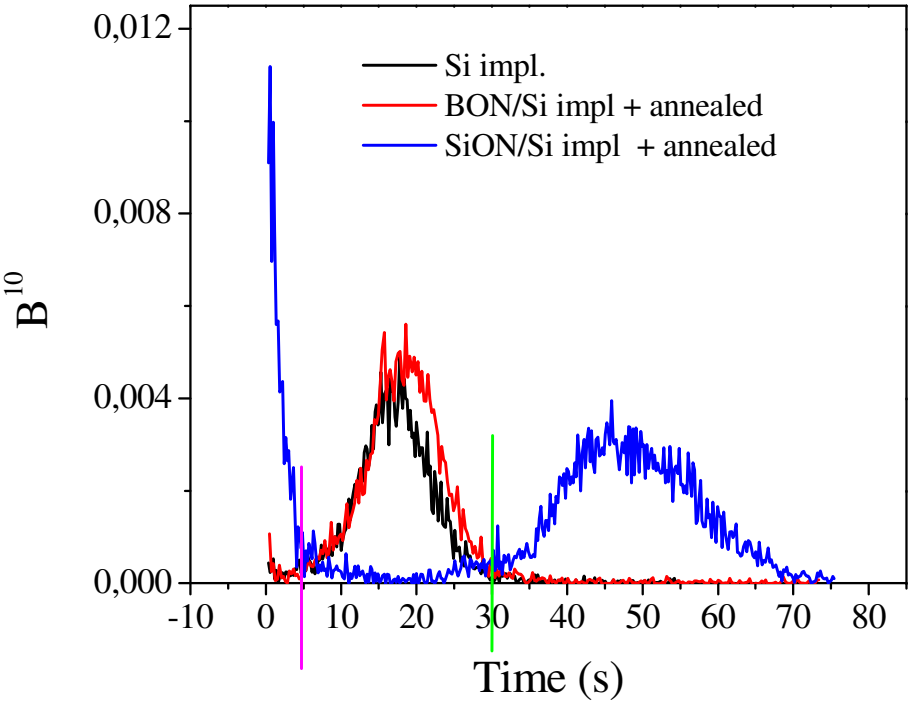
Use of Isotopic Information

Study of B diffusion: BON versus SiON





Intensity	BON	SiON
B^{10}/Si^{29}	$2.134 * 10^{-4}$	$2.632 * 10^{-4}$

Average value of intensities of (B^{10}/Si^{29}) in deposited BON and SiON films

BON is best diffusion blocker of B compared to SiON

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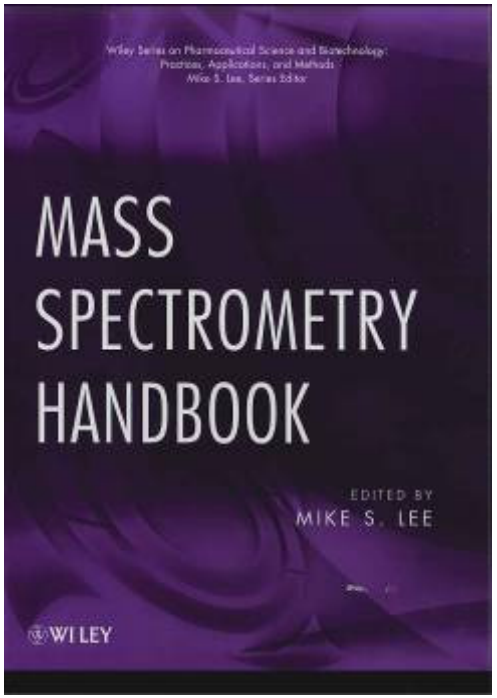
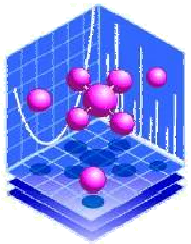
Conclusion

- Isotopic depth profiles of thin/thick layers are possible with Plasma Profiling TOFMS (and GDOES in some cases).



Chapt. 41 by EMDPA partners dedicated to Dick Payling



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Thank you

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