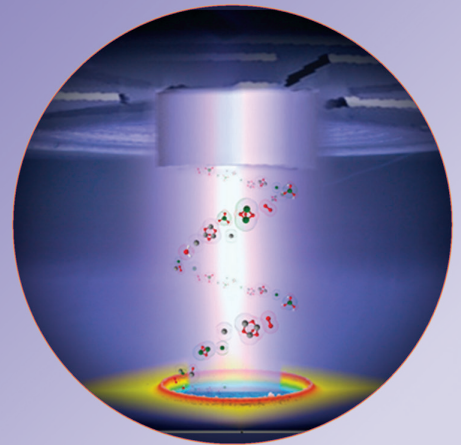


GD Day 2016

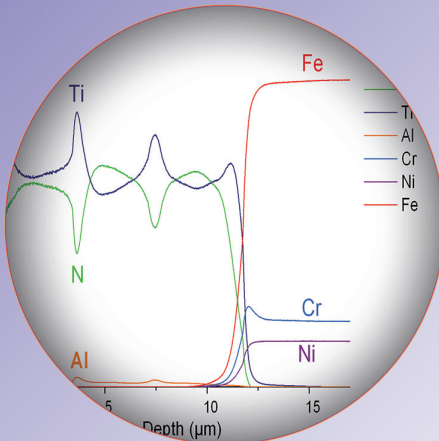
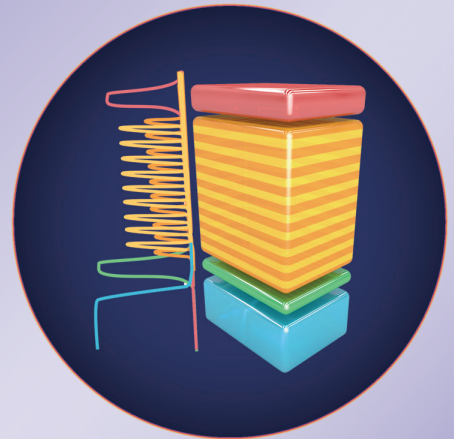
**15 afternoon
& 16
September 2016**



DiP



**8th
GD Day**



**For surface and
depth profile
analysis**

WELCOME!

First of all, thank you for attending the 8th GD Day Symposium.

The GD Day is an international event, initiated by HORIBA Scientific in collaboration with major research organizations. This every two year International Conference illustrates the current state of advanced applied Glow Discharge Spectroscopy through presentations and discussions from today's leaders in the field, and encourages participants to discuss their latest research results and inspire new thoughts.

After Reims in 2014 (with the Société Française du Vide), we are pleased and honoured to welcome you at Soleil, the French Synchrotron facility, prestigious area synonymous of scientific innovations since generations.

In this conference we will demonstrate again that GD is a common language that spans the disciplines, and helps bring them together in a unified voice for innovation and discovery.

Finally, I must once again thank our kind hosts at Synchrotron Soleil for their support in the organization of this event, and for their help to make the event as successful as its reputation has come to demand.

With all good wishes.



Ramdane Benferhat
HORIBA Scientific
Strategy Director
September 2016

8th International GD Day

GD Day 2016

www.gd-day.com

Practical information

Registration

On-line registration to the GD Day is mandatory at www.gd-day.com.

Location

Synchrotron SOLEIL
L'Orme des Merisiers
Rond point du Golf de Saint Aubin
91190 Saint Aubin

An identity card or a passport is mandatory to enter the site.

Poster guidelines

Poster boards are provided for poster presenters to display their posters.
Poster format is A0 vertical.
Posters will be on display during the whole symposium.

Synchrotron visit

A visit of the Synchrotron SOLEIL is organised on Thursday 15th afternoon. The visit is forbidden to people with pacemaker.

Gala Dinner

The Gala Dinner will be held at the Synchrotron Soleil on Thursday evening.

HORIBA is Dedicated to Problem Solving and Enriching Lives

Smartphones, tablet PCs, electric vehicles.

Today we are always surrounded by new products based on various technological innovations. They promise richer and higher-quality lives.

Food products must first be safe so that people can eat with peace of mind, and then they need to be tasty too. The medical world will be revolutionized by iPS cells through regenerative medicine.

The progress of various electric power generation technologies using renewable energy sources such as wind power, solar energy and biomass, will improve the stability of our lives.

Furthermore, the launch of new rocket based on home-grown leading-edge technologies stirred us to expand our dreams to outer space.

What underlines these new technologies and revolutionary products?

Smartphones and electric vehicles use myriad technologies and countless numbers of components.

In other words, components govern product performance.

How are these components and technologies developed?

HORIBA does not manufacture the tangible things you find around you.

What HORIBA does have is the analytical techniques that are indispensable to developing advanced technologies and components.

No advanced technologies or hi-tech components can be created without analytical techniques.

HORIBA's techniques are always there before hi-tech products are developed.

HORIBA's analytical techniques are always hard at work to bring you all the useful devices and safe food products that you find around you, as well as new energy sources.

Yes, we played a role in the taste of that cup of coffee you are probably holding in your hand.

HORIBA Scientific, following light to identify the source of innovation

Carrying on the tradition of commitment to measurement of the founder who invented Japan's first pH meter, HORIBA strives to shed light on the unknown.

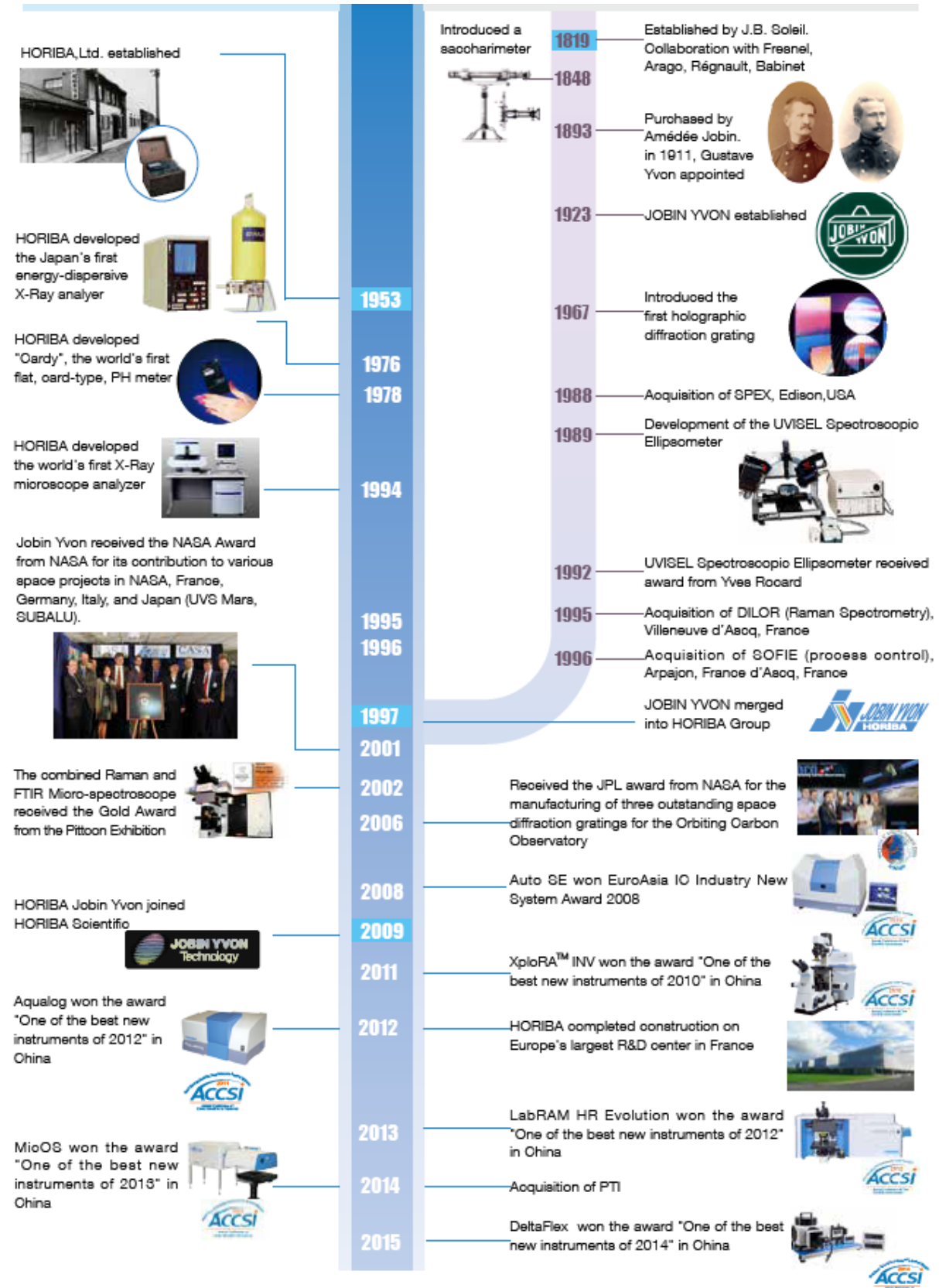
HORIBA Jobin Yvon SAS has spectroscopy technology that covers the entire range of light wavelengths... from infrared rays through visible light and ultraviolet rays to X-rays.

Always one step ahead of high technology - this slogan of HORIBA is also our statement toward researchers working on the global stage, as well as self-admonishment that it is impossible to create anything truly valuable without continuing to stay ahead of technology.



R&D Research Center at Palaiseau, France

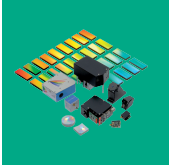
HORIBA Jobin Yvon History Timeline



HORIBA Scientific

Gratings, Original Equipment Manufacturer (OEM) Spectrometers, VUV

Diffraction gratings are the heart of spectroscopic instrumentation. We supply OEM gratings and miniature spectrometers for industrial volume customers who integrate these components into their own instruments. We also manufacture state-of-the-art customized gratings for scientific markets such as synchrotrons, astronomy and high energy lasers. These gratings are installed on the VUV (Vacuum UV) spectrometers that we sell.



Optical Spectroscopy

From the simplest system to the most complicated custom configurations, HORIBA Scientific develops and manufactures optical spectroscopy solutions for research and industry. We offer a wide range of light sources, spectrometers, detectors, readout electronics and application-oriented software.



Typical applications:

Photoluminescence, transmission/reflection, laser pulse characterization, microscopy, imaging, plasma monitoring, NIR spectroscopy...

Raman Spectroscopy, Raman-AFM

Raman scattering provides both chemical composition and molecular structure information in a non-destructive way, without any need for sample preparation. Raman microscopes allow fast acquisition of spatially resolved Raman images.



Combining AFM with Raman spectroscopy enables true nanospectroscopy measurements.

Typical applications:

Pharmaceuticals, material science, biology, polymers, geology, Raman-AFM, TERS, SERS...

Fluorescence

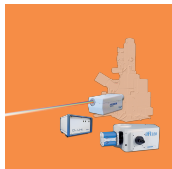
Spectrofluorometry is a highly sensitive technique for the characterization of molecules, molecular interactions and materials. Both steady-state and dynamic (fluorescence lifetime) analysis supply information on concentration, shape and microenvironment of molecules or complex networks (e.g. binding process, membranes, aggregates, ...).



Typical applications:

Biology, pharmaceuticals, material science, photovoltaics, environment, chemistry, polymers...

CathodoLuminescence (CL) for SEM



CL is a fast and non-destructive materials characterization technique to analyze the structural composition and properties of luminescent or optical materials. With high spatial resolution and sensitivity, CL provides high resolution imaging and spectroscopic analysis which allows the detection of trace elements, defects and impurities from FUV to NIR.

Typical applications:

Semiconductors, optoelectronics, dielectrics, ceramics, geology, mineralogy, forensics, life sciences...

Particle Size Analysis

Laser diffraction and dynamic light scattering analyzers are able to determine size and size distribution of particles from 0.3 nanometer to 5 millimeters from samples in powder, suspension or emulsion state. These instruments can incorporate small volume pumping systems for precious materials, high throughput automation, dry powder dispersers and temperature controlled flow systems.



Typical applications:

Nanoparticles, ceramics, polymers, minerals, cement, food, inks, environment, cosmetics, pharmaceuticals...

Surface Plasmon Resonance imaging (SPRi)



SPRi monitors label-free biomolecular interactions in real-time. It provides high-throughput information on kinetic processes (association & dissociation), binding affinity, analyte concentration and molecule detection.

Typical applications:

Antibody screening, high-throughput protein interaction analysis, cell sorting, DNA point mutation investigation...

Forensics

These instruments provide the tools to assist the police with the examination, capture, enhancement and comparison of all types of evidence. In addition to finger and palm prints, evidence can include fingerprints on porous and non-porous surfaces, documents, biology, trace evidence, shoe prints, gun shot residue, bite marks/bruises, human bone fragments, etc.



Typical applications:

Criminology, security...

Your Partner in Science

Spectroscopic Ellipsometry

Ellipsometry is a non-destructive optical technique allowing the accurate characterization of thin films, surfaces and interfaces. Spectroscopic ellipsometry is mainly used to determine thin film thickness (from 1 Å to 30 µm) and optical constants (n,k).

Typical applications:

Material science, photovoltaics, flat panel displays, nanotechnology, semiconductors, optoelectronics, optical coatings, surface characterization...



RF Glow Discharge Optical Emission Spectrometry

RF Glow Discharge Optical Emission Spectrometry (GD-OES) is a fast sputtering technique for applications involving surface and interface analysis of materials and coatings - conductive or non-conductive. It provides quantitative depth profiles of all elements, including light ones with excellent depth resolution and sensitivity.

Typical applications:

Metallurgy, semiconductors, photovoltaics, plasma coating...



Plasma-Profiling Time-of-Flight Mass Spectrometry (PP-TOFMS™)

PP-TOFMS™ offers a powerful, fast and user-friendly characterization tool for advanced multi-layered materials. PP-TOFMS™ provides quantitative depth profiles of all elements (including isotopes) with nanometer depth resolution and ppm to sub-ppm sensitivity.

Typical applications:

Solid-state lighting, microelectronics, photovoltaics, nuclear, corrosion, retro-engineering...



Inductively Coupled Plasma Spectrometry



Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is able to determine elements in virtually all types of samples. It is based on the detection of photons emitted by ions and atoms after excitation by a plasma source.

Typical applications:

Agrochemistry, biology, chemistry, petrochemistry, environment, material science, metallurgy...

Carbon/Sulfur and Oxygen/Nitrogen/Hydrogen Analyzers



These analyzers determine the gases emitted during combustion of the sample by specific non-dispersive infra-red (NDIR) analyzers or thermal conductivity detectors (TCD). These gases are CO, CO₂, SO₂, H₂ and N₂.

Typical applications:

Metallurgy, cement, ceramics, catalysts, battery, soils, solar cell, waste...

Sulfur and Chlorine Analyzers in Petroleum Products



These instruments measure sulfur and chlorine in various petroleum products. The analysis is done using energy dispersive X-ray fluorescence. The determination of Sulfur and Chlorine from 1 ppm to 10 % is obtained by generating characteristics X-rays in liquid samples

Typical applications:

S & Cl in oil, diesel, biofuel, gasoline...

Sample Preparation

Whatever your analytical solutions include, whether it's ICP-OES, ICP-MS, AA, XRF, elemental analyzers..., HORIBA Scientific can provide you many sample preparation devices such as: automatic digestion stations, automatic sample dilution, electric fluxers, grinders, microwave, nickel capsules and pelletizing presses, furnace, heating blocks, and more.



Certified reference materials

Full range of single- or multi-element, inorganic or organic certified reference materials for AA, ICP-OES, ICP-MS, CI... Available in catalogues or customized (matrix and analytes concentration).



ABOUT SOLEIL

SOLEIL, the French synchrotron radiation facility

SOLEIL **explores** matter to better understand its structure and properties, thanks to an extremely brilliant light: the synchrotron radiation. Emitted by electrons circulating almost at the speed of light, this radiation can be used to analyze any sample down to the atomic scale.

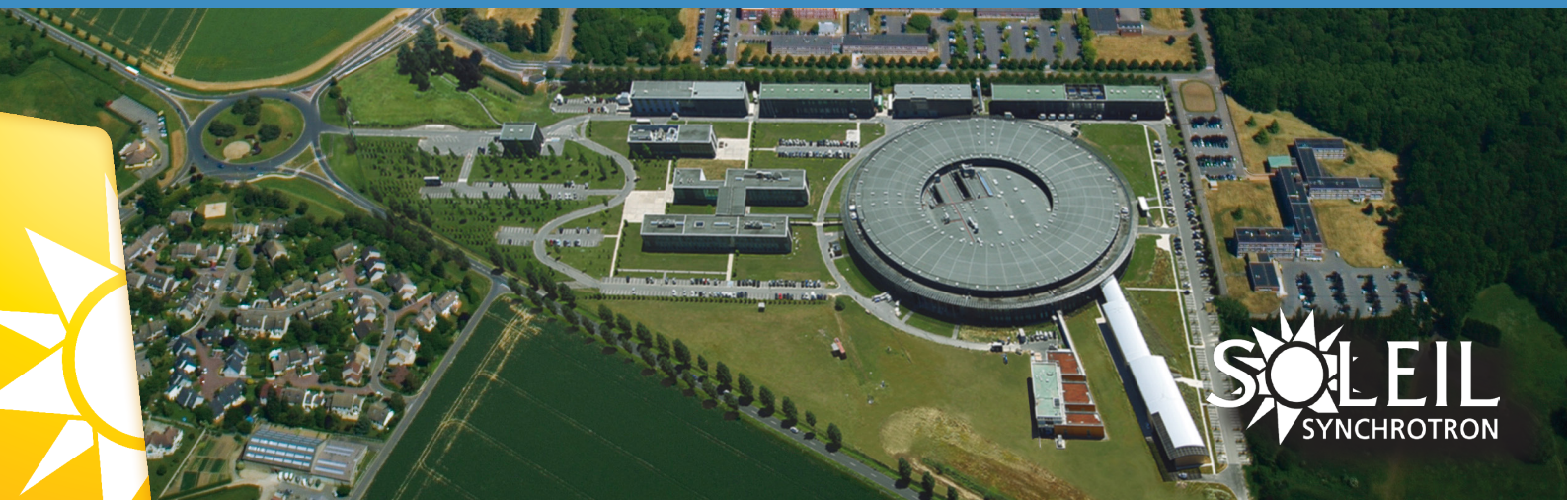
Within the Paris-Saclay scientific and technological cluster, SOLEIL **radiates** across France and throughout the world. The performance of its synchrotron radiation production and matter analysis equipments places SOLEIL amongst the leading large scale research facilities.

SOLEIL is a major **research** center whose groups develop in house or in partnership their own thematic studies on many topics that preoccupy the scientific community today.

SOLEIL also makes its analysis stations or "beamlines" available to scientists working on very varied areas of research, and so accompanies each year more than 2,500 academic or industrial users from around the world.

Whether they are research scientists, industrialists, students or school children, people of all ages with an interest in science are welcomed daily at SOLEIL.

An essential research tool for advances in many different fields.



At the center: an electron accelerator...

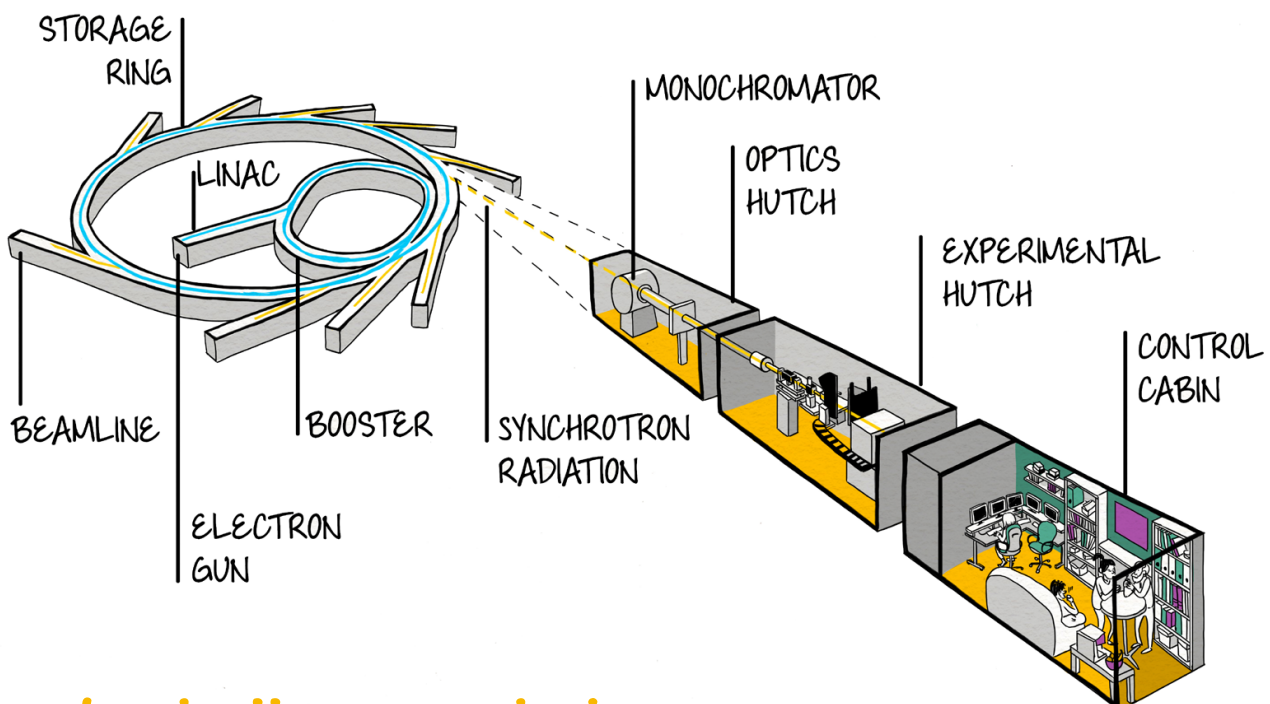
Comparable in size to the Colosseum in Rome, the synchrotron building houses at its center the various high-tech facilities that generate the precious radiation.

Torn from a metal chip the size of a coin, electron bunches are gradually accelerated to nearly the speed of light, hence taken to a very high energy, and then injected into a storage ring with a 354m perimeter where they circulate right round the clock.

Throughout their almost circular path guided by magnetic fields, electrons lose some of their energy as light radiation. At each bend an extremely brilliant light is emitted over a range of wavelengths from infrared to X-rays and covering the visible and ultraviolet ranges.



Here, unlike at the "particle colliders" such as CERN in Geneva, we do not set out to cause collisions between particles: electrons must not stop circulating, so as to create a continuous radiation.



André Bouchard / fr / 2015

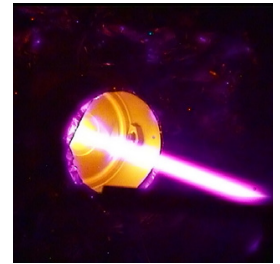
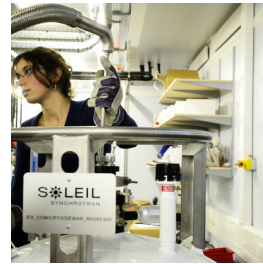
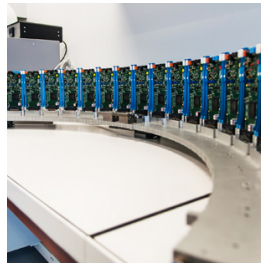
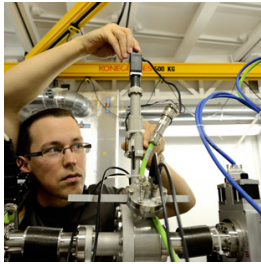
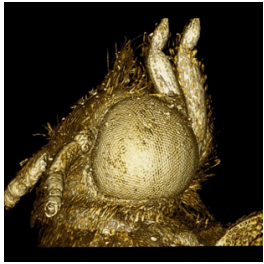
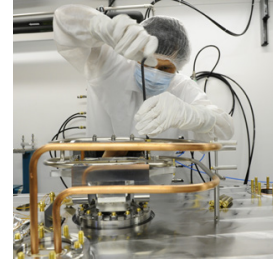
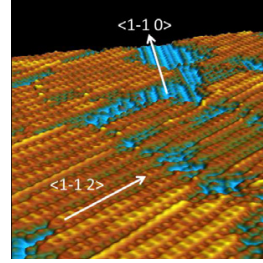
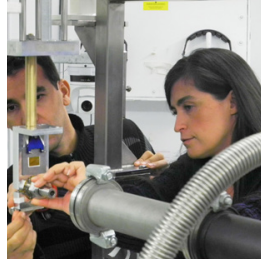
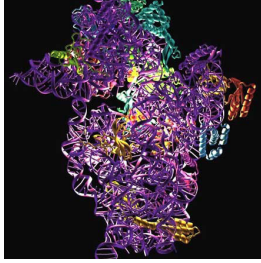
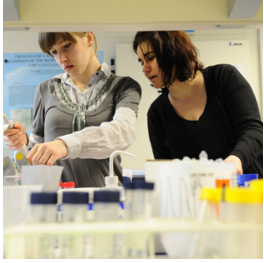
... And all around there are : 29 customized laboratories

While the electrons continue circulating, the radiation they produce is diverted out of the ring at 29 points to be used in 29 "beamlines" built around the electron accelerator.

A beamline is a very specialized laboratory equipped to prepare and analyze samples to study and that can then save and process the data collected. The beamlines are all different, but complementary, designed for specific wavelength ranges, certain analysis techniques and different types of samples. These samples can be solids (surfaces, materials, cells or

living tissue, etc.), gels, liquids or gases, on which light can be focused as a pencil down to a thousand times finer than a hair.

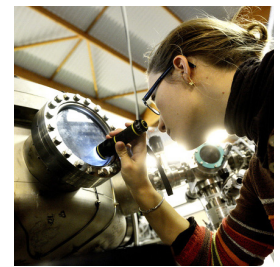
The SOLEIL groups that designed and built the beamlines maintain them and run them every day, to develop their own research topics and host scientists from other laboratories. These external users come to SOLEIL to take advantage of this very high-tech equipment.



The infinitely small within range of the beam

Upon entering the beamline, before arriving on the sample under study, synchrotron radiation passes through different optical systems that select the wavelength and focus it for that experiment. When the extremely bright light reaches the sample, penetrating into the matter composing it, the matter responds, deviating photons, or emitting new photons or electrons. Not in a haphazard way, of course. The quantity, energy and trajectory of these photons and electrons are all essential information.

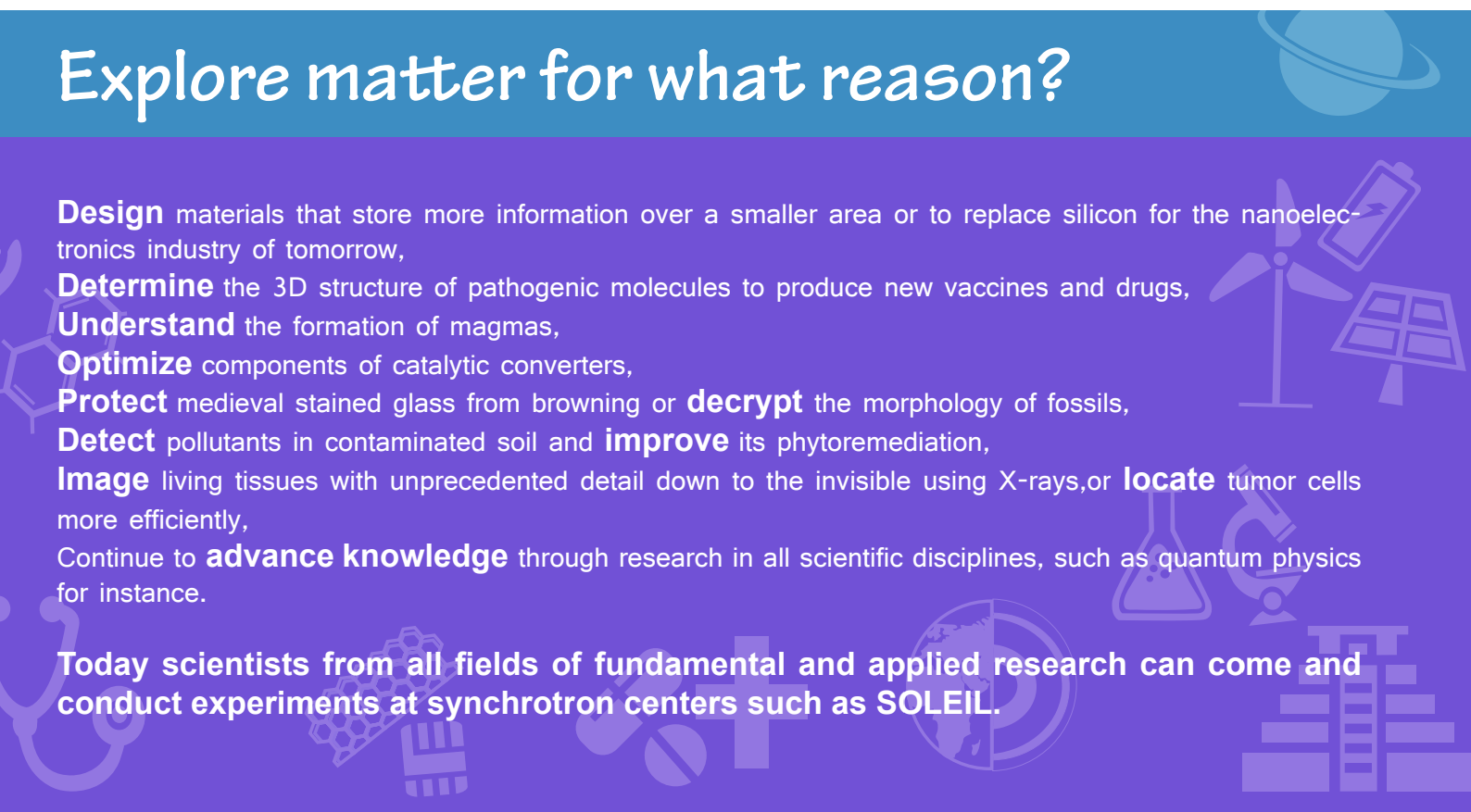
Recorded by very specific detectors, these data are then decoded by researchers, who can deduce the structure and geometry of the surface or in 3D, but also the chemical, electronic and magnetic properties of the sample, right down to the atomic scale.



Explore matter for what reason?

- Design** materials that store more information over a smaller area or to replace silicon for the nanoelectronics industry of tomorrow,
- Determine** the 3D structure of pathogenic molecules to produce new vaccines and drugs,
- Understand** the formation of magmas,
- Optimize** components of catalytic converters,
- Protect** medieval stained glass from browning or **decrypt** the morphology of fossils,
- Detect** pollutants in contaminated soil and **improve** its phytoremediation,
- Image** living tissues with unprecedented detail down to the invisible using X-rays, or **locate** tumor cells more efficiently,
- Continue to **advance knowledge** through research in all scientific disciplines, such as quantum physics for instance.

Today scientists from all fields of fundamental and applied research can come and conduct experiments at synchrotron centers such as SOLEIL.



SOLEIL and its network...

SOLEIL is run as a French civil company founded in 2001 by the CNRS and CEA, which hold 72% and 28%, respectively, of the shares.

The Région Ile de France and the Conseil Départemental de l'Essonne contribute to the project and are essential partners. The Région Centre-Val de Loire is also strongly associated with SOLEIL.

French national education, French and foreign universities, foundations, clusters, industrial users ... SOLEIL has a broad network of partners, including, since its creation, the Paris-Saclay University.

SOLEIL synchrotron also has scientific and technical collaborations and close links with other synchrotrons in Europe and around the world.



They encounter each other at SOLEIL each year

- 350 permanent staff, including 150 researchers and nearly 60 other professions, from technicians (CAP) to post-graduates
- About 2,500 external users from academic and industrial backgrounds, to whom time is allocated on the beamlines (i.e. from the opening of SOLEIL to users in 2008, there has been a total of 25,000, from nearly 1,800 laboratories)
- More than 5,000 visitors from all countries and walks of life: schools, general public, industrialists, researchers and officials ...

SOLEIL in figures

- A construction budget of 400 million euros, about the price of an Airbus A380
- A building 185 meters in diameter (equivalent to 2 football fields), on a 16 hectare site
- 29 beamlines measuring between a few tens up to 200 meters long
- A power consumption of 6 MW, equivalent to that of a town of 8,000 inhabitants
- Light beams stable to 1/1000 mm over several meters
- 5,000 hours of synchrotron radiation delivered per year for experiments on beamlines
- 40% of "beamtime" requests by external users accepted
- 500 scientific articles published annually on the results obtained at SOLEIL

8th International GD Day

Program

Thursday 15 September 2016

13:30 GD Day - Session 1

Chair: Yuriy Popov, HORIBA, Moscow, Russian Federation

- 13:30 **O1** Introduction of the GD Day
P. Chapon, HORIBA Scientific, France
- 13:50 **O2** Possibilities and limitations for analysis of chemical depth profiles in CdTe thin film solar cells
O. Zywitski, FEP, Germany
- 14:10 **O3** Development and characterization of coatings on selected metals and alloys obtained by plasma electrolytic oxidation
K. Rokosz, University of Koszalin, Poland
- 14:30 **O4** Plasma profiling TOFMS analysis for microelectronic applications
Y. Mazel, CEA Leti, France

14:50 GD Day - Session 2

Chair: Patrick Chapon, HORIBA Scientific, Longjumeau, France

Poster talks (3 min/poster) and workshops presentation

- P1** Breakthrough on GDOES analysis applied to rough metal surfaces
S. Cremer, Arcelor Mittal, France
- P2** Influence of CIGS surface conditioning on GDOES depth profile measurement results
W. Hempel, ZSW, Germany
- P3** Depth profiling protective coating titanium nitride based on glow discharge optical emission spectrometry
A. Batrakov, MPEI, Russia (Presented by A. Kuznetsov)
- P4** Depth profiling of Zr-Nb alloy after plasma immersion Titanium implantation and Hydrogen saturation
T. Priamuskhov, University of Tomsk, Russia
- P5** Use of complementary techniques for depth profiling of mobile screen protection covers
B. Bleisteiner, HORIBA Scientific, Germany (Presented by S. Gaiaschi)
- P6** The use of GDOES in failure analysis and quality control
A. Raffaelli, University of Udine, Italy
- P7** Ferroelectric materials with Tetragonal Tungsten Bronze (TTB) type structure: Synthesis and characterization
A. Laaraj, LIMAT University of Casablanca, Maroc
- P8** Pulsed radiofrequency glow discharge time of flight mass spectrometry for VOCs analysis: Development of a new source
N. Bordel, University of Oviedo, Spain
- P9** Improvement of inorganic gas diffusion barriers by a low energy Ar plasma treatment
J.E. Bourée, PICM, France
- W1** DIP workshop
S. Gaiaschi, HORIBA Scientific, France

- P10** Bulk analysis of trace elements in pure Au and Ag by Profiler HR
V. Galuschenko, Moscow Mint, Russia
- P11** Smart solid sample analysis - Some examples for direct analysis by electrothermal vaporisation as add-on for ICP
P. Perzl, Spectral Systems, Germany
- P12** Surface sample preparation for EPMA using GDOES
S. Khromov, NTNU, Norway
- P13** Optical characterization of thin films by spectroscopic ellipsometry
J.P. Gaston, HORIBA Scientific, France
- P14** A new film thickness measurement technique: Differential Interferometric Profiling - Similarities and complementarities with ellipsometry
O. Acher, HORIBA Scientific, France
- P15** Characterization of CIGS solar cells through glow discharge optical emission spectrometry and differential interferometry profiling
S. Gaiaschi, HORIBA Scientific, France
- P16** Synergy of GD-OES & DIP with EDXRF techniques for layers thickness and elemental composition determination
J. Marciano, HORIBA Scientific, France
- P17** Antifungal activity against *Candida albicans* biofilm of composite layers based on silver doped hydroxyapatite-polydimethylsiloxanes
C.S. Ciobanu, NIMP, Romania
- P18** Structural and antimicrobial properties of silver doped hydroxyapatite thin films deposited on PDMS/Si
C.L. Popa, NIMP, Romania
- W2** HORIBA Device Monitor (HDM) applied to GDS
Y. Popov, HORIBA, Russia
- P19** Using power coupling efficiency for ALD thin film oxides quantification.
D. Frey, EMPA, Switzerland
- P20** Presentation of a calibration kit for GDOES
N. Higa, HORIBA, Japan
- P21** Preparation of nanoparticle-based composite coatings
O. Sublemontier, CEA, France
- P22** Evaluation of inhibitory effect of glycerol-iron oxide layers on MRSA
S.L. Iconaru, NIMP, Romania
- P23** XPS analysis of native oxide layers on GaSb (100) surface – Application to depth profiling of AuGeNi/n-GaSb
R.V. Ghita, NIMP, Romania
- P24** Neon plasma jet at atmospheric pressure. Spatio-temporal distribution of ambient air species
L. Chauvet, University of Toulouse, France
- P25** Neon plasma jet at atmospheric pressure. Application to mass spectrometry detection of volatile samples
L. Thérèse, University of Albi, France

8th International GD Day

- P26** Structural and biological evaluation of iron oxide-dextran nanostructures thin films
S.A. Predoi, ICHB, Bucharest, Romania
- P27** Improving layer thickness determination by the combination of depth profile modeling and DIP
M. Laquitaine, ENSSAT, Lannion, France
- P28** Optimizing GDOES sputtering of metal/polymer multilayer systems by plasma gas switching during the test
A. François-Heude, Vallourec Research Center France, France
- W3** HJY Service for GD
R. Toutain, HORIBA Scientific, France
- P29** New strategies to improve the analytical performance of pulsed glow discharge time of flight mass spectrometry
L. Lobo, University of Oviedo, Spain
- P30** Glow discharge optical emission spectrometry and differential interferometry profiling for thickness determination of SiO_xN_y layers
S. Gaiaschi, HORIBA Scientific, France
- P31** Characterization and corrosion behaviour of pure titanium in sulfuric medium
S. Dubent, CNAM Paris, France
- P32** GD-OES crater engineering: the challenge of wet chemical and/or Ar cluster sputtering curing for nanometric XPS analyzes
A. Loubat, ILV, France
- P33** GD group on LinkedIn.
V. Naik, ASE India
- P34** Scaling laws between mono and multi-point configuration in positive DC corona discharge in air
D. Raouti, University of Saida, Algeria
- P35** Measurement of homogeneity of reference materials of special alloys by GD - atomic emission spectrometry
I. Ermakova, Vniiofi Russia.
- P36** Corrosion product films on Mg alloys
P. Volovitch, ENSCP, Paris, France
- P37** Local electrochemical techniques used for spatially-resolved surface analysis
S. Verret, Bio-Logic SAS, Seyssinet-Pariset, France
- P38** On-line measurement of the reactivity of Al-Li alloy during a surface pretreatment sequence
O. Gharbi, Institut de Recherche de Chimie Paris, France
- P39** Reserved

17:30 Coffee break, poster session and Synchrotron visit

19:20 Cocktail

19:45 Gala Dinner at the Synchrotron Restaurant

8th International GD Day

Friday 16 September 2016

9:00 GD Day Session 3

Chair: *Sofia Gaiashi, HORIBA Scientific, Longjumeau, France*

- 9:05 **05** Novel use of glow discharge optical emission spectroscopy (GDOES) to study corrosion of AA2024 T3 in the presence and absence of inhibitors
R. Bingham, University of Manchester, UK
- 9:30 **06** Challenge on depth profiling characterizations by combining GD-DIP and XPS: The absolute GGI determination!
A. Loubat, ILV, France
- 9:55 **07** Electrochemical analyses of intermetallic layers in Zn/Mg coating exposed by controlled GD sputtering of the coating
A. Lanzutti, University of Udine, Italy
- 10:20 **08** Ionic migration of perovskite film studying by GDOES system
H. Lee, PICM, France

10:45 Coffee break and poster session

11:15 GD Day Session 4

Chair: *Olivier Acher, HORIBA Scientific, Palaiseau, France*

- 11:20 **09** Applications of GD-TOFMS for direct analysis of innovative materials
J. Pisonero, University of Oviedo, Spain
- 11:45 **010** Characterization of zinc-rich layers on aluminium
M. Stepanova, NTNU, Norway
- 12:10 **011** GDOES studies of minor alloying elements incorporation into oxide scales during high temperature oxidation of Ni-based superalloys
W. Nowak, Rzeszow University, Poland

12:35 Lunch and poster session

14:40 GD Day Session 5

Chair: *Simon Richard, HORIBA Scientific, Palaiseau, France*

- 14:45 **012** Hydrogen PEM electrolysis: Used of GD-OES for fast characterization of innovative coating
N. Queromes, Areva, France
- 15:05 **013** Magnetically boosted glow discharge optical emission spectroscopy for analytical applications: Pros and cons
N. Bordel, University of Oviedo, Spain
- 15:25 **014** Characterization of thin films on glass by GD-OES
H. Montigaud, St Gobain, France
- 15:45 Round Up & Conclusion of the 8th GD Day.

16:00 End of the 8th GD Day

8th International GD Day

Conferences

O1

Recent Developments & Applications in GDOES

P. Chapon, S. Gaiaschi, Y. Popov

HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

patrick.chapon@horiba.com

Following a brief welcome message to the 8th GD Day with practical information on the agenda of the event, an introduction review on recent developments and applications – some being illustrated in various presentations of the program – will be made.

Highlights will be pulsed operation, DIP, UFS and software functions.

O2

Possibilities and Limitations for Analysis of Chemical Depth Profiles in CdTe Thin Film Solar Cells

Olaf Zywitzki, Richard Belau

Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP,
Winterbergstrasse 28, 01277 Dresden, Germany

olaf.zywitzki@fep.fraunhofer.de

The efficiency of CdTe thin film solar cells depends on the amount of solar light absorption, effective separation of generated charge carriers and low barriers at electrical contacts. These different requirements on CdTe thin film solar cells are significantly influenced by chlorine, sulfur and copper diffusion processes during necessary thermal treatments. The aim of our GD-OES investigations was to optimize the depth resolution and the detection limits for all elements of interest. For this purpose the effect of sputtering power, duty cycle and sputtering pressure was investigated. The remaining limitations for the depth resolution are the roughness of the layers itself and the significant different sputter rates between metallic back contact layer, CdTe absorber layer, CdS buffer layer, fluorine doped SnO₂ front contact and float glass substrate.

The results have shown that the chlorine diffusion during a thermal activation treatment with CdCl₂ depends mainly on the as deposited CdTe microstructure. For a columnar microstructure with small grains a significant higher amount of chlorine was detected in comparison to a block-like microstructure with large grains. In addition a chlorine peak can be detected within the thin CdS buffer layers. These can be explained by the faster grain boundary diffusion in comparison to the bulk diffusion.

Simultaneously, sulfur diffusion from CdS layer into the CdTe layer could be detected by GD-OES depth profiling, which reduces the band gap of the CdTe layer and the CdS layer thickness. These effects increase the quantum efficiencies in short -and long- wavelength range of spectrum. The investigation of copper doping at the back contact of the solar cells by GD-OES is very challenging because of the low concentrations and some line interferences. Nevertheless some interesting results can be also obtained by these investigations. All results show that GD-OES depth profiling is a powerful method for a better understanding of the occurring diffusion processes and thus for further optimization of CdTe thin film solar cells.

O3

Development and Characterization of Coatings on Selected Metals and Alloys Obtained by Plasma Electrolytic Oxidation

Dr Krzysztof Rokosz

Koszalin University of Technology, Koszalin, Poland

rokosz@tu.koszalin.pl

Plasma Electrolytic Oxidation (PEO) is also known as Micro Arc Oxidation, Micro Arc Discharge Oxidation, Micro Plasma Oxidation, Anodic Spark Deposition, Anodic Spark Oxidation as well as Spark Anodizing.

That treatment is widely used to create the porous coatings on light metals and their alloys, such as aluminum, magnesium and their alloys as well as on biomaterials such as titanium, niobium, tantalum, zirconium and their alloys. All the PEO processes on titanium and its alloys as well as on niobium were performed at two voltages of 180 V and 450 V, respectively, during three minutes of treatment in the electrolyte based on orthophosphoric acid H_3PO_4 within copper nitrate $Cu(NO_3)_2$.

It has been found that the thickness of the coating and its chemical composition depend both on the electrolyte composition and the PEO potential. It was also recorded that the higher PEO potential was used, the thicker coating was obtained. The copper inside the coating appeared as Cu^+ and Cu^{2+} ions, while titanium, niobium and zirconium appeared as Ti^{4+} , Nb^{5+} and Zr^{4+} , respectively. Additionally, it must be pointed out that three sub-layers, i.e. outer (porous), inner (semi-porous), and transition (adjacent to the matrix) may be separated in the PEO coating formed on all metals and alloys.

Plasma Profiling TOFMS Analysis for Microelectronic Applications

Yann Mazel¹, J.-P. Barnes¹, E. Nolot¹, S. Legendre², A. Tempez²

¹ Univ. Grenoble Alpes, F-38000 Grenoble, France
CEA, LETI, MINATEC Campus, F-38054 Grenoble, France

² HORIBA Scientific, Avenue de la Vauve, Passage Jobin Yvon, 91120 Palaiseau, France

yann.mazel@cea.fr

A direct chemical depth profiling technique is key for materials innovation (development and process) in current strategic technologies (micro and nanotechnology, energy, industrial renewal, information and communications, quality of life..).

Plasma profiling time of flight mass spectrometry (PP-TOFMS) combines a pulsed radio frequency glow discharge source with an orthogonal time of flight mass spectrometry (P-RF-GD-oTOFMS). It has been demonstrated as a potentially high throughput method for the characterisation of a variety of multilayered materials including nano-structures¹⁻³. This instrument is actually a major breakthrough as it changes the way surface and depth profiling analysis is regarded, being ultra fast, easy to use and low cost. This instrument has been installed in the cleanroom of the CEA LETI and is being tested for a broad panel of microelectronics materials.

Results obtained on thin conductive oxides (doped zinc oxide) and novel chalcogenides materials will be presented, amongst other microelectronic materials. The PP-TOFMS profiles will be compared with TOF-SIMS depth profiles, performed on the platform for nanocharacterisation (PFNC) at the CEA Grenoble. Aspects of composition determination, dopant quantification, and interface monitoring will be discussed.

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O5

Novel Use of Glow Discharge Optical Emission Spectroscopy (GDOES) to Study Corrosion of AA2024 T3 in the Presence and Absence of inhibitors

Ruth Violet Bingham, George Thompson

Corrosion and Protection Centre, School of materials, The University of Manchester, Manchester M13 9PL, UK

djmillspace@gmail.com

Recent interest in environmentally-friendly alternatives to chromate-based corrosion inhibitors has led to the development of a range of novel coating formulations. The work described herein is aimed at developing a novel methodology for investigating the mechanism of self-healing and active corrosion protection of the new coatings.

An experimental procedure has been developed to model a defect in the coating by fixing coated specimens in close proximity to the uncoated AA2024 T3, each separated by a narrow gap containing sodium chloride solution. After exposure to the corrosive environment, elemental depth profiles of the uncoated specimens were acquired by glow discharge optical emission spectroscopy (GDOES). The depth profiles of selected elements (notably aluminium, oxygen and copper) were shown to have characteristics which can be correlated with surface roughening/intensity of corrosion, thickness of the corroded layer and de-alloying/redistribution of copper. An unanticipated inhibitory effect was noted in the case of a coating doped with $\gamma\text{-Al}_2\text{O}_3$ (γ -alumina or AluO_x). The study was then extended to the detection of corrosion inhibitors deposited in the model defect

Challenge on Depth Profiling Characterizations by Combining GD-DIP and XPS: The Absolute GGI Determination!

Anaïs Loubat¹⁻², Sofia Gaiaschi³, Muriel Bouttemy², Mathieu Frégnaux², Damien Aureau², Jackie Vigneron², Arnaud Etcheberry²

¹ Institut Photovoltaïque d'Ile-de-France (IPVF), 8 rue de la renaissance, 92160 Antony, France

² Institut Lavoisier de Versailles (ILV), UMR 8180 CNRS-UVSQ, IPVF, 78035 Versailles, France

³ HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

anais.loubat@ipvf.fr

The CIGS (Cu(In,Ga)Se₂) thin film absorbers are good candidates for high yield photovoltaic cells. It is well known that the device performance mainly rely on the absorber properties and in this context, its fine optimization requires an accurate chemical characterization of surface, volume, back and front interfaces. Indeed, the possible variations in composition, impurities diffusion and interfaces nature are three critical points that influence the final device performance. Especially for CIGS absorbers, the control and determination of the gallium gradient, through the $GGI = Ga/[Ga+In]$ ratio determination, is a key parameter.

Multiple chemical characterization techniques can be applied to achieve the absolute GGI determination. Among them, GD-OES is convenient for obtaining the fast elemental depth profile. This technique relies on the fast sputtering (typically several $\mu\text{m}/\text{min}$) of a representative area of the sample by a high density and low energy RF plasma. An excellent depth resolution can be obtained, depending on the surface roughness. Moreover, one of the most recent advances in GD-OES is the real time measurement of the sputtered crater depth thanks to the addition of a Differential Interferometry Profiling (DiP) within the GD-OES source. This module gives a direct access to layer thickness and erosion rates.

In this work, the characterization by GD-OES-DIP of chemically etched CIGS samples was performed for the first time and coupled with XPS surface characterizations. Indeed, a previous study has shown the strong complementarity and potential of GD-OES and XPS coupling [1]. Furthermore, the CIGS samples are particularly challenging for DiP and XPS as they are possibly rough, partially transparent and oxidized at the surface. Different etching times on different samples were investigated by XPS//GD-OES coupling. Roughnesses have been checked by AFM measurements and CIGS layer thicknesses by GD-DIP//ICP-OES and profilometer. Thanks to this approach, two main information were highlighted: The impact of surface roughness on the layer thickness determination with DiP and the absolute determination of GGI ratio all over the CIGS layer by XPS and GD-OES coupling.

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Acknowledgements

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07

Electrochemical Analyses of Intermetallic Layers in Zn/Mg Coating Exposed by Controlled GD Sputtering of the Coating

A. Lanzutti¹, F. Andreatta¹, J.Rodriguez², M. Mouanga², L. Fedrizzi¹, M.-G. Olivier²

¹ University of Udine, Department of Chemistry Physics and Environment,
Via del Cottonificio, 108-33100 Udine, Italy

² University of Mons - UMONS, Faculty of Engineering Materials Science Department,
Place du Parc, 20 - 7000 Mons, Belgium

alex.lanzutti@uniud.it

The GD instrument is a powerful tool to analyze the elemental distribution of different types of coating, including diffusive coatings. This provides information on the chemical composition as a function of depth. In the last years, this instrument was also used to produce craters at a precise depth in the coating in order to expose regions of material that could be analyzed by other experimental techniques. This experimental approach has been followed for the investigation of diffusive Zn/Mg coatings by the complementary use of the GD instrument and surface analysis and local electrochemical techniques. These coatings are considered for application in the automotive industry since the addition of magnesium into the metallic coating allows to improve corrosion resistance without increasing coating thickness.

In this work the GD instrument was used as a tool to expose each layer of the Zn Mg coating by plasma sputtering in order to investigate the electrochemical behavior of the coatings. Qualitative/quantitative profiles obtained by GDOES analyses were compared with the accuracy of the plasma erosion, each crater was analyzed by SEM in cross section. The different coating layers exposed in the GD craters underwent electrochemical characterization by means of electrochemical micro cell. SVET analyses were also carried out on regions of the sample surface containing GD craters.

The results obtained by the complementary use of GDOES, surface analysis and electrochemical techniques highlighted the possibility to determine the corrosion behavior of each exposed layer. This is important in order to determine the corrosion protection mechanism of Zn/Mg coatings.

Ionic Migration of Perovskite Film Studying by GDOES System

Heejae Lee¹, Heeryung Lee¹, Arthur Marronnier¹, Denis Tondelier¹, Bernard Geffroy^{1,2} and Yvan Bonassieux¹

¹ LPICM, Ecole polytechnique, CNRS UMS-7647, 91128 Palaiseau, France

² LICSEN, CEA Saclay, 91191 Gif Sur Yvette, France

heejae.lee@polytechnique.edu

In recent years, the perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) solar cells have been studied steadily due to their potential properties: low-cost processing and possibility to produce large area in a fast by low temperature processes.¹ The perovskite film has a crystalline structure. Many different solvents are being developed and gradually adopted for high-performance inorganic-organic hybrid perovskite solar cells. In this study, 12.7% of power conversion efficiency (PCE) is obtained by the solution-processed perovskite solar cells (PSCs) with 21.9 mA/cm² of short circuit current (J_{sc}).

However, the PSCs have several unusual characteristics in current-voltage curve, such as hysteresis. Many reasons were reported to explain and the ionic migration (I, Cl or MAI) is one of the reasons of the hysteresis.² In this study, the GDOES measurement was used to verify the ionic migration in perovskite film by applied voltage. As figure 1, we can check the shift of Cl and I distribution in perovskite film depending on applying voltage.

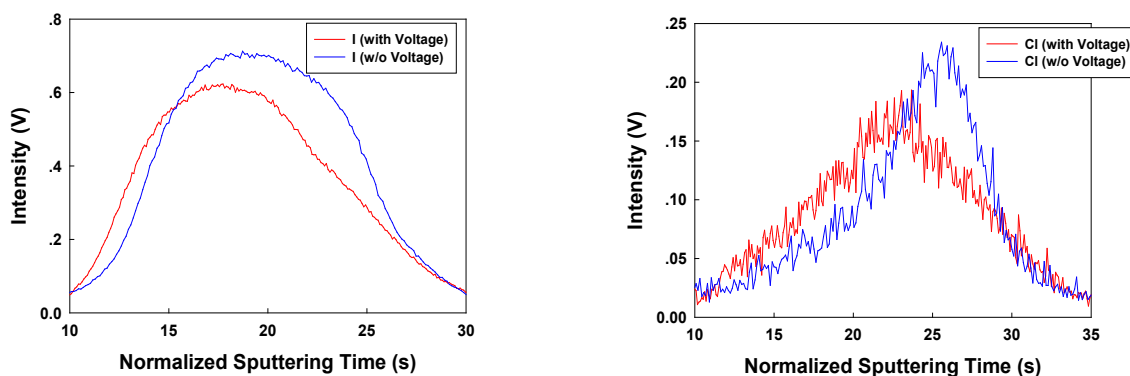


Figure 1: The GDOES measurement result of perovskite film depending on voltage; (a) I, (b) Cl ionic migration can be studied, respectively.

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Applications of GD-TOFMS for Direct Analysis of Innovative Materials.

Jorge Pisonero¹, Cristina González¹, Jonatan Fandiño¹, Alfredo Sanz-Medel² and Nerea Bordel¹

¹ Department of Physics, University of Oviedo, Escuela Politécnica de Mieres, 33600, Spain;

² Department of Physical and Analytical Chemistry, University of Oviedo, Faculty of Chemistry, 33007, Spain;

pisonerojorge@uniovi.es

Manufacturing industry requires the development and characterization of challenging materials (e.g. photovoltaic cells, production of high wear-resistant coatings, hard-disks, Ni and Co super-alloys, etc.). In this context, the ability to accurately analyse and characterise bulk and layered materials is essential to the development of new products and processes.

Atomic spectrometry techniques have long been used for elemental chemical characterization. In particular, for the analysis of layers and coatings, a range of techniques is available, including Secondary Ion Mass Spectrometry (SIMS), Secondary Neutral Mass Spectrometry (SNMS), Auger Electron Spectroscopy (AES) or X-Ray Photoelectron Spectroscopy (XPS). These techniques provide very valuable information about the chemical composition of the surfaces/coatings; however they also have some major drawbacks, such as high operating costs, complex sample pre-treatment and handling, low sample throughput and/or severe matrix effects that result in difficult quantification procedures. In order to overcome some of these drawbacks Glow Discharge Time-of-Flight Mass Spectrometry is proposed as a complementary methodology that provides an ideal solution for fast and accurate bulk and layer analyses [1,2].

In this work, we evaluate the advantages and limitations of this technique and we discuss about recent progresses and new applications.

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O10

Characterisation of Zinc-rich Layers on Aluminum

M. Stepanova¹, O. Lunder^{1,2}, J.H. Nordlien^{1,3}, K. Nisancioglu¹

¹ Department of Materials Science and Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

² SINTEF Materials and Chemistry, NO-7465 Trondheim, Norway

³ Sapa Precision Tubing, Precision Tubing Technology Centre, NO-4265 Håvik, Norway

mariia.stepanova@ntnu.no

Zn-rich layers, formed by thermal-arc spraying of Zn followed by heat treatment for inward diffusion, are widely used for protection of Al alloys against pitting corrosion [1-4]. However, the effect of the Zn concentration depth-profile on the corrosion properties has not been much studied. The purpose of this work is to investigate the feasibility of using glow discharge optical emission spectroscopy (GD-OES) for rapid quantitative determination of Zn depth profiles in such layers, although the calibration of the instrument for the Al-Zn system is reported to be particularly difficult due to a large difference in the Ar-sputtering rates of Al and Zn [5].

Five AlZn binary standards with concentrations varying from 7 to 95 wt% Zn were cast from high purity (99.99%) components. Other certified standards were also available for Al alloys. Calibration was performed based on the theory of relative sputtering rates [6]. Zn thermal-arc sprayed coatings on 3XXX-series aluminium alloy were subjected to heat treatment at various temperatures and durations to produce Zn-rich layers with varying Zn levels and depth profiles. These were examined by GD-OES, scanning electron microscopy and X-ray energy dispersive spectroscopy.

The results show that GD-OES calibration of the AlZn system is possible even by a limited number of AlZn standards covering entire concentration range of the system. Calibration of additional alloying elements is also possible. The accuracy depends on the choice of the spectral lines and the errors introduced in determining the sputtering rates of the standards. The Zn-rich layers produced had thicknesses varying from 35 to 80 μm . The measured Zn concentration profiles were correlated by use of solutions to Fick's 2nd law, which resulted in the estimation of effective diffusion coefficients for Zn in Al in the temperature range from 350°C to 430°C. The diffusion coefficients were in turn correlated with respect to the Arrhenius law. This was possible despite the fact that the as-sprayed Zn coating and produced Zn-rich layers are non-uniform. Surface profiling also showed that, with increasing temperature and time of heat treatment, increasing amounts of the constituent elements Fe, Mn, Si and Mg of the Al alloy substrate become incorporated into the layer.

Acknowledgments

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O11

GD-OES Studies of Minor Alloying Elements Incorporation Into Oxide Scales During High Temperature Oxidation of Ni-based Superalloys

W. Nowak¹, **B. Wierzba**¹, **J. Sieniawski**¹, **A. Jalowicka**², **D. Naumenko**²,
and **W. J. Quadakkers**²

¹ Department of Materials Science, Faculty of Mechanical Engineering and Aeronautics, Rzeszow University of Technology, al. Powstancow Warszawy 12, 35-959 Rzeszow, Poland

² Institute for Energy and Climate Research, IEK-2, Forschungszentrum Jülich GmbH, 52425, Jülich, Germany

w.nowak@prz.edu.pl

Ni-base superalloys are commonly used in the hottest sections of aeroengines and power generating gas turbines due to a combination of excellent mechanical properties at elevated and room temperature and exceptional high-temperature corrosion and oxidation resistance. For obtaining improved mechanical properties, in particular grain boundary strengthening, modern Ni-based superalloys contain minor additions (between 0.01 and 1 at %) of elements such as Hf, Zr or B. However, these minor elements can participate in the oxidation process due to their high affinity to oxygen. The oxidation of the mentioned elements leads to their depletion from the alloy and might result in a change of the mechanical properties.

Analysis of the light elements like e.g. B in the oxide scale and alloy using SEM/EDX is difficult because of the small precipitate size of the formed oxides, low concentration and low peak intensity in the EDX spectra.

For investigating the behaviour of the mentioned minor alloying elements, especially B, during high temperature oxidation, selected Ni-based alloys were exposed at 1050°C up to 100 hours in oxidizing atmospheres. The post-exposure investigation included a number of analytical methods such as glow discharge optical emission spectroscopy (GD-OES), light optical and scanning electron microscopy as well as X-ray diffraction.

It is shown that GD-OES is a powerful tool for the analysis of minor alloying elements such as B in the oxide scales, which provides the data necessary to elucidate the corresponding oxidation mechanisms, types of formed oxides as well as indirect estimation of elements depletion.

O12

Hydrogen PEM Electrolysis: Used of GD-OES for Fast Characterization of Innovative Coating

Nicolas Quéromès

Société AREVA H2Gen, 8 avenue du Parana, 91940- Les Ulis

nicolas.queromes@arevah2gen.com

The collaborative project « Novel materials and system designs for low cost, efficient and durable PEM (Proton exchange Membrane) electrolyser » is a 4-years project within the framework of the European Joint Undertaking Hydrogen and Fuel Cells (FCH JU). It has started in September 2012 under the coordination of SINTEF (Norway).

Partners from industry and research center work together to deal with different aspects of PEM electrolysis as membrane and catalyst development, coatings of bipolar plates and current collectors etc. GD-OES is a very suitable technic for fast investigation of new coating and material developed within the project.



<https://www.sintef.no/projectweb/novel>

O13

Magnetically Boosted Glow Discharge Optical Emission Spectroscopy for Analytical Applications: Pros and Cons

J. Pisonero, N. Bordel

Physics Department, University of Oviedo, 33006 Oviedo, Spain

bordel@uniovi.es

Low pressure radiofrequency glow discharge (rf-GD) sources, coupled to either optical emission spectroscopy (OES) or to mass spectrometry (MS), are powerful techniques for direct solid analysis of materials. Nevertheless, there is still a great interest in the development of new approaches to further improve the sensitivity and depth profile capabilities of this technique. In this sense, the application of external magnetic fields (e.g. magnetically boosted GD) has been shown to produce enhancements in the excitation and ionization efficiencies of the GD plasma. The combination of an external magnetic field and the electric field applied between anode and cathode, causes the electrons circulate around the magnetic field lines, and thus the electron residence time in the plasma is enhanced, which leads to a substantial increase in the collision probability [1].

Several works have shown that sensitivity improves when using magnetically boosted glow discharges coupled to optical emission spectroscopy [2-3] although this combination have not yet been fully exploited for analytical purposes. The possible degradation of the crater shapes and, as a result, a worsening of the resulting depth resolution when layered samples are analyzed can be behind this lack of practical applications.

But, on the other hand, it has been demonstrated that, when using magnetic fields stronger than a given threshold, sensitivities can enhance more than one order of magnitude. Therefore a critical evaluation about the benefits and drawbacks of using magnetic fields in combination with GD-OES is needed in order to set the application niche of the magnetically boosted GDOES.

This presentation will show the state of the art of this technique and possible developments to take advantage of the enhanced sensitivities achieved.

Acknowledgements

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O14

Characterization of Thin Films on Glass by GD-OES

H. Montigaud

Surface du Verre et Interfaces
UMR 125 CNRS/Saint-Gobain, Aubervilliers, France

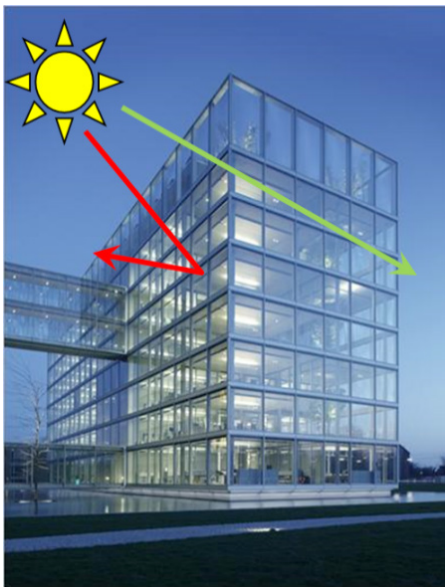
herve.montigaud@saint-gobain.com

Saint Gobain produces high performance glazing combining interesting optical properties such as transparency and high thermal isolation based on IR reflection. These functionalities are obtained by the addition of thin layers stack at the glass surface. The number of the layers can reach 20 and their thicknesses are in the range 0.3 nm to 50 nm. These stacks of coatings, deposited industrially by PVD process have to present homogeneous performances on the whole surface of the 6 x 3.2 m² flat glass substrate. This need to control the stack at the nano-scale in terms of thickness, composition, gradient...

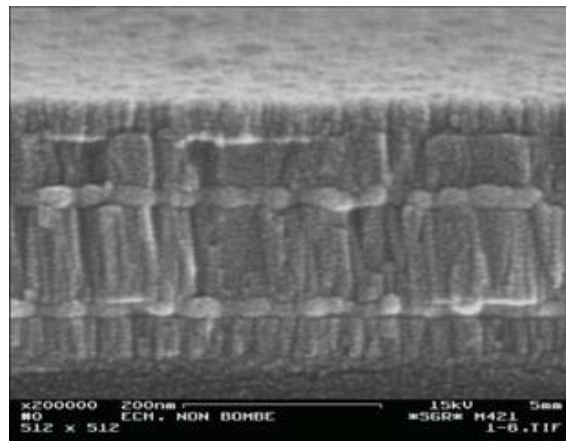
The characterization of the stack is performed by techniques such as SIMS (depth profiling), SEM (largest thicknesses, defect), TEM (thickness, local composition, crystallinity)...

Regarding its specific advantages, high erosion rate (1 $\mu\text{m}/\text{min}$) combined with a depth resolution in the nano scale, GD-OES is an interesting technique for the analysis of these thin coatings at glass surface.

The presentation presents some examples of characterization of optical stacks. The results are compared with those obtained with other techniques and elements are proposed to explain the differences observed.



SG Solar Control product



Solar control stack : example of SEM picture from cross section

O

Hydrogen Enhanced Oxidation - Atomic Scale Simulation and Experimental Evidences-

Tetsuo Shoji, Nishith Kumar Das and Jian Xu

Frontier Research Initiatives (FRI) on Long-term Materials Reliability,
New Industry Creation Hatchery Center
Tohoku University, Sendai, Japan

tshoji@fri.niche.tohoku.ac.jp

It is well known that the most of the structures and equipments show some kind of aging degradation in service and may cause some failures of critical components to cause serious accidents. Therefore, an extensive efforts have been paid to inspect and to evaluate these ageing degradation. One of the most common degradation is oxidation related degradation such as, for example, general corrosion (GC), pitting corrosion (PC), stress corrosion cracking (SCC) and grain boundary attack (GBA). Atomic scale simulation of oxidation of Fe, Fe-Cr and Fe-Cr-Ni by gaseous water (no electrochemical double layer) demonstrated that the hydrogen atoms released by dissociation of water molecule at a metal surface diffuse into metal and enhance an oxidation of metal by oxygen, major oxidant. Several experimental verification of this hydrogen enhanced oxidation were made and DG-OES can reveal an hydrogen concentration at metal/oxide interface suggesting an strong interaction between vacancy and hydrogen.

Presenter cannot attend but presentation will be available.

Posters

P1

Breakthrough on GDOES Analysis Applied to Rough Metal Surfaces

S. Cremel¹, E. Gagaték¹ and P. Chapon²

¹ Arcelormittal Research & Development, Voie Romaine, 57280 Maizières-lès-Metz, France

² HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

sebastien.cremel@arcelormittal.com

GDOES is widely used in steel industry as a fast and powerful method for analyzing steel products, coated steel products. Industrial samples, especially Press Hardening Steels (PHS) after Hot forming treatment exhibit a strong surface oxidation and roughness (fig. 1) leading to difficulty in analysis (strong leaking and Ar plasma strongly contaminated by Oxygen and Nitrogen from the atmosphere)



Fig. 1 Typical oxidized and rough surface of a treated PHS steel

An interesting solution has been found by using a hermetic protective bell that surrounds the sample (fig. 2) this bell is linked to an independent high purity Argon bottle that allows saturating in Argon the whole atmosphere around the sample and avoiding plasma contamination by Oxygen and Nitrogen at thus any kind of modification of emission intensities.



Fig 2: Argon saturation protective bell prototype

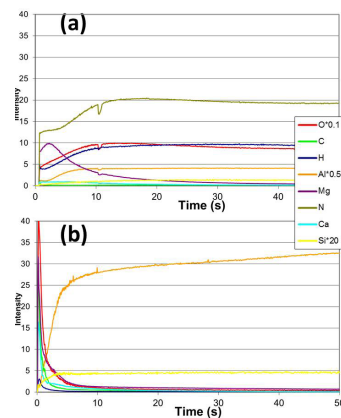


Fig 3: GDOES depth profile without (a) or with (b) the Argon saturation protective bell

Figure 3 shows how improvement of depth profiles quality is clear on a high surface roughness Automotive Aluminum molden piece. Using the bell allows acquiring a relevant depth profile no more contaminated by strong O and N signals, optical emission intensities are in agreement with a smooth sample and surface layer and interface are well resolved. On this specific product GDOES can now be used to characterize fine (nanometric) MgO passivation layers on aluminum alloys, before that X-Ray Photo Electron Spectroscopy were required.

This new tool is now implemented at ArcelorMittal surface analysis lab, helping us analyzing complex industrial samples. The following steps are to test repeatability of profiles and study dependency of Optical Emission with Argon flow value in the Argon saturation protective bell.

P2

Influence of CIGS Surface Conditioning on Sputtering Condition of GDOES Depth Profile Measurement

W. Hempel, W. Wischmann

Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW),
Industriestraße 6, 70565 Stuttgart, Germany

wolfram.hempel@zsw-bw.de

GDOES has evolved into an important tool for fast depth profiling. For instance CIGS absorber of 3 µm in thickness can be measured within 10 to 15 minutes. But in detail differences in measurement conditions occur, when samples are treated differently. In Table 1 different tested treatment methods and their effect are summarized:

	Treatment	Effect
	as grown	sample after CIGS coevaporation step
	water rinse	removing of particles
	Na ₂ S etching	removing of oxidized CIGS surface layer
	CdS bath deposition	buffer layer and protection against surface oxidization
	Plasma cleaning	removing of surface contamination, application of GDOES profiler
	KCN etching	removing of Cu ₂ Se
	CdS etching	removing of CdS by hydrochloric acid

Table 1: Used treatment methods

All these treatment methods influence the conditioning of CIGS surface. Some of these techniques remove sodium and organic remains from the surface. These differences of surface layer lead to a change in sputtering conditions and have a mayor effect on sputtering rate (Fig. 1), although sputter parameters keep constantly. Associated to this a Gallium depletion appears for first seconds of measurement. Gallium enrichment occurs at end of sputtering of absorber layer. This effect points to the influence of the sputtering conditions on the composition in the sputter crater. This was already reported in references [1] [2]. Therefore it is necessary to define the same surface conditioning to be able to compare all measurements with each other. Finally a copper peak is visible near the surface of absorber layer, which couldn't be correlated to any treatment method.

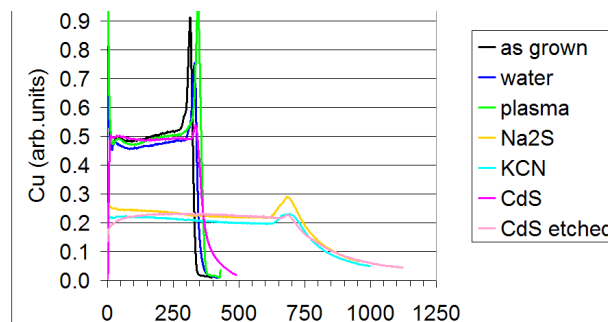


Fig. 1: Sputtering time in dependence to different treatment methods

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P3

Depth Profiling Protective Coating Titanium Nitride Based on Glow Discharge Optical Emission Spectrometry

A. A. Batrakov, A. V. Ryzhenkov, O. S. Zilova, G. V. Kachalin, A. A. Burmistrov, A. P. Lepekhov

National Research University «MPEI», Russia

Batrakovaa@mail.ru

This poster presents elemental depth profile analysis based on glow discharge optical emission spectrometry for titanium nitride protective coatings created by ion-plasma method. It solves the problem of availability of required standard samples with a high concentration of nitrogen (more than 2%) needed for calibration of the spectrometer glow discharge.

P4

Depth Profiling of Zr-1Nb Alloy After Plasma Immersion Titanium Implantation and Hydrogen Saturation

Tatiana S. Priamushko, Egor B. Kashkarov, Alina N. Sutygina

Tomsk Polytechnic University, Tomsk, Lenin str., 30, 634050, Russia

tatyana.pryamushko@gmail.com

Hydrogen can be a reason of embrittlement and degradation of the mechanical properties of zirconium alloys [1]. Plasma immersion ion implantation (PIII) is promising to protect zirconium alloys from hydrogen embrittlement [2]. Moreover, surface modification by PIII improves the mechanical strength, corrosion and wear resistance of material. However, it is necessary to investigate the depth distribution of elements (including H) to describe the mechanism of accumulation and interaction of hydrogen with a modified layer. Thus, the aim of this work is to study the hydrogen sorption kinetics and accumulation mechanism in Zr-1Nb alloy after PIII of titanium.

The samples of Zr-1Nb alloy with a size of 20×20×1 mm were prepared. It is known that the state of the surface strongly influences the penetration of hydrogen [3]. Thus, the samples were mechanically polished to the average roughness R_a of 0.06 μm and subjected to argon bombardment at $U=1500$ V and $I=0.3$ A for 3 minutes. PIII of titanium were performed with the following parameters: $I=70$ A, $U=0.5-1.5$ kW, $\nu=100$ kHz; $P=0.15$ Pa, $t=15$ min. Coaxial plasma filter was used to reduce the microdroplet content on the surface. Gas-phase hydrogenation of samples was performed using Gas Reaction Controller technique at $T=400$ °C, $P=1.95$ atm for 1 hour. Elemental composition and depth distribution of elements were investigated by glow discharge optical emission spectroscopy using GD-Profilier 2 technique.

The results revealed that the modified layers primarily consists of Ti, Zr, O and small impurities of Nb and N elements. The intensity of the hydrogen absorption process decreases with increase in the bias voltage from 500 V to 1000 V. However, the further increase in the bias up to 1500 V leads to the formation of thinner layer and rough morphology that are strongly influenced on the hydrogen absorption rate. The depth distribution of hydrogen in the modified layers is similar for all samples implanted at different bias voltages. Hydrogen accumulated at the modified layer and tends to decrease from the surface to the depth of the material. However, the hydrogen content in the modified layers is different and related to the concentration of titanium and oxygen, thickness of the layer, and defect structure caused by titanium ions implantation.

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P5

Use of Complementary Techniques for Depth Profiling of Mobile Screen Protection Covers

B. Bleisteiner

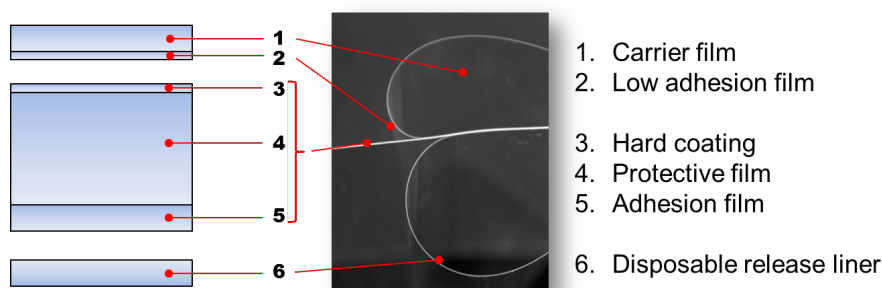
HORIBA Scientific, Neuhofstrasse 9, D-64625 Bensheim, Germany

bernd.bleisteiner@horiba.com

Everybody knows the annoyance: just bought a new mobile and a small inattention is causing the mobile screen to be broken by falling on the ground. To avoid this scenario, industry is supplying mobile screen protection covers. Besides protecting mobile screens from breaking, such protection films also avoid scratching the display when carrying the phone in the pocket and they are also dirt-repellent.



The manufacturers of mobile screen protection covers offer different concepts either based on polymer or glass. HORIBA Scientific was asked to demonstrate analytical methods for the layer analysis of plastic protection covers. The poster presents the results generated on a multilayer polymer film analyzed by GD-OES and Raman spectroscopy.



Both analytical techniques are perfectly complementary: GD offers information of the elemental composition, while Raman spectroscopy gives molecular information. Thanks to GD it was possible to discover that these protection covers employ ionic polymer compounds, which cannot be detected by Raman spectroscopy. In contrast, Raman enabled to identify the type of polymers used.

P6

The Use of GDOES in Failure Analysis and Quality Control

A. Raffaelli, A. Lanzutti, F. Andreatta, M. Magnan, L. Fedrizzi

University of Udine, Department of Chemistry Physics and Environment,
Via del Cottonificio, 108-33100 Udine, Italy

alberto.raffaelli@uniud.it

The GD instrument is a powerful tool to analyze the surface quality of a material by means of in depth elemental distribution profiles. Several cases of failure of mechanical components are related to the surface conditions of material, in particular in the case of surface treatments like thermochemical processes or the application of different types of coatings.

In this work, selected examples of application of the GDOES technique for quality control and failure analysis are presented. In these case histories, the GDOES was employed for the analysis of the bulk composition and for the acquisition of elemental distribution profiles. GDOES results were confirmed by the use of complementary surface analysis techniques like SEM-EDXS and by the investigation of the surface morphology of the samples.

The case histories presented in this work confirm that the GDOES is very useful for the assessment of the quality of a material and for the failure analysis of different mechanical components.

P7

Synthesis and Characterization of Tungsten Quadratic Bronze Ferroelectric Materials

A. Laaraj, L. Zerhouni, E. ELmoussafir, Y. Guaaybess, R. Adhiri, M. Moussetad

LIMAT, Faculty of Sciences Ben M'sik, Casablanca, Morocco

abdelali.laaraj@gmail.com

Recently, a number of phases with “tungsten quadratic bronze” structure have attracted a great interest because of their properties on ferroelectricity and nonlinear optics. In fact, since the 1970 years the nonlinear dielectric behavior of ferroelectric ceramics has attracted attention of scientific community. Indeed, these materials have been used in many applications such as electro-optical, pyroelectric, piezoelectric, and nonlinear optical. For the environmental reasons, several efforts are made in order to find the new ferroelectric materials free of lead. For this purpose, in the present work, the new ferroelectric materials of tungsten quadratic bronze structure derived from the lead niobate were successfully prepared and characterized. Noting that, the substitution was made at the level of the square sites (A) and pentagonal sites (B).

The aim of this study is to elaborate and characterize the ceramics, also to link their physical properties to their composition including to the nature of substitutions in Site A (coordination number 12) and B (coordination number 15), and to their chemical homogeneity and microstructure. We mention that, the powders are prepared by solid phase reaction then, they shaped and densified at high temperature by thermal treatment. The homogeneity, microstructure and purity of the obtained phases will be determined using XRD, Raman spectroscopy and MEB.

Keywords:

Solid reaction; Phase transition; Ferroelectrics; X-Ray Diffraction; Raman spectroscopy

P8

Pulsed Radiofrequency Glow Discharge Time of Flight Mass Spectrometry for VOCs Analysis: Development of a New Source

J. Fandiño¹, A. Sanz-Medel², J. Pisonero¹, N. Bordel¹

¹Department of Physics. University of Oviedo.

²Department of Physical and Analytical Chemistry. University of Oviedo

bordel@uniovi.es

The accurate identification of gaseous compounds, such as volatile organic compounds, is a key issue in analytical chemistry. Gas Chromatography (GC) is one of the most used techniques to separate and identify these compounds with no degradation. After their separation there are two typical detections modes: Flame Ionization Detection (FID) and Mass Spectrometry (MS). The most common ion sources used in GC-MS are electron ionization and chemical ionization. Alternatively, different ion sources such as atmospheric pressure ionization, inductively coupled plasma or low pressure glow discharge are also used.

In this work the capabilities of a low pressure pulsed glow discharge to act as ionization source for GC-MS are studied. Pulsed glow discharges present three temporal regimes along the discharge pulse [1] with different ionization mechanisms. At the beginning of the pulse, the so-called *prepeak*, ionization is mainly produced by electron impact and information about the sample is mostly the elemental composition. The *plateau* takes place during the stable part of the discharge pulse and ionization is generated by several mechanisms (charge transfer, Penning ionization and electron impact). As a result, fragments of the molecular samples are formed in the plasma during this temporal regime, and structural information can be obtained.

The afterpeak or afterglow corresponds to the post-pulse time and the most important process is Penning ionization. In this temporal region, molecular ions (M^+) or protonated ions ($(M+H)^+$) from the sample are obtained.

The main goal of this work is the coupling of a gas chromatograph to a radiofrequency pulsed glow discharge time-of-flight mass spectrometer (rf-pGD-ToFMS) for the analysis of volatile organic compounds (VOCs). A new GD source has been designed to optimize the sample entrance in the discharge and its potential is evaluated and compared with the results offered by the previous source. In addition the fragmentation patterns and their intensity are studied as a function of the GD parameters.

Acknowledgements

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P9

Improvement of Inorganic Gas Diffusion Barriers by a Low Energy Argon Plasma Treatment

**P. Alpuim^{1,2}, S. Majee³, P. Chapon⁴, M.F. Cerqueira¹, D. Tondelier³, B. Geffroy^{3,5},
Y. Bonnassieux³, J.E. Bourée³**

¹ Centro de Física, Universidade do Minho, 4710-057 Braga, Portugal

² INL – International Iberian Nanotechnology Laboratory, 4715-330 Braga, Portugal

³ Laboratoire de Physique des Interfaces et des Couches Minces, CNRS, Ecole polytechnique, Université Paris-Saclay, 91128 Palaiseau, France

⁴ HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

⁵ Laboratoire d'Innovation en Chimie des Surfaces et Nanosciences, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France

jean-eric.bouree@polytechnique.edu

Efficient gas-diffusion (permeation) barriers are needed for organic electronic devices on flexible substrates because the oxygen or water molecules degrade rapidly the active organic layers. So a reliable thin film encapsulation is mandatory associated with a water vapor transmission rate (WVTR) not exceeding 10^{-5} g/(m².day).

To reach this goal, our interest was focused in the fabrication of stacked silicon nitride (SiN_x) single layers (50 nm thick) deposited by hot-wire chemical vapor deposition (HWCVD) process at low-temperature (~100°C), with a specific argon plasma treatment between two successive layers. Several plasma parameters (RF power density, pressure, duration of treatment) as well as the number of single layers have been explored in order to improve the quality of permeation barriers deposited on polyethylene terephthalate. More precisely, maximum Ar⁺ energy was highlighted as the crucial parameter making it possible to minimize WVTR, as determined by the electrical calcium test method, all the other parameters being kept fixed. Thus fixing the plasma treatment duration at 8 min for a stack of five SiN_x single layers, a minimum WVTR of 7×10^{-5} g/(m².day), measured at room temperature, was found for a narrow window of maximum ion energy around 30 eV.

An additional study based on the choice of two specific maximum Ar⁺ energy values (30 eV and 100 eV) allowed to confirm, with the help of glow discharge optical emission spectroscopy, X-ray photoelectron spectroscopy and X-ray reflectometry, that for SiN_x single layers deposited on c-Si substrate the surface layer is densified for 30 eV while this surface is severely damaged for 100 eV.

The interpretation of these experimental results has been made using the analogy with low-energy ion beam epitaxy of Si. So the reduction in the permeability is interpreted as due to the rearrangement of atoms at the interfaces when average transferred ion energy to target atoms exceeds threshold displacement energy for Si.

Keywords:

Silicon nitride, Hot-wire CVD, Low-temperature deposition, Ar plasma treatment, Permeation barrier

P10

Bulk Analysis of Trace Elements in Pure Au and Ag by GD-Profilier HR

V. Galuschenko

Moscow Mint, Russia

galuschenko_v_v@goznak.ru

Moscow Mint makes the routine analysis of pure gold and silver (99.9 and 99.99% grade) by GD-Profilier HR spectrometer. The possibility of reliable measurement of trace concentration of impurity elements is noted. Concentration of matrix elements (gold and silver) is defined as difference of 100% minus the sum of impurity. Results of analyses are confirmed by parallel measurements on ICP spectrometer and spark optical-emission spectrometer.

P11

Smart Solid Sample Analysis - Some Examples for Direct Analysis by Electrothermal Vaporisation as Add-on for the ICP (ETV-ICP OES/MS).

Peter R. Perzl

Spectral Systems, Munich, Germany

Perzl@t-online.de

ETV-ICP-OES is a scientifically well investigated, understood and established method for direct solid sampling analysis of metallic impurities in different matrices of solids and solutions. It becomes more and more established in modern laboratories as fast, powerful and cost effective systems in the routine analysis especially when they are equipped with an automatic sampler. The field of application is far diversified and is extended from general inorganic raw materials beyond ceramics, carbon, geological and environmental samples to organic materials like plastics, human, animal or plant tissues, as well as blood, serum, liquids of all kinds including petroleum products.

A commercially available and well optimised ETV device is being presented that is installed in about 100 industrial and research labs meanwhile.

The working principle is to evaporate some mg of solid sample in a graphite furnace at temperatures up to 3000°C, converting the vapour into an aerosol and transferring it directly into the injector tube of the ICP-torch. Thus the transport efficiency reaching up to 100% nearly the entire amount of trace elements is reaching the plasma, enhancing the sensitivity up to a factor of 50 compared to liquid ICP analysis.

By using a halogenated reaction-gas as a modifier even the carbide forming and high boiling elements are converted into easy volatile halogenides so that there is no limitation in the analytes.

The sample undergoes an arbitrary temperature program that easily can be adapted to the analytical needs, for example to a certain extend even speciation analysis can be performed, spectral interferences avoided by sequentially running several temperature steps.

An analysis usually takes a total time of about two minutes, except sample preparation (weighing, drying).

A great advantage is the possibility to calibrate with dried liquid standard solutions to be pipetted directly into the graphite boats, as very often solid CRMs are not available.

With an autosampler for 50 solid samples routine analysis becomes very fast, especially when using a synchronised simultaneous spectrometer with a suited software.

Technology, handling and some applications of this ETV system combined to modern ICP-spectrometers on the basis of several solid materials are presented.

For more information visit: www.spectral-systems.de

P12

Surface Sample Preparation for EPMA Using GDOES

Sergey Khromov, Morten Peder Raanes, Mariia Stepanova, Marisa Di Sabatino Lundberg

Department of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU),
A. Getz vei 2B, 7491 Trondheim, Norway

sergey.khromov@ntnu.no

Al-Si cast alloys are in high demand for automotive applications and there is an indication that additions of Ni to these alloys can significantly improve their high temperature mechanical properties. Accurate quantification of Ni concentrations is therefore important to assess the influence of Ni on the microstructure and mechanical properties of the resulting alloy.

In this work we present a study of three Al-Si cast alloy samples with varying Ni concentrations, namely 0.5, 1, and 2 wt.%. Glow discharge optical emission spectroscopy (GDOES) was used to measure the chemical composition while electron probe microanalysis (EPMA) was used to make elemental mappings and reveal the microstructure. Samples for EPMA were prepared by mechanical polishing with SiC and diamond papers down to 1 μm . We also studied the possibility of using GDOES at various analytical conditions (power and pressure) as a final polishing step for EPMA.

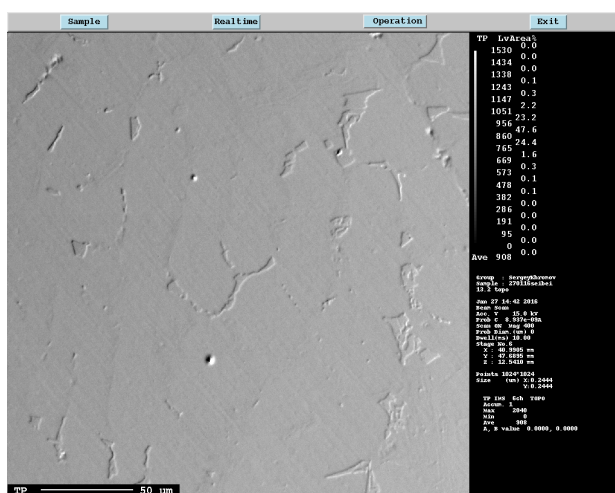


Figure 1. SE micrographs of the sample (1% Ni) surface outside (left) and inside (right) the GDOES crater.

The results of the GDOES analysis confirm the target levels of Ni for all the three samples investigated. EPMA analyses were conducted both outside and inside the areas of the crater made by GDOES sputtering. The results seem to indicate that GDOES cannot be used as a final polishing step for EPMA and that the presence of Ni can significantly change the sputtering rate during GDOES analysis, thus affecting the GDOES quantification.

P13

Optical Characterization of ITO Films Prepared in Different Atmospheres Using Spectroscopic Ellipsometry

J.P. Gaston, C. Eypert

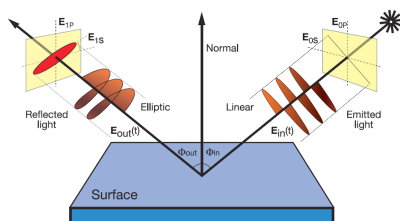
HORIBA Scientific, Avenue de la Vauve, Passage Jobin Yvon, 91120 Palaiseau, France

jean-paul.gaston@horiba.com

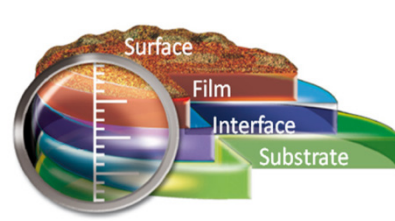
Indium tin oxide (ITO) thin films show interest due to their unique characteristics of high conductivity, high optical transmittance over the visible wavelength region, and excellent adhesion to the substrate. For these reasons, ITO is often used to make transparent, conductive coatings for liquid crystal displays, flat panel displays, plasma displays, touch panels, and electronic ink applications. ITO is also commonly used in organic light-emitting diodes, solar cells, and various other optical coating applications.

A suitable technique for characterizing thin films of ITO is spectroscopic ellipsometry, which is a surface sensitive, non-destructive, non-intrusive optical technique that measures the change in the polarization state of light reflected from the surface of a sample. It is widely used to determine film thickness and optical constants (n, k) and provides significant advantages for nano-material characterization such as determination of film thickness with Ångstrom resolution and determination of optical constants that allow the deduction of a wide range of physical properties. This technique gives also the possibility to perform dynamic studies in real time

In the work presented here, ITO films were deposited onto silicon substrates by DC sputtering and then annealed at 500° C in various atmospheres such as air, vacuum (0.6 bar), and N₂ (1 bar). The films were then studied using ex-situ spectroscopic ellipsometry, over a wavelength range from 190 to 2100 nm, to observe changes in the optical properties of the films before and after annealing in various atmospheres. The resulting optical constants show that all of the annealing treatments, regardless of the atmosphere, improved the transparency of the ITO layer.

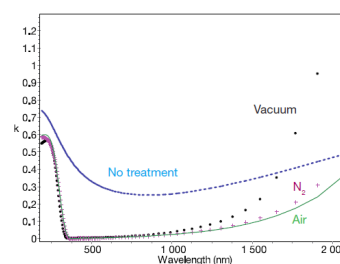
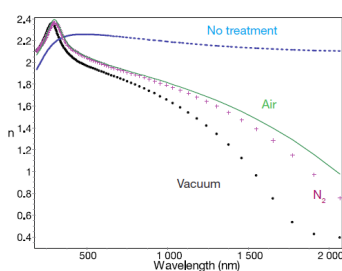


Change the polarization state of the light reflected from the surface of a sample



Main properties determined by Spectroscopic Ellipsometry

The ITO optical constants were determined using a combination of a Drude oscillator (to model the absorption in the NIR range) and a double New Amorphous Formula (to model the absorption in the UV range).



P14

A New Film Thickness Measurement Technique: Differential Interferometric Profiling (DIP) Similarities and Complementarities with Ellipsometry

Simon Richard, Patrick Chapon, Sofia Gaiaschi and Olivier Acher

HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

olivier.acher@horiba.com

The precise determination of thickness and composition profiles of films and multilayers is key to many fields of Material Science, and ellipsometry has become a very popular technique for these applications. Among the other profiling techniques, Glow Discharge Optical Emission Spectroscopy (GD-OES) has grown very popular among some Material Science sub-communities, as a very convenient tool to obtain fast and reliable atomic composition profiles on thin and thick films [1]. In a GD-OES instrument, a few-mm-sized crater is plasma-etched while simultaneously analysing the optical spectrum of the plasma, allowing the determination of the different atomic element present in the layer. If the composition of different layers can be determined using GD-OES, their thickness cannot, as the etch rate varies with material composition.

Recently, we have introduced the Differential Interferometric Profiling (DIP) technique attached to GD-OES, and established its capability to measure film thicknesses and etch rates [2]. It is based on a two path laser interferometer, one beam probing the bottom of the etched crater, while the reference beam reflects on the unetched surface (Fig. 1a). The interferometer is a polarization interferometer, using a division of amplitude polarimetric detection that provides real time information. It determines the complex quantity $r(t)/r(0)$ where $r(t)$ is the complex normal incidence reflection coefficient of the sample at etching time t , $r(0)$ being the reflection coefficient at etch start. It is convenient to write:

$$R(t)/R(0) = \rho(t)e^{-i\Delta(t)}$$

This equation is useful to discuss the similarities and difference with ellipsometry. As in ellipsometry, the thickness information is retrieved from the complex reflection coefficient of the sample. In some cases, the information provided by the DIP setup is more straightforward than in the case of ellipsometry. As an example, for opaque films, the measured quantity $\Delta(t)$ is simply related to the depth $d(t)$ by $\Delta(t) = 2\pi d(t)/\lambda$, and oscillations of the experimentally determined phase allow precise etched thickness and etch-rate determination (Fig 1b). However, in a regime where layers are optically thin, full optical modelling of the structure is needed, in a similar way to in-situ real-time ellipsometry. It is anticipated that information on composition gradients during the etching process can be obtained, which can be useful to optimise the GD-OES parameters.

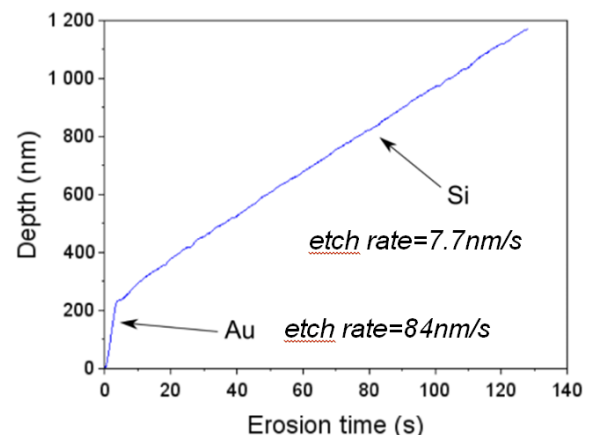
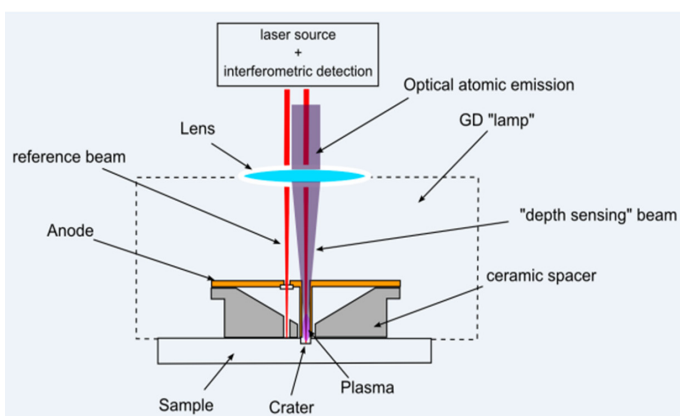


Fig. 1 a) principle of Differential Interferometric Profilometer attached on a GD-OES setup; b) experimental record of $d(t)$ on a Au/Si layer, and corresponding determination of etch rate and sample structure.

As a conclusion, the combination of GD-OES and DIP constitute a powerful tool in Material Science. It is expected to be a very appropriate complement to ellipsometry. It can provide information on optically opaque materials such as relatively thick metal layers, and it determines directly atomic elemental composition information, that are out of reach of ellipsometry. But it is also anticipated that the ellipsometry community can have much impact on the development of the DIP technique, as its optical material and multilayer modelling tools are very relevant to this technique.

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P15

Characterization of CIGS Solar Cells Through Glow Discharge Optical Emission Spectrometry and Differential Interferometry Profiling

**Sofia Gaiaschi¹, Anaïs Loubat², Simon Richard¹, Muriel Bouttemy², David Alamarguy³,
Patrick Chapon¹, Arnaud Etcheberry²**

¹HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

²Lavoisier Institute of Versailles (ILV), UMR 8180 CNRS-UVSQ, IPVF, 45 avenue des Etats Unis,
78035 Versailles, France

³GeePs | Group of electrical engineering – Paris
UMR CNRS 8507, CentraleSupélec, Univ Paris-Sud, Sorbonne Universités, UPMC Univ Paris 06
11 rue Joliot Curie, Plateau de Moulon F91192 Gif sur Yvette CEDEX

sofia.gaiaschi@horiba.com

The growth of the photovoltaic technology relies on the improvement of existing materials and manufacturing technologies, as well as on the development of new ones.

In the case of CIGS solar cells the chemical engineering of the absorber layer remains a permanent challenge. The variation of composition, the diffusion of impurities and the nature of the interfaces are three critical points that influence the performance of these devices.

Multiple characterization techniques are applied. Among them, Radio Frequency Glow Discharge Optical Emission Spectrometry (GDOES) is used for fast elemental depth profile. The technique relies on the very fast sputtering (typically $\mu\text{m}/\text{min}$) of a representative area of the sample by a high density and low energy RF plasma. An excellent depth resolution can be obtained, depending on the surface roughness.

The most recent advance in GDOES is the real time measurement of the depth of the sputtered crater thanks to the addition of a Differential Interferometry Profiling (DiP) module within the GD source. It gives a direct access to layers thickness and erosion rates.

In this work the characterization by GDOES and DiP of chemically etched CIGS samples was performed for the first time. These materials are challenging for DiP as they are possibly rough and partially transparent. Different surface roughness levels were investigated, corresponding to different etching times, and their impact on the layer thickness determination with DiP was evaluated.

P16

Synergy of GDOES & DIP with EDXRF Techniques for Layers Thickness and Elemental Composition Determination

Jocelyne Marciano, Sofia Gaiaschi, Patrick Chapon

HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

jocelyne.marciano@horiba.com

Nowadays, a great effort is put into improving product performance while reducing product costs. One of the solutions considered by the modern manufacturing world is based on coatings.

Coatings can be used in a variety of applications: from electronics to anti-corrosion and wear resistance. New layer systems are usually developed in order to satisfy specific requirements and these are often multi-layer systems, which may include very thin layers (< 100 nm). In order to optimize the manufacturing process, it is of great importance to determine the thickness/composition of the different coatings and therefore it is crucial to have access to reliable techniques providing such information within just a single measurement.

In this perspective, Glow Discharge Optical Emission Spectrometry (GDOES) is an ideal method as it easily gives access to the elemental depth profile. It relies on the very fast sputtering (typically $\mu\text{m}/\text{min}$) of a representative area of the sample by a high density and low energy radio frequency plasma. Moreover, thanks to the addition of the Differential Interferometry Profiling (DiP), it can now also provide the direct measurement of layers thickness.

However, Energy Dispersive X-rays Fluorescence (EDXRF) is another interesting method as it is a non-contact and non destructive technique. As GDOES, it can be applied to both metals and dielectrics, with the advantage of being able to efficiently analyze both transparent and opaque materials, whereas DiP can presently be applied straightforwardly only to non-transparent samples. EDXRF relies on a X-ray source to excite all the elements in the sample, and on an energy dispersive detector for the simultaneous collection of the emitted fluorescence radiation. Once the XRF spectrum is acquired, the composition and the thickness of the different layers can be obtained by calculating how they should be based on the obtained X-ray fluorescence intensity.

In this work multilayered coatings were studied both by GDOES+DiP and EDXRF in order to investigate the synergy of these methods and to assess the agreement between such techniques.

P17

Antifungal Activity Against *Candida Albicans* Biofilm of Composite Layers Based on Silver Doped Hydroxyapatite-polydimethylsiloxanes

C.S. Ciobanu¹, C. L. Popa¹, S.L. Iconaru¹, S. Gaiaschi², P. Chapon², A.M. Prodan^{3,4}, A. Groza⁵, M. Ganciu⁵, D. Predoi^{1,*}

¹ National Institute of Materials Physics, 405 A Atomistilor Street, P.O. Box MG 07, Magurele 077125, Romania;

*Corresponding author: dpredoi@gmail.com

² HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

³ Emergency Hospital Floreasca Bucharest, 8 Calea Floresca, Sector 1, 014461 Bucharest, Romania

⁴ Carol Davila University of Medicine and Pharmacy, 8 Eroii Sanitari, Sector 5, 050474 Bucharest, Romania

⁵ National Institute for Laser, Plasma and Radiation Physics, 409 Atomistilor St. P.O. BOX MG 36, Magurele 077125, Romania

ciobanucs@gmail.com

The development of nanotechnology has brought improvements to the field of nanomedicine, providing biomaterials that are able to mimic the human body tissues to a certain point. Nevertheless, in this area, there are still many challenges to overcome. Even though we live in an era of technology advances, the medical field is still struggling to find new and more effective methods for fighting off viruses, bacteria and fungi.

Candida species are considered the most dangerous human fungal pathogens responsible for deep tissue and mucosal infections, especially in the oral cavity, being proven that up to 50% of hospital-related *C. albicans* infections are deadly. In this context, the goal of this research was an in vitro evaluation of the effects of various composite layers based on silver doped hydroxyapatite/polydimethylsiloxane (Ag:HAp-PDMS/Ti) or hydroxyapatite/polydimethylsiloxane (HAp-PDMS/Ti), prepared by combining corona discharge at atmospheric pressure and sol-gel dip coating method, on *Candida albicans* (*C. albicans*) adhesion to layers surfaces.

This study was focused on surface and structural characterization of HAp-PDMS/Ti, and Ag:HAp-PDMS/Ti by different techniques: Scanning Electron Microscopy (SEM), Glow Discharge Optical Emission Spectroscopy (GDOES) and Fourier Transform Infrared Spectroscopy (FTIR). The morphological studies revealed that the PDMS polymer interlayer improved the quality of the coatings. The structural investigations revealed the presence of the basic constituents of both apatite and PDMS structure in the thin films. All the functional groups characteristic to apatite and PDMS were found in the IR spectra. The GDOES depth profiles indicated the formation of a composite material as well as the successful embedding of the HAp and Ag:HAp into the polymer. On the other hand, the in vitro evaluation of the antifungal properties of Ag:HAp-PDMS/Ti demonstrated its fungicidal effect. The results obtained in this study provide complex insight on the potential mechanism involved in the antifungal activity of silver ions against *C. albicans* biofilms and also emphasize the potential uses of these types of coatings in medical applications.

Acknowledgments

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P18

Structural and Antimicrobial Properties of Silver Doped Hydroxyapatite Thin Films Deposited on PDMS/Si

C. L. Popa¹, C.S. Ciobanu¹, S.L. Iconaru¹, S. Gaiaschi², P. Chapon², A.M. Prodan^{3,4}, R. Ghita¹, A. Groza⁵, M. Ganciu⁵, D. Predoi^{1,*}

¹National Institute of Materials Physics, 405 A Atomistilor Street, P.O. Box MG 07, Magurele 077125, Romania;

*Corresponding author: dpredoi@gmail.com.

²Horiba Jobin Yvon S.A, 16-18, rue du Canal, 91165 Longjumeau, France

³Emergency Hospital Floreasca Bucharest, 8 Calea Floresca, Sector 1, 014461 Bucharest, Romania

⁴Carol Davila University of Medicine and Pharmacy, 8 Eroii Sanitari, Sector 5, 050474 Bucharest, Romania.

⁵National Institute for Laser, Plasma and Radiation Physics, 409 Atomistilor St. P.O. BOX MG 36, Magurele 077125, Romania.

dpredoi@gmail.com.

Due to the constant and rapid progress of modern medicine during the last years, the need for new and improved materials with application in the medical field has increased. Nowadays, one of the major problems encountered are the apparition of post operative infections which could cause serious problems and pose a great risk to the patients. In order to avoid post operative infections, the attention of researchers worldwide has been focused on developing novel materials which could serve as biocompatible and antimicrobial coatings, combining nanotechnology and materials science. The most investigated element known for its excellent antimicrobial properties is silver. On the basis of previous results, this study was focused on the preparation and characterization of silver doped hydroxyapatite (AgHAp) with polydimethylsiloxane (PDMS) (AgHAp-PDMS/Si) layers obtained by thermal evaporation technique. The AgHAp ($x_{Ag} = 0.5$) powder was deposited by thermal evaporation technique as solid layer on a silicon substrate previously coated with a PDMS layer and the AgHAp-PDMS/Si layers were characterized by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR). The phase composition of the silver doped hydroxyapatite with PDMS (AgHAp-PDMS/Si) layers was investigated by infrared spectroscopy analyses. Glow Discharge Optical Emission Spectroscopy (GDOES) was used for the evaluation of constituent elements distributed in the studied layers. In the GDOES depth profile spectrum of the AgHAp-PDMS/Si layer we marked of the surface of the polymer/substrate interface by the Si depth profile curve behavior. The antimicrobial activity of AgHAp-PDMS/Si layers was tested against *Candida albicans* strain. The results of the antimicrobial assay revealed that the microbial activity decreases significantly for the surveyed time intervals on Ag:HAp-PDMS/Si layers. The results obtained in this study showed that silver doped hydroxyapatite with PDMS (AgHAp-PDMS/Si) layers have excellent antimicrobial activity. Therefore, the deposited AgHAp-PDMS/Si layers are a good candidate for coating different surfaces with medical applications.

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P19

Using Power Coupling Efficiency for ALD Thin Film Oxides Quantification

D. Frey

EMPA Thun, Switzerland

Damian.Frey@empa.ch

Reference materials for GD-OES with high oxygen concentrations providing high oxygen signals are hard to find. There is only one conductive oxide commercially available.

In nonconductive samples the erosion rate, and therefore the signal intensity, is strongly dependent on the power coupling efficiency. A complete oxygen calibration curve can be obtained by changing only one parameter which influences the power coupling efficiency.

In this study Al_2O_3 and ZrO_2 discs of varying thicknesses are used to quantify oxygen in ALD thin film oxides.

P20

Presentation of a Calibration Kit for GDOES

Naoki Higa^{1,2}, Akira Fujimoto²

^{1,2}HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

²HORIBA Scientific, 2-6, KandaAwaji-cho, Chiyoda-ku Tokyo 101-0063, Japan

naoki.higa@horiba.com

Rf-GD-OES for quantitative analysis require calibration curves to be built. For that certified reference materials (CRM) ideally must have a composition similar to the measured samples.

But to cover the larger dynamic range of calibration curves used for depth profiles, the number of CRMs should be high. And moreover, it's difficult to find or prepare adequate CRMs when samples have an unknown composition.

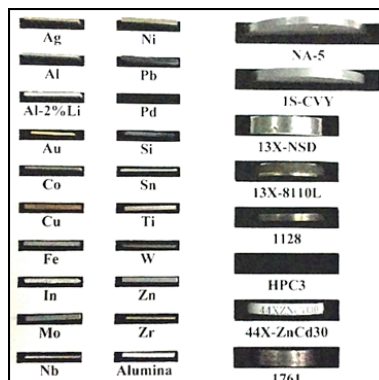
Quantitative depth profiles are however required even in such cases and the "Semi-quantitative kit" was developed for these needs.

The normal "Semi-quantitative kit" is constructed from 18 pure metals and 10 alloys. Around 40 elements (include metals such as Fe, Cu, Al, semi-conductive elements such as Si, and light elements such as C and O) are covered by this "Semi-quantitative kit".

The kit comes as a box with samples well identified and elements measured précised.



The "Semi-quantitative kit" makes easier to gain obtain quantitative depth profiles. Of course accuracy has limits depending on the type of samples measured and also when available measurement times are limited but this kit has already been proved to be useful in Japan as it was already sold to more than 7 customers.



P21

Preparation of Nanoparticle-Based Composite Coatings

O. Sublemontier

CEA, France

olivier.sublemontier@cea.fr

We propose a method for the elaboration, in a single step and in a confined chamber, of composite coatings made of nanoparticles embedded in a matrix. The process combines a beam of nanoparticles with Physical Vapor Deposition. The association of the two techniques is made possible by routing nanoparticles by aerodynamic means to the substrate, either immediately after their synthesis in the gas phase, or from atomized colloidal suspensions. The simultaneous deposition of the particles and the matrix is performed on the same substrate. The process allows a virtually unlimited selection in the respective chemical compositions of nanoparticles and the matrix, and a moderate temperature of the substrate.

Different source types of nanoparticles are possible. A laser-driven pyrolysis reactor can be used for the in-situ synthesis. Laser pyrolysis is an efficient method to synthesize various high purity nanopowders, oxides and non-oxides, in a gas phase bottom-up approach. An atomizer that produces an aerosol from colloidal suspensions of previously synthesized nanoparticles can alternatively be used. The particle stream is formed by means of an aerodynamic lens system. This system is currently used to produce a collimated beam of particles under vacuum for further gas phase characterization or for precision 3D micro printing. It allows for long-term stable and high transmission of particles in a wide range of size and density. We show that it is possible to get an angle-controlled divergent beam of nanoaerosols by optimizing the geometry of a classical lens. In this way, homogenous deposition of nanoparticles is performed on large areas. We demonstrate the adaptation of the technique with pressure environment required for running a classical magnetron sputtering device. The latter is used for depositing the material constituting the matrix of the composite film.

The deposition of a large variety of materials is conceivable by this means. The possibility to elaborate large and homogenous nanostructured films were investigated with different types of nanoaerosols with different sizes and densities. In addition, in situ characterization of the deposits are carried out by spectroscopic ellipsometry during the film growth.

Numerous application domains are already considered for this kind of nanostructured coatings, including photovoltaic, photocatalysis, aesthetic coatings, hard covering, biomedical and self-healing films. The development of the process is carried out in the frame of the HYMALAYAN project funded by the French Research National Agency (ANR) under Grant No ANR-14-CE07-0036. It is open to new potential applications.

P22

Evaluation of Inhibitory Effect of Glycerol-Iron Oxide Layers on MRSA

S. L. Iconaru¹, C.L. Popa¹, C.S. Ciobanu¹, S. Gaiaschi², P. Chapon², A.M. Prodan^{3,4}, M. Beuran^{3,4}, C. Turculeț^{3,4}, D. Predoi^{1,*}

¹National Institute of Materials Physics, 405 A Atomistilor Street, P.O. Box MG 07, Magurele 077125, Romania

²HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

³Emergency Hospital Floreasca Bucharest, 8 Calea Floresca, Sector 1, 014461 Bucharest, Romania

⁴Carol Davila University of Medicine and Pharmacy, 8 Eroii Sanitari, Sector 5, 050474 Bucharest, Romania

dpredoi@gmail.com

During the last years, iron oxide particles such as magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), with various coatings and nanometric size, have been used in biological applications for diagnosis and/or cancer treatment. Recently, functionalized magnetic nanoparticles have been involved in numerous new biomedical and diagnostic applications such as magnetic resonance imaging (MRI), contrast agents, targeted drug delivery, molecular biology, DNA purification, cell separation, and hyperthermia therapy. Due to the particular magnetic properties of iron oxide nanoparticles and their biocompatibility researches have focused on developing iron oxide thin films for various biomedical applications.

The main goal of this study was to obtain, characterize and evaluate the antimicrobial activity of glycerol-iron oxide thin films deposited by spin coating method. The inhibitory effect of glycerol-iron oxide thin films on Methicillin-Resistant *Staphylococcus aureus* (MRSA) was evaluated.

The glycerol-iron oxide thin films were deposited by spin coating method on a silicon (111) substrate and their structural properties were studied by X-ray diffraction (XRD) and scanning electron spectroscopy (SEM). The XRD studies evidenced that the crystal structure of glycerol-iron oxide nanoparticles was not changed after the spin coating deposition.

On the other hand, the SEM micrographs revealed that the size of the glycerol iron oxide microspheres increased with the increase of glycerol, thus exhibiting a narrow size distribution. More than that, glow discharge optical emission spectroscopy (GDOES) technique was used for investigating qualitative depth profile of glycerol-iron oxide thin films. The GDOES spectra revealed the presence of the main elements: Fe, O, C, H, and Si in the composition of glycerol-iron oxide thin films. The antimicrobial activity of glycerol-iron oxide thin films was qualitatively evaluated by measuring the zone of inhibition after 18 hours of incubation at 37°C. The results of the qualitative assay showed that the MRSA bacterial strain presented an inhibition zone which increased when the glycerol amount in the samples increased. Furthermore, glycerol-iron oxide thin films showed better antibacterial performance when the amount of glycerol increased. The present research proposes a new antimicrobial product that could be successfully used in various medical applications involving inhibition of antibiotic-resistant bacterial strains.

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P23

GDOES and XPS Analysis of Native Oxide Layers on GaSb (100) Surface Application to Depth Profiling of AuGeNi/n-GaSb

R.V. Ghita¹, C.C. Negrila¹, F. Frumosu¹, C. Logofatu¹, L. Trupina¹, S. Gaiaschi², P. Chapon²

¹National Institute of Materials Physics, Magurele, Bucharest, Romania

²HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

ghitar@infim.ro

Gallium Antimonide and related based semiconductor compounds devices have potential use in cutting-edge applications for mid-infrared optoelectronics and thermophotovoltaics ($E_g \sim 0.73$ eV at 273 K). A major problem to be overcome in the technology of III-V compounds is the poor quality of oxide/semiconductor interfaces. The performance and reliability of GaSb devices largely depend on surface preparation techniques in order to reduce the reverse current level and surface instabilities. The present work is dedicated to the GDOES and XPS studies of Ga and Sb native oxides phases developed on n-GaSb and p-GaSb, and their evolution route to a passivating layer. In our studies, the GDOES method was used for qualitative determination of the constituent elements in the films. The elemental distribution from coating to substrate with GaSb were investigated using GDOES depth profile. We investigate the characteristics of Au/Ge/Ni contact layers deposited in medium vacuum using a controlled Ar⁺ ion etching coupled with a XPS analysis that conducted to accurate depth profiling of contact metal layers. Data extracted from this analysis are dedicated to the technological research in order to design and realize a photosensitive structure of Schottky type. In this view, the formation of ohmic contacts on n-GaSb represents a technological skill considered in general a real state-of-art in obtaining semiconductor devices [1].

Acknowledgements

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P24

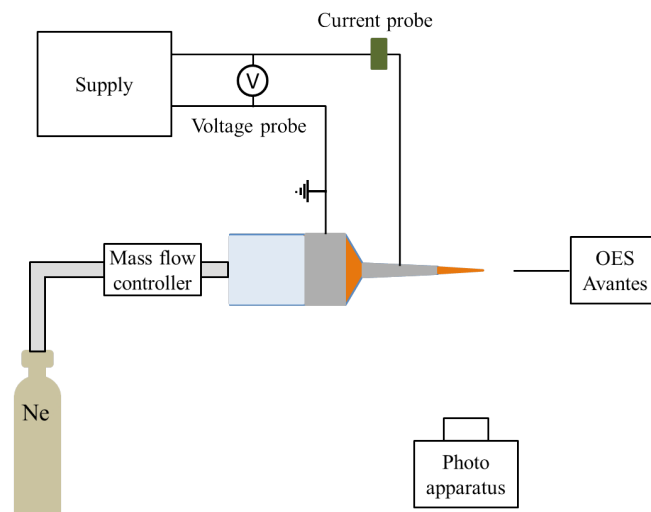
Neon Plasma Jet at Atmospheric Pressure. Spatiotemporal Distribution of Ambient Air Species.

Laura Chauvet, Bruno Caillier, Laurent Therese and Philippe Guillot

Laboratoire Diagnostics des Plasmas Hors Equilibre (DPHE), Université de Toulouse,
Institut National Universitaire Champollion, Albi, France.

laura.chauvet@univ-jfc.fr

The source developed in our laboratory is based on Dielectric Barrier Discharge (DBD) geometry. It allows the formation of a plasma jet in open air that can be directed toward the surface to be analyzed. This asymmetric plasma source consists of a dielectric cylinder ending by a dielectric cone with smaller diameter. The conductive electrodes surround each part of the device (cylinder and cone). The source is fed with high purity neon introduced into the source through a mass flow controller connected to the back of the source. The source is powered with a symmetric square alternative voltage. The frequency delivered by the power supply can vary from 10 kHz to 100 kHz, and the amplitude can reach a maximum of 3 kV (6 kV peak to peak voltage). The rising/falling time is about 100 ns.



Optical measurements were performed with an optical spectrometer (Avantes 2048-2) placed in front of the source exit to get the optical emission spectra. An iCCD camera (Princeton PIMAX-2K-RB) is placed on the side of the plasma jet to obtain the spatiotemporal distribution of the species. Optical filters with different central wavelength (band pass region of 10 nm for each) were added to select the species of interest.

In this work, emission spectra of the discharge were used to characterize the emission lines of interest corresponding to the buffer gas and to the ambient air species - i.e. O, H, OH, N₂ and N₂⁺. In the same time, the spatiotemporal evolution of the jet during the positive and the negative half periods of the signal were observed with the iCCD camera. The optical filters coupled with the iCCD camera are used in order to study spatial distributions of neon gas and air species present within the jet during the period (Ne, 703 nm and 584 nm, N₂, 380 nm, N₂⁺, 390 nm and O, 777 nm). These distributions will be presented and commented.

P25

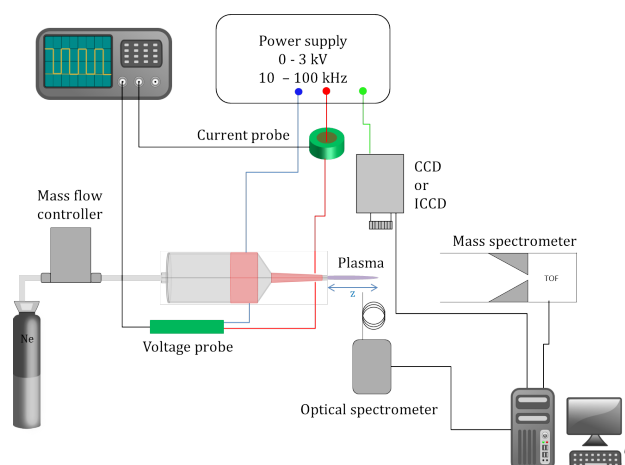
Neon Plasma Jet at Atmospheric Pressure. Application To Mass Spectrometry Detection of Volatile Samples.

Laura Chauvet, Cristina Muja, Laurent Therese and Philippe Guillot

Laboratoire Diagnostics des Plasmas Hors Equilibre (DPHE), Université de Toulouse,
Institut National Universitaire Champollion, Albi, France.

laurent.therese@univ-jfc.fr

In direct sample analysis domain, atmospheric pressure sources are widely investigated for ambient desorption/ionization mass spectrometry and atmospheric-pressure ionization mass spectrometry [1-3]. Dielectric barrier discharge (DBD) can be used to generate low temperature plasmas at atmospheric pressure and create soft ionization [2]. Coupled to mass spectrometry detection, high selectivity and sensitivity can be obtained but its efficiency is influenced by the plasma properties. A dielectric barrier discharge source has been developed to be associated with a Time Of Flight Mass Spectrometer (TOF-MS, CTOF-ToFwerk AG, Thun, Switzerland) for analytical investigations. This source is composed of a large cylindrical dielectric chamber with a capillary termination. The different electrodes cover both the cylindrical chamber (ground) and the capillary tube (HT). The power supply generates a square alternating voltage (20 kHz). The plasma is created inside the cylinder and a plasma jet is going out of the capillary tube. The source is operated in flowing Neon.



The aim of this study was to characterize the discharge in open air by mass spectrometry in positive and negative mode. Different mass spectra will be presented and commented. The results reflect two different behaviors: the molecules which did not undergo fragmentation and a molecule that has undergone fragmentation (chloroform). Non fragmented molecules are those of ethanol, acetone, diethyl ether and toluene. Next we tried to realize some quantitative experiments. From this work, a calibration curve has been plotted. The sample was ethanol (purity > 99%). These experiments were conducted with neon. Calibration curves were plotted for the protonated ion ($m/z = 47$) and the protonated dimer ($m/z = 93$).

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P26

Structural and Biological Evaluation of Iron Oxide-Dextran Nanostructures Thin Films

S. A. Predoi¹, S.L. Iconaru², C.L. Popa², C.S. Ciobanu², S. Gaiaschi³, P. Chapon³, M. Beuran^{4,5}, C. Turculeț^{4,5}, A.M. Prodan^{4,5}

¹International Computer High School Bucharest, Balta Albina Street, nr. 9, Bucharest, Romania

²National Institute of Materials Physics, 405 A Atomistilor Street, P.O. Box MG 07, Magurele 077125, Romania

³HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

⁴Emergency Hospital Floreasca Bucharest, 8 Calea Floresca, Sector 1, 014461 Bucharest, Romania

⁵Carol Davila University of Medicine and Pharmacy, 8 Eroii Sanitari, Sector 5, 050474 Bucharest, Romania

prodan1084@gmail.com

Due to their outstanding properties and their potential use in biomedical application, iron oxide nanoparticles and their composites have received increasing attention in the last years. These materials are highly biocompatible and can be easily conjugated with bioactive molecules. Recent studies have evidenced the use of nanoscale iron oxide nanoparticles as light scattering labels and luminescent optical markers, as contrast agents for magnetic imaging, etc.

This study is focused on the obtaining of the polymer nanocomposite thin films containing iron oxide nanoparticles (magnetite or maghemite). Another goal of this research was the study of the physico-chemical and biological of layers based on iron oxide nanoparticles (IONPs) in a dextran matrix. Structural and morphological properties of dextran coated iron oxide thin films obtained were investigated by X-ray analysis (XRD) and scanning electron microscopy (SEM). The adsorption of dextran on the surface of IONPs was investigated using X-ray Photoelectron Spectroscopy (XPS), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) coupled with an Energy Dispersive X-ray detector (EDX), Glow Discharge Optical Emission Spectroscopy (GDOES) and Fourier Transform Infrared (FTIR) Spectroscopy.

Dextran coated iron oxide continuous thin films were obtained by spin coating technique. The iron oxide nanoparticles were synthesized by an adapted by co-precipitation method and presented granular surface morphology. The XRD results of iron oxide nanoparticles and dextran coated iron oxide nanoparticles thin films revealed that they could be indexed into the spinel cubic lattice type (ICSD card no.01-083-0112) with a lattice parameter of 8.36 Å. More than that, the XPS results showed that the thin films have the expected composition of dextran coated maghemite γ -Fe₂O₃ powders. The GDOES investigation showed the presence of a material composed mainly of carbon, iron and oxygen, specific to the materials used for the obtaining of the thin films.

The expression of F-actin in Hep G2 cells adhered to dextran nanoparticles and dextran coated maghemite (γ -Fe₂O₃) nanoparticles with different iron oxide concentrations was also investigated. The results of the biological assessment proved that Hep G2 cells adhered very well to the dextran coated iron oxide thin films with various iron oxide concentrations. The biological evaluation revealed that the Hep G2 cells exhibited a normal actin cytoskeleton, which suggest that these cells underwent normal cell cycle progression. The results obtained in this study, highlighted the potential of these thin films for being used as biosensors for different xenobiotics.

Acknowledgments

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P27

Improving Layer Thickness Determination by the Combination of Depth Profile Modelling and DiP

Maëva Laquittaine¹, Simon Richard³, Sofia Gaiaschi², Patrick Chapon²

¹ENSSAT, Lannion, France

¹ HORIBA Scientific, Avenue de la Vauve, Passage Jobin Yvon, 91120 Palaiseau, France

² HORIBA Scientific, 16-18 rue du canal, 91165 Longjumeau cedex, France

maeva.laquittaine@horiba.com

Glow Discharge Optical Emission Spectroscopy (GDOES) is commonly used to analysing depth profile composition of multi-layer materials and coatings [1,2]. Thin layers down to the nanometer level can be « resolved ». However in many situations the eroded crater shape has a significant impact on GD analysis and especially on the shape of the interfaces. This leads to layer broadening on one side and uncertainty on interface positioning on the other side. Several approaches have been proposed to correct for this effect, either empirical [3], or based on sputtering process modelling and deconvolution [4]. In this poster we present our work on the improvement of layer thickness determination thanks to the combination of the modelling of GD signals and an in situ measurement of the depth as a function of time (DiP [5]). The modelling strategy is to describe the erosion rate as a polynomial function of the radial coordinate, resulting in a non flat crater shape, and to model the sample as a stack of layers, with thickness as a parameter. Then we can calculate the corresponding depth profile, and fit to the data. For this purpose, we have to adjust several parameters including polynomial coefficients of the erosion rate and layer thickness. In a nutshell, we succeed to refine the determination of layer thickness thanks to a better understanding of erosion rate and crater shape impacts on depth profile.

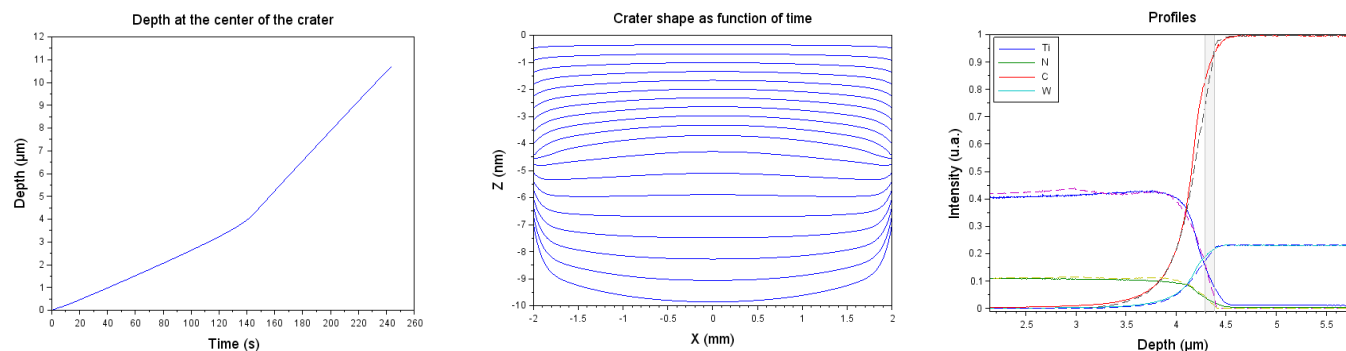


Figure 1 : Modelisation of TiNCW sample
a) DiP measurement b) Crater shape modelling
c) Experimental and modelled profiles with an estimated uncertainty on interface position

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P28

Optimizing GDOES Sputtering of Metal/Polymer Multilayer Systems by Plasma Gas Switching During the Test

Alexandre François-Heude¹, Sophia Gaiashi², Patrick Chapon²

¹Vallourec Research Center France, Aulnoye-Aymeries

² HORIBA Scientific, 16-18 rue du Canal, 91165 Longjumeau cedex, France

alexandre.francoisheude@vallourec.com

Determining a suitable set of operational conditions in GDOES can be difficult in case of thick metal/polymers hybrid systems since each layer requires different power or pressure for the analysis. By the way, recent RF-GDOES developments suggest Ultra Fast Sputtering to be a way to accelerate analysis of polymer (by introducing oxygen in the common plasma gas, i.e. argon). However, such conditions are not suitable for metal surface since oxygen can passivate them and slows down experiments on these surfaces.

The present work aims at determining the feasibility to improve efficiency of analysis of a metal/polymer multilayer system by switching the plasma gas during the GDOES analysis. Depth-profiling analyses are therefore carried out with optimized conditions for both the organic coating and the electroplating. The difficulty is that this operation requires stopping the test to purge oxygen of the chamber after analysis of the polymer in UFS mode and repositioning the specimen tested area in front of the anode, to continue with metal analysis. The investigated coating system consists in an epoxy paint (30-30 μm) on Cu-Sn-Zn ternary alloy electroplated on steel. It has been shown that the procedure can be performed easily and results in good aspect of both the sputtered crateria (homogeneous with clear edges, absence of electric arc) and the glow discharge depth profiling (no abnormal signal fluctuation).

The organic coating sputtering rate has been estimated from the time to consume the whole coating thickness (which had been preliminary determined by the magnetic induction (ISO 2178) and eddy current (ISO 2360) methods by using a dual-probe device). It was estimated that UFS (650 Pa, 35 W, anode of 4 mm diameter) enables to increase sputtering rate by a factor of 10 compared with the argon plasma alone (650 Pa, 20 to 25 W, anode of 2 to 4 mm diameter). Sputtering rates were estimated to increase from 0.5 to 5-6 $\mu\text{m}\cdot\text{min}^{-1}$ thus reducing the coating sputtering duration from 4000 to 500 sec and to divide the overall analysis duration by a factor of 2. Above all, it has enabled to avoid coating thermal degradation and occurrence of electric arc. The analysis of the underlying electroplating with the argon plasma alone has resulted in a satisfying GDOES depth-profiling, i.e. without metal surface alternation, at a sputtering rate of 2.3 $\mu\text{m}\cdot\text{min}^{-1}$, as measured by DiP.

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P29

New Strategies to Improve the Analytical Performance of Pulsed Glow Discharge Time Of Flight Mass Spectrometry

Lara Lobo, Rocío Muñiz, Rosario Pereiro, Alfredo Sanz-Medel

Department of Physical and Analytical Chemistry, Faculty of Chemistry, Julián Clavería 8 33006, Spain

laraloborevilla@hotmail.com

Glow discharges (GDs) either with optical emission or mass spectrometric detection are well recognized atomization/excitation/ionization sources for the analysis of solid materials (conductive and insulating) with depth resolution capabilities in the nanometric range and limits of detection at the ppb-low ppm level. During the last years, the combination of a pulsed GD (PGD) source with a time-of-flight mass spectrometer (TOFMS) has received much attention and recent developments are now opening new fields of application due to its particular features.

Typically, glow discharges are run in an Ar discharge and positive ions are traditionally detected. However, the determination of certain elements can be hindered due to the lower first ionization potential of Ar (compared to e.g. halogens) or because the concentration is below the limits of detection. In this line, novel approaches to broaden the potential applications of this analytical technique are proposed in this communication:

- i) The detection of negative ions in GDs will be thoroughly investigated for the determination of halogens in polymeric materials. Not only elemental information, but also the possibility of using this feature to obtain characteristic molecular information will be presented.
- ii) Efforts to improve the limits of detection will be also be pursued by the use of alternative discharge gases. In particular, Ar+He and Ar+O₂ mixtures will be shown

P30

Glow Discharge Optical Emission Spectrometry and Differential Interferometry Profiling for Thickness Determination of SiO_xN_y Layers

Sofia Gaiaschi¹, Rosa Ruggeri², Francesca Monforte², Simon Richard¹, Patrick Chapon¹

¹HORIBA Scientific, 16-18 rue du canal, 91165 Longjumeau cedex, France

²IMM-CNR UMR Strada VIII n. 5 Zona Industriale, Catania, Italy

sofia.gaiaschi@horiba.com

Silicon oxynitrides (SiO_xN_y) are used in a variety of applications, such as optical and protective coatings and most importantly, dielectric thin films. They offer high dielectric constants and chemical inertness. In addition their optical properties are adjustable over a large range of values.

Pulsed Radio Frequency Glow Discharge Optical Emission Spectrometry (RF-GDOES) relies on the very fast sputtering (typically $\mu\text{m}/\text{min}$) of a representative area of the investigated sample by a high density and low energy RF plasma, providing the Fast Elemental Depth Profile of thin and thick films, with nanometre depth resolution. A full elemental coverage can be obtained going from H (121 nm) to K (766 nm).

The most recent advance for this technique is the real time measurement of the depth of the sputtered crater depth thanks to a new Differential Interferometry Profiling (DiP) module integrated to the GD source. While this method gives a direct access to layers thickness and erosion rates when applied to metallic layers, its application to transparent materials such as SiO_xN_y requires a modeling step based on the optical properties of the sample.

In this work SiO_xN_y layers deposited by Low Temperature Plasma Enhanced Chemical Vapor Deposition were studied and a wide range of chemical compositions was investigated. The coupling of RF-GDOES and DIP allowed to determine the layers thicknesses. A comparison with Spectroscopic Ellipsometry will be presented.

P31

Characterization and Corrosion Behaviour of Pure Titanium in Sulfuric Medium

Sébastien Dubent

CNAM Paris - Laboratoire de Matériaux Industriels, 292, rue Saint Martin, 75141 Paris, France

sebastien.dubent@cnam.fr

Although titanium is a chemically very reactive species, it is extremely oxidizable and, thanks to the formation on the surface of a protective oxide layer of a few nanometers thick, is deemed to have a high corrosion resistance. This very adherent natural oxide layer reforms spontaneously if scratching of the surface in the presence of air or water. However, very reductive conditions, as in sulfuric medium, decrease the protective nature of the layer and can cause corrosion. Therefore, in the case of the use of titanium in the design of electrolyzers for hydrogen production, the risk of degradation of parts is real. In addition, the presence of hydrogen in the system increases this risk and can exacerbate damage. Indeed, the production of hydrogen can be followed by adsorption with diffusion of hydrogen molecules in the phase of the material (phase α for pure titanium). However, if the solubility limit of hydrogen in titanium is reached, there may be hydrides precipitation causing metal embrittlement. These two phenomena, corrosion and hydrogenation, can cause a decrease in the lifetime and efficiency of electrolyzers, hence the need to determine the exact origin and to characterize the nature of the damages.

P32

GD-OES Crater Engineering: The Challenge of Wet Chemical and/or Ar Cluster Sputtering Curing for Nanometric XPS Analyzes

Anaïs Loubat^{1,2}, Sofia Gaiaschi³, Muriel Bouttemy², Mathieu Frégnaux², Damien Aureau², Jackie Vigneron², Arnaud Etcheberry²

¹ Institut Photovoltaïque d'Ile-de-France (IPVF), 8 rue de la renaissance, 92160 Antony, France

² Institut Lavoisier de Versailles (ILV), UMR 8180 CNRS-UVSQ, IPVF, 78035 Versailles, France

³ HORIBA Scientific, 16 rue du Canal, 91165 Longjumeau cedex, France

anaïs.loubat@ipvf.fr

Photovoltaic cells based on CIGS (Cu(In,Ga)Se₂) absorbers are among the most efficient in photo-conversion. As part of the manufacturing cycle in which the absorber is involved, the fine control of the overall composition in the CIGS layer and at its interfaces with the front and back contact layers are crucial for the success of the final stack processes. To achieve an absolute determination of this chemical composition, GD-OES and XPS coupling is a promising tool providing at first sight complementary advantages: GD-OES high etching rate and XPS surface chemical (composition and chemical environment) diagnostic. Particularly, specific in-depth location can be precisely reached by live GD-OES profiling monitoring and supplemented by XPS analyses directly performed in the GD crater. Dimension (large sputtering area of 4 mm) and flat bottom topography totally match with the XPS spot size (400 μm) and morphology requirements.

A previous study of GD-OES and XPS coupling on CIGS absorbers [1] has already shown great potentials. Nevertheless, the question of the preservation of the original chemical information in the bottom crater is a crucial point. Indeed, D. Mercier & al. have shown that surface modifications are depicted in the GD crater, mainly arising from redeposit materials due to inward flux and metallic droplet formation inherent to the low Ga melting point. The depth modification could be limited by GD condition adjustment such as the gas nature and the gas flux direction but could not be totally avoided. As a consequence, an intermediate step to restore the crater at the end of the GD profiling and prior to XPS chemical characterization is mandatory.

In this contribution, we will focus on this intermediate step by considering two ways for the crater curing. On the one hand, the potentiality of ex-situ wet chemical engineering (HCl, KCN and Bromine dipping) will be presented. On the other hand, a physical curing approach based on the use of Arⁿ⁺ cluster sputtering, directly performed inside the XPS analysis chamber, will be evaluated. Actually, this new generation of ion source enables a better control and thus, a considerable decrease of the erosion damages. Finally, a combination of these two processes will be evaluated.

References

[1] D. Mercier, M. Bouttemy, J. Vigneron, P. Chapon, A. Etcheberry, "GD-OES and XPS coupling: A new way for the chemical profiling of photovoltaic absorbers", Appl. Surf. Sci. 347, pp. 799–807, 2015.

Acknowledgements

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P33

The GD - Group on LinkedIn

Vinay Naik

ASE India, India

vinay.n@advscientific.com

Group Established in Nov 15 -2011. The GD-OES & GD-MS group is designed for Professionals – GD users of course but mainly Researchers and Engineers in various fields such as Corrosion, Spectroscopy, Nanomaterials, Surface Analysis, Elemental analysis, PV, Electronic industry etc

The screenshot shows the LinkedIn group page for "GD-OES/ MS(Glow -Discharge Optical Emission SPectrophotometer/ Mass Spectrometer". The page header includes the LinkedIn logo and navigation links like "What is LinkedIn?", "Join Today", and "Sign In". The group name is prominently displayed, along with "190 members" and a "Join" button. Below the name are tabs for "Discussions", "Promotions", "Jobs", and "Search". A grey banner contains an information icon and text: "About the GD-OES/ MS(Glow -Discharge Optical Emission SPectrophotometer/ Mass Spectrometer Group", "GD-OES & GD-MS Professional group", "Have something to say?", and "Join LinkedIn for free to participate in the conversation. When you join, you can comment and post your own discussions." The main content area features a diagram of a GD-OES/MS system on the left and a spectral plot on the right. The diagram labels components like "Excitation Tube", "Sample", "Excitation Source", "Excitation Gas", "Excitation Gas Inlet", "Excitation Gas Outlet", "Excitation Gas Inlet Valve", "Excitation Gas Outlet Valve", "Excitation Gas Inlet Filter", "Excitation Gas Outlet Filter", "Excitation Gas Inlet Filter Valve", "Excitation Gas Outlet Filter Valve", "Excitation Gas Inlet Filter Valve", "Excitation Gas Outlet Filter Valve", "Excitation Gas Inlet Filter Valve", "Excitation Gas Outlet Filter Valve". The spectral plot shows intensity versus wavelength with various peaks labeled. To the right of the plot is a section titled "About this Group" with details: "Created: November 15, 2011", "Type: Professional Group", "Members: 190", and "Owner: Vinay N.". At the bottom right, there is a "Find career opportunities" button with the LinkedIn logo.

Welcome to the group !

This group is intended to share technological advances, published papers and various up-coming applications of GD-OES/MS in surface engineering, so feel free to introduce yourself and share about your activity in this field and possibly ask questions so that the community can help in return.

Our MEMBERS Our STRENGTH 424 members.....

P34

Scaling Laws Between Mono and Multi-Point Configuration In Positive DC Corona Discharge in Air

D. Raouti¹, S. Flazi², D. Benyoucef³, A. Mokadem^{4,5}

¹ Université de Saida, Faculté des Sciences et de Technologie, Département d'Electrotechnique, BP 138 Cité ENNASR, Saida, Algeria

² Département d'Electrotechnique, Faculté des Sciences et de Technologie, Université d'USTOMB Oran, BP 1505 El-M'Naouar Oran, Algeria,

³ Laboratoire Génie Electrique et Energies Renouvelables, Chlef university, Algeria,

⁴ Laboratoire Matériaux (LABMAT), Ecole Nationale Polytechnique (ENP), BP1523 Oran Mnaouer, Oran, Algeria

⁵ Université Hassiba Benbouali, Chlef, Algeria

raouti1@yahoo.fr

This work is devoted to the study of the electrical behavior of DC point-to-plane air corona discharges. We specifically aim at looking for possible scaling laws that could exist when passing from a mono-point to plan, to multi-points to plan reactor geometry. The electrical parameters are obtained based on experimental data of the discharge voltage and current, thanks to the simulation of our model, proposed and validated, in references [1, 2]. The discharge is represented by variable, in series resistor and capacitor. First, both electrical parameters of the discharge are determined in several operating points relative to the voltage magnitude and inter-electrode distance. This step is done for all the following geometric configurations of electrodes: - mono tip / plan, - close bi tip / plan – distant bi tip / plan remote. Thereafter, we compare the discharge resistance and capacity for the three configurations, phase by phase, for the same operating points.

References

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2. D. Raouti, S. Flazi, D. Benyoucef, Modeling and Identification of Electrical Parameters of Positive DC Point-to-Plane Corona Discharge in Dry Air Using RLS Method, IEEE Transactions on Plasma Science, 2016

P35

Measurement of Homogeneity of Reference Materials of Special Alloys by GD - Atomic Emission Spectrometry

Muravskaya N.P., Ivanov A.V., Ermakova I.I., Zyablikova I.N.

FGUP «VNIIOFI», 119361, Russia, Moscow, Ozernaya st. 46,

Ermakova@vniiofi.ru

Federal State Unitary Enterprise VNIIOFI is one of the leading metrological institutes of Russia. The field of activity of institute is very extensive and indissolubly connected with measurements and control of their quality. For this reason Federal State Unitary Enterprise VNIIOFI is a keeper of a large number of primary measurement standards (national standards). The department of certification and testing is a keeper of the primary measurement standard of mass (molar) fraction and mass (molar) concentration of components in the liquid and solid substances and materials based on spectral methods (GET 196-2015). One of the methods which is realized in the standard is the GD - atomic emission spectrometry provided by spectrometer Profiler 2.

Due to the increasing requirement of various industries, such as an aerospace engineering, in improvement of quality of the products, annually producers of reference materials develop and issue new material types, in particular alloys. A job of institute is carrying out testing and types approval of these materials.

One of the serious problems is research of homogeneity of monolithic samples. As a rule, such analyses are made by means of the X-ray fluorescent analysis. However, recently, in search of new solutions and upgrade of materials producers had begun focus on a microalloying and entering of nanoinclusions, and sensitivity of the X-ray fluorescent analysis became not enough. That is why has appeared the requirement in search of new methods of the analysis for distribution of microcomponents in samples volume.

Specialists of Federal State Unitary Enterprise VNIIOFI successfully realize research of homogeneity of monolithic samples by the GD method. The method has a number of advantages in comparison with the X-ray fluorescent analysis. First, GD has the better accuracy and sensitivity, that allows to analyze microcontents of elements in a sample. Secondly, at the expense of replaceable anodes the spectrometer gives the chance of locally analysis of impurity that is necessary for the nanostructured materials. Thirdly, the method allows to research difficult impurity which are usually lost in case of chemical decomposition of samples. For example, such impurity is silicon.

Finding GD - atomic emission spectrometry perspective, in Federal State Unitary Enterprise VNIIOFI are conducted works on metrological providing for this method: development of measurement procedures (including reference) for the alloying impurity and microimpurity in alloys with various bases, inclusion of a measurement procedures of research of homogeneity of materials in programs of tests for reference material and the international comparison of a standard.

P36

Corrosion Product Films on High Purity Mg Alloys

¹A. Maltseva, ¹A. Michot Mignucci, ¹C. de Faria Barros, ¹K. Ogle, ¹P. Volovitch,
²S. Gaiaschi, ²P. Chapon, ³N. Birbilis

¹IRCP, PSL Research University Chimie ParisTech, 11 rue P. et M. Curie 75005 Paris France

²HORIBA Scientific, HORIBA Jobin Yvon S.A.S., 16-18, rue du Canal 91165 Longjumeau Cédex France

³Department of Materials Engineering, Monash University, Clayton, VIC 3800, Australia

polina.volovitch@chimie-paristech.fr

Enhanced cathodic reactivity of anodically polarized pre-corroded magnesium is usually assigned to enhanced catalytic activity of corrosion product films composed of a thin compact inner oxide and a more porous hydrated oxy-hydroxide layer [1]. Several explanations of this effect are proposed in the literature, among which the formation of local cathodes due to the surface enrichment by more noble elements and the increased cathodic reactivity of the oxide-hydroxide film by itself are the most advanced in the modern state of the art. Several recent works reported Fe enrichment in corroded Mg alloys, the behavior of other elements is less studied; the surface enrichment in Mg-Ca and Mg-Li alloys is not expected however the anomalous cathodic reactivity under anodic polarization is still observed. Study of depth distribution of different impurities in corrosion product films can help to understand the phenomena. Concerning the effect of corrosion product films, the anodic reactivity of Mg decreases at alkaline pH because of the formation of low soluble oxide-hydroxide films. It is important however to understand how these films affect cathodic reactivity as well as if their chemical stability is sufficient to talk about “passivity” at alkaline pH.

To better understand the relation between the solution chemistry, the chemistry and the morphology of corrosion products and their effect on the reactivity, surface film composition, growth kinetics and reactivity of 3 low alloyed magnesium alloys (99 % of Mg, less than 300 ppm Fe) under formed in strong alkaline condition (pH 10.5 – 13.0) films was studied using a combination of analytical and electrochemical methods. Glow Discharge Optical Emission Spectrometry was used for depth profiling of the dense layer and Inductively Coupled Plasma Optical Emission Spectroscopy for direct measurement of selective dissolution. The results demonstrated that the compact layer formed in alkaline pH is enriched by Fe (Fig. 1a, b), Ca and Na, while Mn is selectively dissolved from the surface (Fig. 1a, b). Ca incorporation is higher in deaerated conditions.

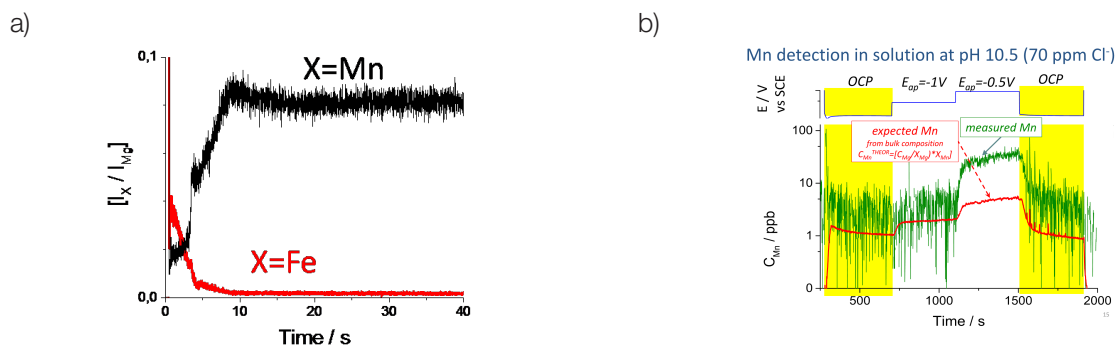


Figure 1. Fe enrichment and Mn leaching from Mg-0.52 wt. % Mn 80 ppm Fe alloy in alkaline conditions and 70 ppm Cl⁻.

a) Post mortem analysis of the layer formed at pH 12.5: relative intensities of Fe and Mn (I_X , $X=Fe$ or $X=Mn$) normalised by Mg signal I_{Mg} , measured by GD-OES, sputtering rates 3 and 150 nm s⁻¹ in oxide and metal substrate.

b) In-situ survey of the layer formation at pH 10.5 Streamline concentration of Mn measured by ICP compared to expected value from the bulk composition and Mg dissolution at open circuit potential (OCP) and under applied anodic potential.

Spatial distribution of corrosion products in thicker porous layer was surveyed by real time μ Raman mapping. Average brucite film growth kinetics monitored in real time by the signal to background ratio at wavelength 3650 cm^{-1} was different from the expected from the simple precipitation model. There was no carbonate ions incorporation in the film at short exposure times. External layer became denser and reach steady state in thickness quicker at $\text{pH} > 11$ than at $\text{pH} < 11$. The role of dissolution –precipitation processes and the effects of solution chemistry in film formation mechanisms are discussed. The barrier properties of the films formed at different pH were compared in flowing solution at $\text{pH} 10.5$. After the formation of the film in stagnant electrolytes ($\text{pH} 13$ or $\text{pH} 10.5$), the solution was replaced by flowing electrolyte ($\text{pH} 10.5$, 0.005 M Cl^-) and potentiostatic and potentiodynamic tests were completed. The results demonstrated different effects on both, electrochemical response and Mg dissolution rate, of films formed at $\text{pH} 12.5$ and 10.5 .

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P37

Local Electrochemical Techniques Used for Spatially-resolved Surface Analysis

Nicolas Murer, Sébastien Verret

Bio-Logic SAS, 4 rue de Vaucanson, 38170 Seyssinet-Pariset, France

sebastien.verret@bio-logic.net

Classical electrochemistry consists in characterizing the global response of a metallic sample, ie the response coming from the entire investigated area. Local electrochemical techniques allow one to obtain spatially-resolved information on the surface properties of a heterogeneous conducting sample. These techniques can be used to extend the understanding of electrochemical mechanisms in the field of corrosion, corrosion protection, energy and sensors applications. Understanding the local response of an electrode allows one to predict and control its global response.

P38

On-line measurement of the reactivity of Al-Li alloy during a surface pretreatment sequence.

¹O. Gharbi, ²N. Birbilis, ¹K. Ogle

¹Chimie-ParisTech, PSL Research University, CNRS - Institut de Recherche Chimie Paris, Paris 75005, France

²Department of Material Science and Engineering, Monash University, VIC 3800, Australia

oumaima.gharbi@chimie-paristech.fr

Surface treatment processes frequently involve metal dissolution and a knowledge of the elementary dissolution kinetics could prove very useful for the development of new improved surface treatment formulations. The corrosion reactions occur within a relatively short time with very large rates; they often involve massive precipitation, and sometimes particle release. For example, surface conditioning for Al alloys generally involves an alkaline etching and acid pickling. Ideally, the aim is to provide a homogenous surface chemistry prior to subsequent surface treatment by removing the intermetallic particles.

However, the electrochemical properties of the intermetallic phases - such as the S-phase (Al_2CuMg) or the S-phase (Al_2Cu) - are sufficiently different from the matrix^{1,2} that certain alloy components will be enriched on the surface due to selective dissolution and / or redeposition. The aim of this study is to quantitatively measure the selective dissolution processes and characterize the residual films that form during these pretreatment steps.

To this end, we have developed an *in situ* measurement of elemental dissolution during a pretreatment sequence for aluminum alloys under simulated industrial conditions using atomic emission spectroelectrochemistry (AESEC). Through a mass balance, the elemental dissolution rates also yield the quantity of residual Cu and Mg. Moreover, it was possible to detect particle detachment and their composition during the pretreatment.

These results are combined with a microscopic analysis of the surface and with conventional electrochemistry to clarify the nature of the residual films formed and their effect on the electrochemical activity of the Al alloy under simulated corrosion conditions³. Finally, additional results GD-OES analysis will be presented to understand the effect of Li addition on the surface chemistry of Al-Li alloys during surface treatment.

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8th International GD Day

Workshops

W1

Dip Workshop

Sofia Gaiaschi

HORIBA Scientific, 16 rue du Canal, 91160 Longjumeau, France

sofia.gaiaschi@horuiba.com

The recent introduction of the Differential Interferometry Profiling (DiP) inside the GD instruments is a powerful advancement for Glow Discharge Optical Emission Spectrometry. Thanks to DiP it is now possible to obtain the direct measurement of the crater depth during the GDOES profiling. Such measurement is straightforward for non transparent materials and it gives direct access to important quantities such as:

- Erosion rate
- Layer thickness
- Crater depth
- Variations in reflectivity

In this workshop we will see how the DiP measurement can be included in a GDOES analysis and how to treat the data in order to obtain the key information about the analysed material.

W2

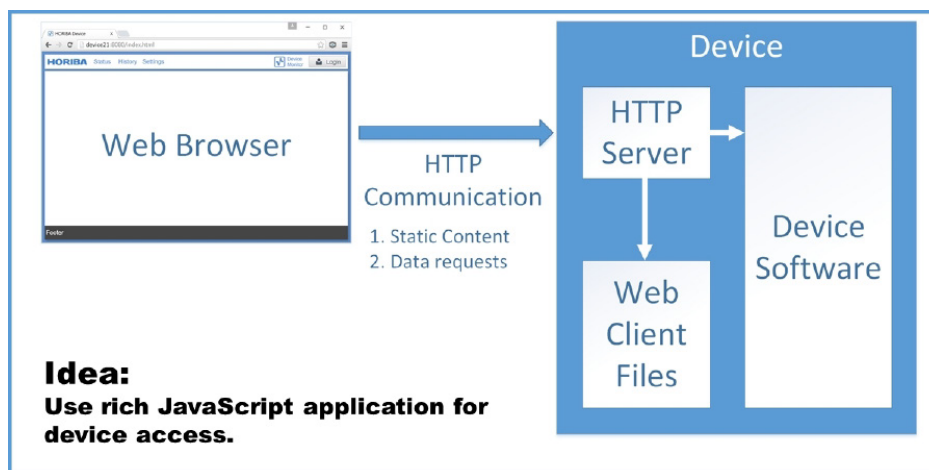
HORIBA Device Monitor

Alexander Karpov, Yuriy Popov

HORIBA Scientific, Russian Federation

ypopov@horiba.ru

HDM is a technology adding web-interface to HORIBA device



1. Browse measurement results
User can browse and find measurement results, display them in various interactive forms and export to his/her local PC.
2. Monitor device status
User can monitor current activity of the device, watch measurement process and current values.
3. Maintain device
Service person can directly access device logs and alarms for problem analysis. Service person can keep track of the status of consumables and reagents

W3

HJY Service for GD

Richard Toutain, Alain Salaville

HORIBA Scientific, 16 rue du Canal, 91160 Longjumeau, France

services.jyfr@horiba.com

We will be pleased to welcome all the participants of the GD Day around a table to discuss and discover all services that HJY can provide around and for the GD-OES spectrometer.

If you are already using a GD, or if it is under process, this workshop will be the opportunity to ask all technical questions you may have.

Richard who is International Service Engineer as well as Alain who is Sales Manager of Customer Support will be your contact persons.

Beside your questions, we will address various topics such as :

- DIP > It is the last worldwide innovation for GDS. It is now possible to measure the actual depth of the GD crater and the erosion rate of the layers. See also the posters P15 and P30 and the Workshop 1 for more on DIP. This unique option can be installed on your existing instrument - We will give you all details you may need.

- Service contracts > We are offering 3 kinds of Service contracts for the GDS. Let discover which one will be more adapted for you.

- Second hand GD > HJY also offer some instruments already used which are totally refurbished and fully tested. We have some units available at the moment that we will introduce in case of interest.

- Accessories 1 >, are you interested in other anode diameters, in the Li bell transfer chamber, in an external profilometer, in a Nitrogen generator, in a cooling device, in a small samples holder ? We have solutions.

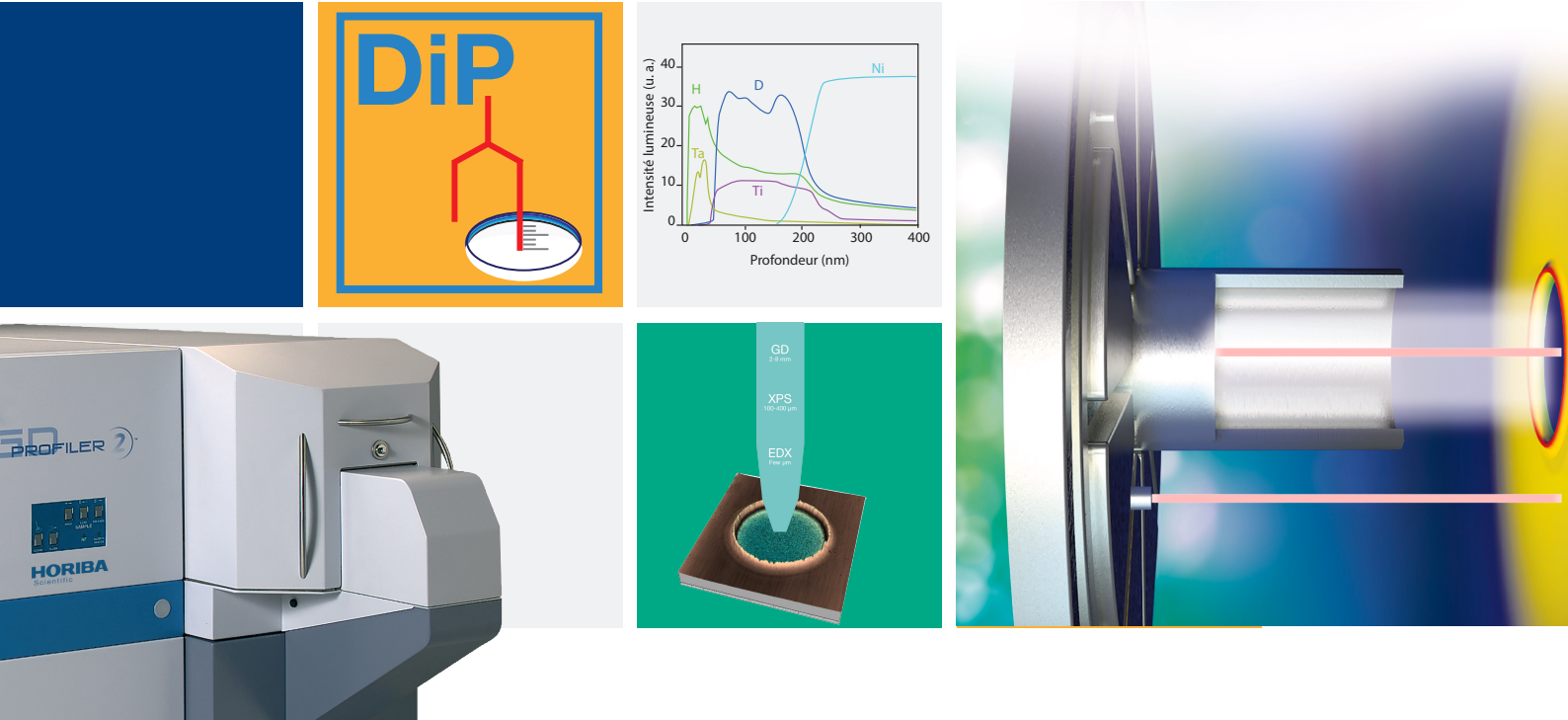
- Accessories 2 > Some other equipments may be required for Sample preparation before GD analysis (grinding/Cutting/Polishing/Pressing...) HJY also has many solutions of potential interest.

- Trainings > Different trainings can be done by HJY specialists either for service, operation or application. It is usually done in our demolab, but also on your site when required. We will share the training catalog with you or provide you with a quotation. HJY is certified as official training center.

- Calibration > You may want to know more about which standard samples to be used to calibrate your instrument: SUS / RM / CRM or you want to know how to purchase the calibration kit described in the poster 20 - We will be pleased to share experience with you.

Multi-Layered Samples

Thickness, elemental profiles and access to interfaces



Elemental profiles by RF-GDOES

Glow Discharge Optical Emission Spectrometry

- Plasma erosion and excitation
- Elements: spectrometric measurement
- Thickness: differential interferometry measurement
- Complementarity XPS/SEM/Micro-Raman
- Fast ~7 nm/sec
- All elements H to U
- Depth resolution: nm
- Crater diameter: 4 mm