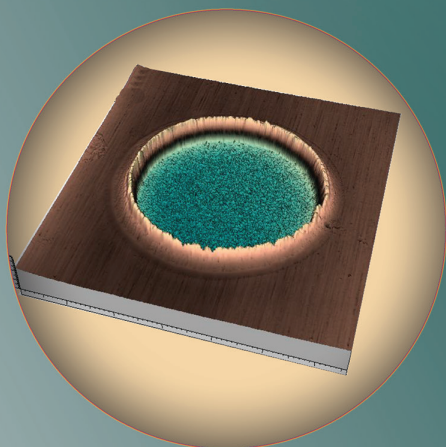
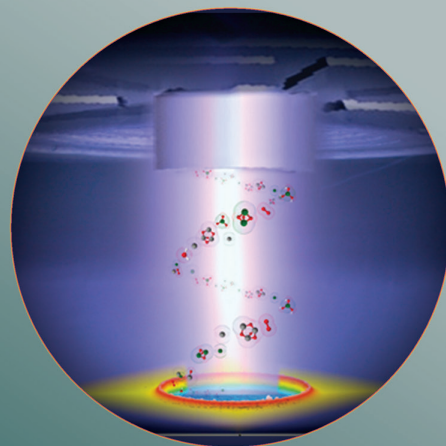
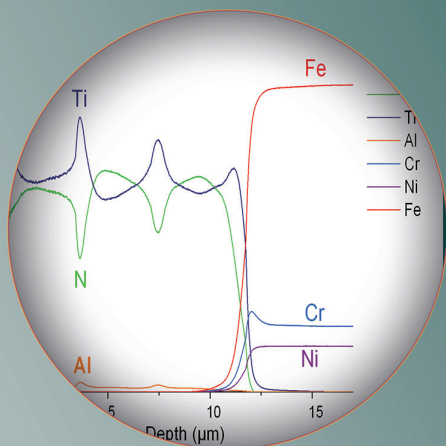
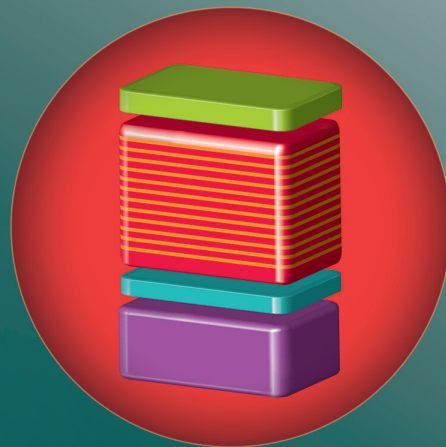


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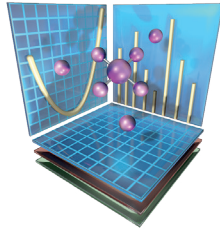
**11 & 12
June 2014
France**



**7th
GD Day**



**For surface and
depth profile
analysis**



GD Day
2014 Symposium

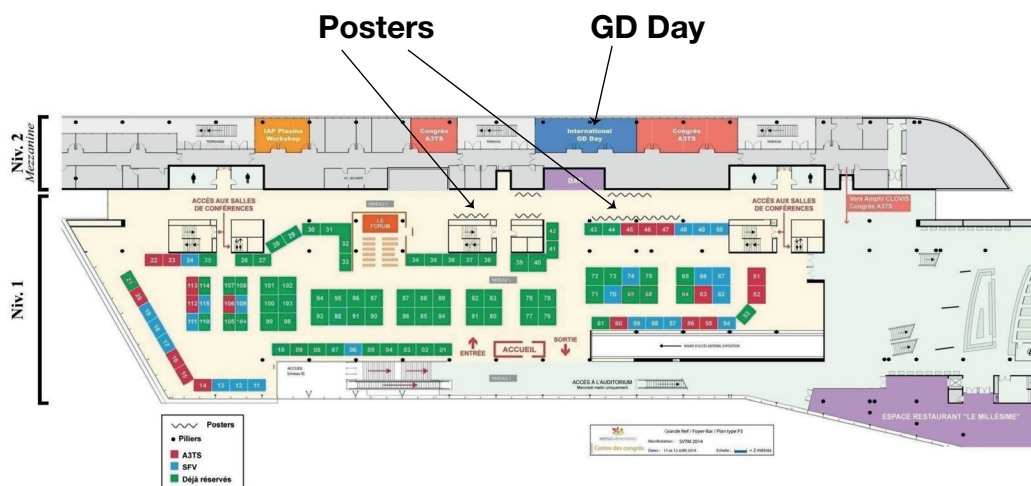
GD Day 2014

www.gd-day.com

Practical information

Location

Centre des Congrès, 12 bd Général Leclerc - 51722 Reims cedex



Poster guidelines

Poster boards are provided for poster presenters to display their posters.

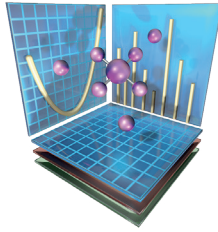
Poster format is A0 vertical.

Posters will be on display during the whole symposium.

Gala Dinner

The historical tour and the gala Dinner will be held on wednesday 11, from 8 pm.

Palais du Tau
2 Place du Cardinal Luçon
51100 Reims



GD Day 2014 Symposium

Wednesday 11 June 2014

13:30 Welcome to the participants of the GD day

Tiberiu Minea - SFV, Patrick Chapon - HORIBA Scientific, Rony Snyders - IAP

13:45 GD Day - IAP Plenary session

Chair: T. Minea, University of Orsay, France

13:45 **O1** Plasma diagnostics with laser and spectroscopic techniques
N. Sadeghi, University of Grenoble, France

14:25 **O2** Thin film and nanostructured materials produced by low temperature plasma processes and their application to solar cells
P. Roca i Cabarrocas, LPICM-CNRS, Ecole Polytechnique, Palaiseau, France

15:05 IAP posters presentation & SFV exhibition

15:45 Coffee break and poster session

16:10 GD Day Session 1

Chair: P. Chapon, HORIBA Scientific, Longjumeau, France

16:15 **O3** Nitrogen incorporation in metallic alloys by plasma immersion surface treatments at moderate temperature.
L. Pichon¹, C. Templier¹, O. Ozturk², J.P. Rivière¹, J. Cormier¹, P. Villechaise¹, J.B. Dubois¹, S. Chollet¹, S. Okur², M. Drouet¹
¹Institut P¹ - CNRS-Université de Poitiers-ENSMA, Chasseneuil-Futuroscope, France
²Izmir Institute of Technology, Izmir, Turquie

16:35 **O4** Rare earth doping of oxides and nitrides for photonics and photovoltaics applications
A. Ziani, C. Davesne, L. Dumont, P. Benzo, J. Cardin, P. Marie, C. Labbé, C. Dufour, X. Portier, F. Gourbilleau
CIMAP/CNRS/CEA/ENSICAEN/UCBN, Caen, France

16h55 **O5** GDOES studies of minor alloying elements distribution in the oxide scales and sub-scale areas of high temperature Ni-based superalloys
W. Nowak, A. Jalowicka, D. Naumenko, E. Wessel, L. Niewolak, L. Singheiser, and W.J. Quadackers
Institute for Energy and Climate Research, Forschungszentrum Jülich GmbH, Jülich, Germany

17h15 **O6** A unique approach of GDOES for improving Scanning Electron Microscopy imaging
K. Kawano, K. Shimizu, G.E. Thompson, Keio University Japan and Manchester University UK

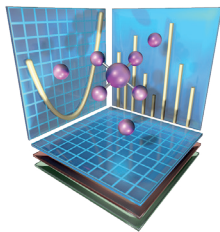
17h35 **O7** Hybrid diffusive/PVD treatments to improve the tribological resistance of Ti-6Al-4V
E. Marin¹, R. Offoia¹, A. Lanzutti¹, M. Regis², S. Fusi², L. Fedrizzi¹
¹Department of Chemistry, Physics and Environment, University of Udine, Udine, Italy
²Lima Corporate Spa, Udine, Italy

17h55 Poster talks (5 min/poster)

P1 Presented within IAP

Endpoint control supervision on dry etch, cleaning, PECVD processes

E. Bluem¹, C. Louis¹, J.P. Vassilakis¹, H. Birk², ¹HORIBA Scientific, Longjumeau, France, ² HORIBA Semiconductor, Oberursel, Germany



GD Day 2014 Symposium

- P2** Bulk and thin films standards for GDOES
P. Kiryukhantsev-Korneev, E.A Levashov, S. Rupasov, National University «MISIS», Moscow, Russian Federation
- P3** Sample of Science: a peer-sharing platform for material scientists
R. Melet, O. Acher, Sample of Science Editorial Office, Palaiseau, France
- P4** Dedicated measurement test bench for study of RF discharge parameters of the GD-source in GD-TOFMS
P. Bulkin¹, S. Legendre^{1,2}, D. Daineka¹, A. Tempez², T. Novikova¹ and P. Chapon²
¹LPICM, CNRS-Ecole polytechnique, Palaiseau, FRANCE, ²HORIBA Scientific, Palaiseau, France
- P5** Plasma and gas flow modeling for GD TOFMS instrument
T. Novikova¹, S. Legendre², A. Tempez², P. Bulkin¹, P. Chapon², ¹LPICM-CNRS, Ecole Polytechnique, Palaiseau, France, ²HORIBA Scientific, Palaiseau, France
- P6** New insights on the understanding of Cu(In,Ga)Se₂/CBD-ZnS/ Windows interfaces for high efficiencies solar cells using advanced composition profiling techniques
T. Hildebrandt¹, C. Olivero², P. Chapon², D. Lincot¹, N. Naghavi¹
¹Institute of Research & Development on Photovoltaic Energy (IRDEP), EDF CNRS Chimie ParisTech, Chatou, France, ²HORIBA Scientific, Longjumeau, France
- P7** Pulsed Radio Frequency Glow Discharge - Time of Flight Mass Spectrometry as a new powerful tool for characterization of materials
R. Pereira¹, B. Fernandez¹, J. Pisonero², N. Borde², A. Sanz-Medel¹, ¹Dept of Physics & Analytical Chemistry, University of Oviedo, Oviedo, Spain, ²Dept of Physics, University of Oviedo, Mieres, Spain



18:15 **End of session**

18:30 **Cocktail SFV-A3TS-GD Day-IAP**

20:00 **Walk through the historical Palais du Tau**

20:30 **Gala Dinner at the Palais du Tau**

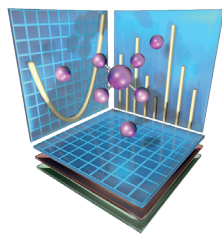
Thursday 12 June 2014

8:30 **GD Day Session 2**

Chair: Y. Popov, HORIBA, Moscow, Russian Federation

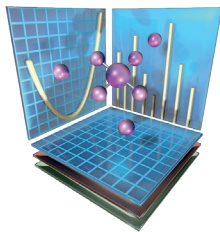
8:35 **O8** Detection of hydrogen absorbed in Mg-based alloys using GD spectrometer.
V. Knotek, P. Novák, D. Vojtěch, Institute of Chemical Technology Prague, Czech Republic

8:55 **O9** Depth profiling analysis of thin film composite membranes by pulsed glow discharge mass spectrometry: Layer modifications due to oxidation in seawater
N. Borde¹, C. González¹, J. Pisonero¹, J. Fuertes¹, R. Sandin², A. Sanz-Medel³, ¹University of Oviedo, Mieres, Spain, ²R&D Dept Acciona Agua SAU Barcelona, Spain, ³Dept of Physical and Analytical Chemistry, University of Oviedo, Oviedo, Spain



GD Day 2014 Symposium

- 9:15 **O10** Is GD sputtering modifying the composition of the material? An XPS study of the surface composition of GD craters
D. Mercier¹, M. Bouttemy¹, J. Vigneron¹, I. Gérard¹, P. Chapon², A. Etcheberry¹
¹Institut Lavoisier de Versailles, Versailles, France, ²HORIBA Scientific, Longjumeau, France
- 9:35 **O11** Composition depth profile of electrodeposited alloy and multilayer films
L. Peter, K. Vad, A. Csik, K. Neuróhr, I. Bakonyi and G. Molnár
Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest, Hungary.
- 9h55 Poster talks (5 min/poster)
- P8** Development of method for preparation calibration samples of Titanium with Hydrogen for GDOES
N.S. Pushilina, V.N. Kudiyarov, A.M. Lider, National Research Tomsk Polytechnic University, Tomsk, Russia
- P9** Quantitative Depth Profile analysis of Magnetostrictive FeGa Thin Films using RF-GDOES.
S. S. Kalyan Kamal¹, N. D. V. Prasad¹, L. Durai¹ and V. Naik², ¹DMRL India, ²ASE India
- P10** Depth Profile analysis of Bi-layer thermal barrier surface coating on steel substrate using RF-GDOES.
P. K. Sahoo, N. D. V. Prasad, L. Durai, DMRL India
- P11** Development of a new GD micro-plasma for analysis of low sample volumes
M. Tabarant, S. Manani, F. Chartier, CEA Saclay, Saclay, France
- P12** RF-GDOES analyses of swelling and Ce migration, on ZrO₂ based sol gel coatings, after different immersion times in no-aggressive media.
A. Lanzutti, F. Andreatta, L. Paussa, E. Marin and L. Fedrizzi
University of Udine, Department of Chemistry, Physics and Environment, Udine, Italy
- P13** Solutions to specific physical and chemical features of sample for analysis by RF-GDOES
C. Olivero, HORIBA Scientific, Longjumeau, France
- P14** Continuous Wave Micro-plasma excited by microwaves in capillary tubes. Comparison between noble gas and molecular mixture operation
O. Leroy¹, G.D. Stancu², F. Bacque¹, V. Guerra³, L.L. Alves³, P. Coche³, P. Leprince¹, T. Minea¹
¹LPGP, UMR 8578: CNRS-University Paris-Sud, Orsay, France, ²Ecole Centrale Paris, Châtenay-Malabry, France, ³Instituto de Plasmas et Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal
- P15** RF GDOES analyses of optical multilayers
O. Zywitzki, R. Belau, Fraunhofer Institute for Electron Beam and Plasma Technology FEP, Dresden, Germany
- 10:30 Coffee break and poster session**
- 10:50 GD Day Session 3**
Chair: A. Tempez, HORIBA Scientific, Palaiseau, France
- 10h55 **O12** Atom probe tomography: a mass spectrometry technique for 3D characterization of nanomaterials
D. Mangelinck¹, Y. Collignon¹, F. Panciera^{1,2}, K. Hoummada¹, M. El Kousseifi¹, H. Benallali¹, C. Perrin¹, M. Descoins¹, A. Portavoce¹, and X. Tan¹
¹IM2NP, Aix Marseille Université, CNRS, Marseille, France, ²STMicroelectronics, Crolles, France
- 11h15 **O13** Ion-plasma modification of reed switch blades
A. Tosltoguzov¹, M. N. Drozdov², O.M.N.D. Teodoro¹, I.A. Zel'tser³, ¹CeFITec, New University of Lisbon, Portugal, ²IPM RAS, Nizhny Novgorod, Russian Federation, ³RMCIIP JSC, Ryazan, Russian Federation



GD Day 2014 Symposium

11h35 O14 Morphological changes of tungsten surfaces by low-flux helium plasma treatment and helium incorporation via magnetron sputtering
*S. Iyyakkunel¹, L. Marot¹, B. Eren¹, R. Steiner¹, L. Moser¹, D. Mathys², M. Düggelin², P. Chapon³, E. Meyer¹,
¹University of Basel, Department of Physics, Basel, Switzerland, ²University of Basel, Center of Microscopy, Basel, Switzerland, ³HORIBA Scientific, Longjumeau, France*

11h55 Poster talks (5 min/poster)

P16 Raman Spectroscopy applied to thin layers analysis
R. Lewandowska, HORIBA Scientific, Lille, France

P17 New Developments in application of micro-wave discharges to surface treatments
*R. Valledor-Gonzalez¹, L. Latrasse², R. Verhoef³, Patrice Raynaud³, Th. Nelis¹
¹Berner Fachhochschule, Technik und Informatik, Bienne, Switzerland, ²Sairem, Neyron, France, ³LAPLACE, Toulouse, France*

12:05 Lunch and poster session

13:15 GD Day Session 4

Chair: S. Legendre, HORIBA Scientific, Palaiseau, France

13h20 O15 Depth profile analysis on Cu(In,Ga)Se₂ solar cells by SIMS/SNMS and GDOES
W. Hempel, ZSW,, Stuttgart, Germany

13h40 O16 GDOES of Materials for Biomedical Applications
P. Kiryukhantsev-Korneev, D.V. Shtansky, National University «MISIS», Moscow, Russian Federation

14h00 O17 Effect of annealing temperature on antibacterial activity of silver doped hydroxyapatite thin films
*C. S. Ciobanu¹, C.L. Popa^{1,2}, S. L. Iconaru^{1,4}, P. Chapon³, R.V. Ghita¹, D. Predoi¹
¹National Institute of Materials Physics, Magurele, Romania, ²Faculty of Physics, University of Bucharest, Bucharest, Romania, ³HORIBA Scientific., Longjumeau Cedex, France, ⁴Institute des Sciences de la Terre D'Orleans (ISTO), 1A, rue de la Férollerie 45071 Orléans, France*

O18 Characterization and antibacterial activity of samarium doped hydroxyapatite thin films
*C.L. Popa^{1,2}, C. S. Ciobanu¹, S. L. Iconaru^{1,5}, P. Chapon³, P. Le Coustumer⁴, D. Predoi¹
¹National Institute of Materials Physics, Magurele, Romania, ²Faculty of Physics, University of Bucharest, Bucharest, Romania, ³HORIBA Scientific., Longjumeau Cedex, France, ⁴Universite Bordeaux, EA 4592 Géoresources & Environnement, ENSEGID, Pessac Cedex, France, ⁵Institute des Sciences de la Terre D'Orleans (ISTO), 1A, rue de la Férollerie 45071 Orléans, France*

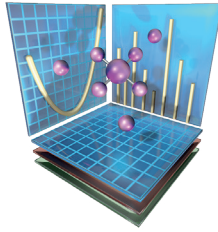
14h25 O19 DBD atmospheric pressure plasma source coupled to OES and a MS
L. Chauvet, P. Guillot, CUFR JF Champollion, Laboratoire DPHE, Albi, France

14h45 Poster talks (5 min/poster)

P18 Spatiotemporal characterization of a DBD atmospheric pressure plasma source
P. Guillot, L. Chauvet, CUFR JF Champollion, Laboratoire DPHE, Albi, France

P19 Chemical analysis of CdTe solar cells by glow discharge techniques
*G. Kartopu¹, A. J. Clayton¹, V. Barrioz¹, S.J.C. Irvine¹, A. Tempez², C. Olivero², P. Chapon², J. Cooper²
¹CSER, Glyndwr University, UK, ²HORIBA Scientific, Palaiseau, France*

P20 & P21 Characterisation of CZTSSe using Spectroscopic Ellipsometry and pulsed RF Glow discharge Optical Emission Spectroscopy - Optical Characterisation of CIGS using Spectroscopic Ellipsometry and Glow Discharge Optical Emission Spectrometry
J.P. Gaston, C. Eypert, C. Olivero, P. Chapon, HORIBA Scientific, Palaiseau, France



GD Day 2014 Symposium

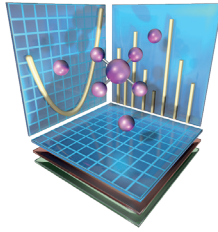
- P22** Quantitative Depth Profiling of Various Anodized Coatings by RF GDOES
F. Li, S. Anderson, Air Liquide Electronics, Balazs NanoAnalysis, USA
- P23** Glow discharge optical emission spectroscopy to analyze thin electrodeposited polyaniline films
V. Moutarlier, S. Lakard, T. Patois, B. Lakard, Université de Franche Comté, France
- P24** Depth Profiling of Phosphorous using PPTOFMS in Laser Doped Emitter
A. Tempez¹, S. Mondal², ¹HORIBA Scientific, France, ²Indian Institute of Technology Bombay, India

15:15 GD Day Final session

Chair: C. Olivero, HORIBA Scientific, Palaiseau, France

- 15h20 **O20** Reserved presentation
S. Richard, HORIBA Scientific, Palaiseau, France
- 15h40 **O21** Dynamics of GDOES induced surface roughening in metal interfaces
R. Escobar Galindo and L. Vazquez, ICMM-CSIC, Spain
- 16h00 **O22** The multiple facets of GD
R. Escobar Galindo, ICMM-CSIC, Spain

16:10 End of the GD Day



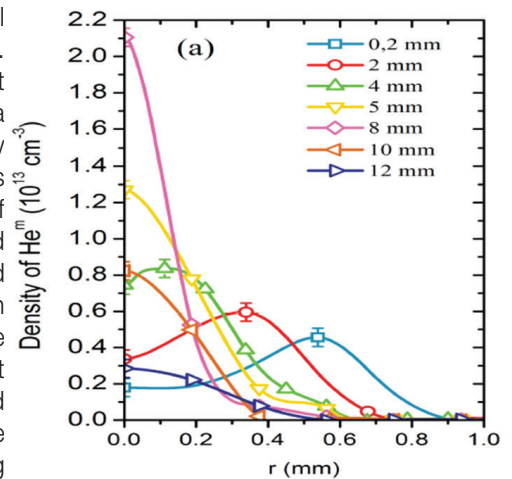
Plasma diagnostics with laser and spectroscopic techniques

N. Sadeghi

Université de Grenoble & CNRS, LIPhy (UMR5588) & LETI (UMR5129), Grenoble, France

Optical diagnostic techniques are usually non-invasive. The most popular and cost-effective is the emission spectroscopy which can provide qualitative information about species present, particularly impurities in rare-gas plasmas, the gas temperature [1] or the sheath dynamics [2].

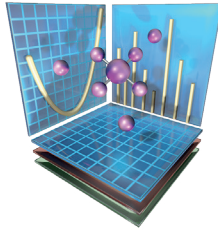
In atmospheric pressure plasmas, neutrals and electron densities can also be estimated from the spectral width of lines when using a high enough resolution spectrometers. The big advantage of the optical absorption spectroscopy (OAS) techniques is to provide the absolute density of monitored species, even if this value is sight of line averaged. However, when a cylindrical symmetry exists, Abel inversion can be applied to obtain the radial distribution of absorbing species. Figure shows the radial distribution of $\text{He}^*(^3S_1)$ metastable atoms at the exit of a helium atmospheric pressure plasma micro-jet, deduced by OAS with a 1083 nm tuneable diode laser as light source. The profile, which has a hollow shape at the exit of the plasma tube (2 mm diameter), gradually becomes centred at 5 mm from the exit. When absorption on a large number of spectral elements is of interest, it is more convenient to use the Broad-Band Absorption Spectroscopy (BBAS), whose detection limit is much improved with a Light Emitting Diode (LED) as light source. An example can be found in [3], which reports on OH radial density measured in an atmospheric pressure Ar-H₂O plasma jet by BBAS with a 308 nm LED. It has been also shown that auto-absorption can lead to important error on the gas temperature deduced from the intensity of rotational lines of OH by emission spectroscopy. The laser induced fluorescence reveals to be a powerful technique for obtaining the velocity distribution function of particles, as was done for Xe⁺ ions in a plasma Hall thruster [4].



References

- [1] P.J. Bruggeman, N. Sadeghi, D.C. Schram and V. Linss, PSST, 23 (2014) 023001.
- [2] C. Lazzaroni, P. Chabert, A. Rousseau and N. Sadeghi, Eur. Phys. J. D 60 (2010) 555.
- [3] T. Verreycken, N. Sadeghi, R. Mensink, R. van der Horst P. Bruggeman, PSST, 22 (2013) 055014.
- [4] S. Mazouffre, D. Gawron and N. Sadeghi, Physics of Plasmas, 16 (2009) 043504.

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GD Day 2014 Symposium

O2

Thin Film and Nanostructured Materials produced by Low Temperature Plasma Processes and their Application to Solar Cells

Pere Roca i Cabarrocas

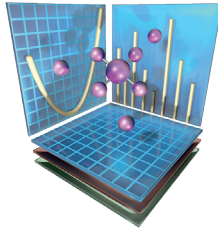
LPICM-CNRS, Ecole Polytechnique, 91128, Palaiseau, France

Over the past decade photovoltaics has emerged as a credible source of energy thanks to the extraordinary progress on crystalline silicon solar cells, which have led to a world market of over 30 GW/year and production costs well below 1 €/Wc. While PV is already cost competitive with respect to grid electricity in many countries, further penetration of this energy requires continuous cost reduction. This involves increasing solar cell efficiency while reducing production costs. In this presentation we will focus on the benefits of dry plasma processes when applied to c-Si solar cells, as well as their application to the deposition of silicon thin films and nanostructured materials.

Hydrogenated amorphous and microcrystalline silicon thin films are routinely produced using silane plasmas. While SiH_3 is often considered as the main radical for the obtaining of such films, we will show that moving the process to conditions where silicon clusters and nanocrystals are produced in the plasma can lead to high deposition rates and improved materials, such as hydrogenated polymorphous silicon and polycrystalline silicon [1,2]. Moreover, by changing the substrate from glass to crystalline silicon, it is possible to produce epitaxial thin crystalline silicon films which can be transferred to foreign substrates for flexible electronic devices [3]. Even more interesting, this low temperature epitaxial process can be extended to germanium and to the production of Si/Ge/Si quantum well structures [4]. Last but not least, combining PECVD with low melting temperature metal particles such as indium and tin opens the way to the growth of silicon nanowires, which allow to achieve efficient light trapping and carrier collection in radial junction solar cells [5].

- [1] Y. M. Soro, A. Abramov, M.E. Guenier-Farret, E.V. Johnson, C. Longeaud, P. Roca i Cabarrocas, and J.P. Kleider. *J. Non Cryst. Solids* **354** (2008) 2092.
- [2] Y. Djeridane, A. Abramov and P. Roca i Cabarrocas. *Thin Solid Films* **515** (2008) 7451.
- [3] M. Moreno and P. Roca i Cabarrocas. *EPJ Photovoltaics* 1, (2010) 10301.
- [4] M. Labrune, X. Bril, G. Patriarche, L. Largeau, O. Mauguin, and P. Roca i Cabarrocas . *EPJ Photovoltaics* **3**, (2012) 30303.
- [5] S. Misra, L. Yu, M. Foldyna, and P. Roca i Cabarrocas. *Solar Energy Materials and Solar Cells* **118** (2013) 90.

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GD Day 2014 Symposium

O3

Nitrogen incorporation in metallic alloys by plasma immersion surface treatments at moderate temperature.

L. Pichon¹, C. Templier¹, O. Ozturk², J.P. Rivière¹, J. Cormier¹, P. Villechaise¹, J.B. Dubois¹, S. Chollet¹, S. Okur², M. Drouet¹

¹ Institut P' – UPR 3346 CNRS – Université de Poitiers – ISAE-ENSMA, Poitiers, France

² Izmir Institute of Technology, Izmir, Turquie

By Plasma Based Ion Implantation (PBII) or Plasma Assisted diffusion treatments, nitriding of several metallic alloys can be achieved at moderate temperature, enabling the formation of a nitrided layer with improved mechanical properties. Nitriding of Austenitic stainless steels (ASS) was widely studied and is already employed in various industrial applications: the incorporation of large amount of nitrogen (up to 25-35 at.%) in solid solution in the initial FCC γ phase at temperature below 400°C enables the formation of the metastable so-called expanded phase γ_N . The induced expansion of the cells leads to important compressive stresses and severe elasto-plastic responses (swelling, lattice rotation,...). These compressive stresses in the nitrided layer and the improved surface hardness significantly improve the mechanical properties (fatigue lifetime, wear resistance,...) while keeping the corrosion resistance as there are no nitrides formation (CrN, FeNx). We have applied similar treatments to Co and Ni-based superalloys as their lattice structure is also austenitic: a corresponding γ_N phase was obtained.

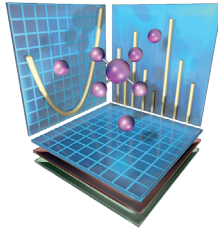
The diffusion process of nitrogen in the γ phase is thought to process by trapping-detrapping of nitrogen by the nitrides former elements (Cr, Mo,...) and/or a concentration-dependant diffusion. This mechanism can explain the unusual experimental nitrogen profiles obtained by GDOES exhibiting a slightly decreasing plateau (few microns after few hours of nitriding at about 400°C) followed by a sharp fall in the bulk. The influences of the major element of the alloys matrix (Co, Fe or Ni) and of the alloying elements composition (e.g: the Cr content) are discussed concerning the surface concentration and the end-level of the nitrogen plateau.

Several Ni-based superalloys have additional structural precipitates of Ni_3Al (γ') or Ni_3Nb (γ or δ) phases. GDOES profiles and SEM observations have enabled to conclude that these precipitates did not significantly modify the γ phase nitriding. However, depending on their accurate composition and microstructure, these precipitates can – or not – incorporate nitrogen to the same extent than the γ phase.

A numerical simulation of the nitrogen diffusion was adapted from the literature, taking into account the cells expansion and the induced elasto-plastics strains. It is demonstrated that the GDOES profiles can be roughly simulated. However, these GDOES profiles result from the averaging on few mm^2 of the profiles in each grain. Because of the important anisotropy of diffusion, the simulation cannot give accurate informations concerning the diffusion coefficient or the detrapping energy.

Finally nitriding results obtained by PBII treatments are compared to plasma assisted nitriding. Thanks to few keV energetic ions implantation and irradiation, the surface sputtering and the sub-surface nitrogen incorporation accelerate the surface kinetic limiting steps at low temperature and then achieve more efficient nitriding treatments.

Luc.Pichon@univ-poitiers.fr



GD Day 2014 Symposium

O4

Rare earth doping of oxides and nitrides for photonics and photovoltaics applications

**A. Ziani, C. Davesne, L. Dumont, P. Benzo, J. Cardin, P. Marie, C. Labbé, C. Dufour, X. Portier
and F. Gourbilleau**

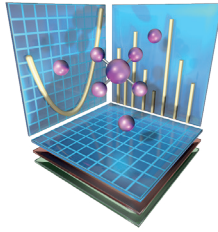
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Oxides and nitrides are widely used in photovoltaic and photonic devices as electrodes or potential candidates for down converter layers by using rare earth dopants. In the present study, Eu and Tb co-doped zinc oxide (Eu,Tb:ZnO) thin films have been grown by RF magnetron sputtering on (100) silicon substrates with different deposition conditions. The goal is to achieve a white light emission for LED application. We will present the structural properties of these films as well as their optical properties and their associated photoluminescence responses (optical excitation). For Eu and Tb elements, the classical chemical analyses by EDX and/or RBS are confusing since the corresponding signals are overlapping and they are not sensitive enough to measure low concentrations (typically < 1 %). As a result, a quantitative determination of the corresponding atomic percentages in the film is hardly obtainable by these techniques. In this work, we will present Eu and Tb concentration measurements from plasma profiling time of flight mass spectroscopy (PP-TOFMS) allowing a decorrelation of the two species. PP-TOFMS couples a plasma source fed with pure Ar and created under a pulsed RF potential with an orthogonal time of flight mass spectrometer (TOFMS). To confirm the reliability of this technique, the dopant concentration profiles measured in other materials commonly used for LEDs or photovoltaic applications will be shown as example. In particular, the Tb-doped and the Tb-Yb-codoped Silicon Nitride systems will be discussed.

Furthermore, the case of Eu doping in a ZnO matrix is complicated since two electronic configurations of ions are generated in the matrix: Eu^{2+} and Eu^{3+} . Using X-ray photoemission spectroscopy, the presence of these two ions has been demonstrated and is in agreement with previous works [1]. It results a much lower luminescence efficiency of the Eu^{3+} than expected. We have also shown that Tb and Eu codoping in ZnO promotes the Eu^{3+} emission via an energy transfer mechanism from Tb towards Eu [2].

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GD Day 2014 Symposium

O5

GD-OES studies of minor alloying elements distribution in the oxide scales and sub-scale areas of high temperature Ni-based superalloys

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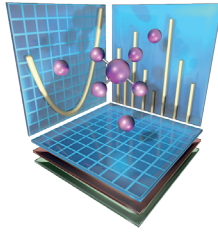
Ni-base superalloys are commonly used in the hottest sections of aeroengines and power generating gas turbines due to a combination of excellent mechanical properties at elevated and room temperature and exceptional high-temperature corrosion and oxidation resistance. Apart from the major alloying elements, Cr, Co, Al, W, Ti, Ta, modern Ni-based superalloys contain minor (between 0.01 and 1 at.%) additions of elements such as Hf, Zr or B for obtaining improved mechanical properties, in particular grain boundary strengthening. However, these minor elements also possess a high affinity to oxygen and can therefore participate in the oxidation process.

Analysis of the distribution of the mentioned elements in the oxide scale and alloy using SEM/EDX is difficult because of small precipitate size of the formed oxides, low concentration and especially for B, low peak intensity in the EDX spectra.

To investigate the behaviour of the above minor alloying elements, in the present work several Ni-based alloys were exposed at 1050 °C up to 100 hours in oxidizing atmospheres. After exposure the oxidized samples were investigated with a number of surface analytical methods, including glow discharge optical emission spectroscopy (GDOES), light optical and scanning electron microscopy as well as X-ray diffraction.

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

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O6

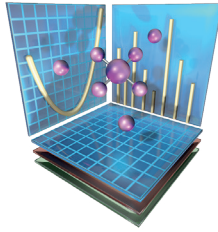
A unique approach of GDOES for improving Scanning Electron Microscopy imaging

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It is now well established in the scientific community that Glow Discharge Optical Emission Spectroscopy (GDOES) has become one of the most suitable instruments to determine the variation of chemical composition with depth underneath a surface. Unlike previous studies, aim of the present work is not to remark the indubitable benefits offered by GDOES to depth profiling. Instead, it is proposed an alternative and novel application, based on applying the sputtering precision and accuracy offered by GDOES to the enhancement of available scanning electron microscopes' (SEMs) resolution. Glow discharged argon ion plasma can be successfully used to sputter, quickly and without damages, a well-defined area on a selected metallic sample, providing an ideal surface where specific characteristics, including grain structure, intermediate particles and defects are emphasized and made easier to recognize. Furthermore, this unique ability of GDOES can be used for surface cleaning after SEM surface observation. The specimen surface is contaminated through an electron beam irradiation and associated with hydrocarbon accumulation. However, the surface can be observed repeatedly after GDOES, because each individual treatment nearly completely removes hydrocarbon from the surface without inflicting any damage. In the present study practical approaches to the use of GDOES for surface preparation of commercial stainless steels and a magnesium alloy, and for cross-section cleaning of an aluminum alloy are described.

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GD Day 2014 Symposium

07

Hybrid diffusive/PVD treatments to improve the tribological resistance of Ti-6Al-4V

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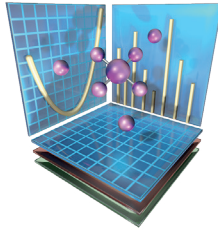
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Titanium alloys are nowadays used for a wide range of biomedical applications, thanks to their combination of high mechanical resistance, high corrosion resistance and biocompatibility. Nevertheless, the applicability of titanium alloys is sometimes limited due to their low microhardness and tribological resistance and thus cannot be successfully applied on prosthetic joint couplings. A wide range of surface treatments have been used in order to improve the tribological behaviour of titanium alloys and in particular PVD coatings such as CrN and TiN, but the low microhardness of the titanium substrate often resulted in coating failure due to cracks and delamination. For this reason, hybrid technologies based on diffusive treatments and subsequent PVD coatings may improve the overall coating resistance. In this work, conventional PVD coatings of CrN or TiCN, deposited on Titanium Grade 5, have been characterized and then combined with a standard thermal diffusive nitriding treatment in order to improve the tribological resistance of the titanium alloy and avoid coatings delamination. The different treatments have been studied by means of Scanning Electron Microscopy both on the sample surface and in cross-section. In-depth composition profiles have been obtained using Glow Discharge Optical Emission Spectrometry (GDOES) and localized Energy Dispersive X-Ray Diffraction on linear scan-lines. The micro-hardness and adhesion properties of the different treatments have been evaluated using Vickers micro-hardness tests at different load conditions and observing the indentations by means of SEM in order to evaluate delaminated areas and the cracks shape and density. The tribological behaviour of the different treatment has been tested in dry conditions and in solution, in alternate pin-on-flat configuration, with a frequency of 0.5 Hz. After testing, the surface has been investigated by means of stylus profilometry and SEM observations both on the surface and in cross-section. The standalone PVD coatings showed a limited tribological resistance due to the low hardness of the substrate, which resulted in fractures and delamination. The combination of a diffusive process and a subsequent PVD coating showed a stronger effect in improving the tribological resistance of the substrate.

Keywords: Ti-6Al-4V, PVD, titanium hardening, nitridation, TiN

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GD Day 2014 Symposium

P1

Endpoint Control Supervision on Dry etch, Cleaning, PECVD processes

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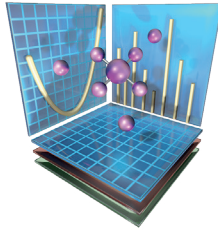
To address new requirements in Advanced Endpoint Control for semiconductor Dry Etch, Cleaning and PECVD industry, HORIBA has introduced a unique generation of Sensor, named *EV-140*. This instrument is dedicated to Run to Run control, chamber health monitoring, fault detection... to ensure system throughput and predict preventive maintenance if necessary. Plasma Optical Emission Spectroscopy information is complex. Hence, extraction of principal relevant wavelengths with Elements Time Trend view (gas, by-products) and then easy process control with Endpoint Recipe creation must be done even when Low open area, Bosch process, high selective chemistry, rotating magnetic field... Those 2 process Engineering steps are eased with the combination of HORIBA Softwares: *Recipe Designer 7* and *Sigma_P*.

Hardware and software are jointly developed so that *EV-140* may be adapted to all etchers (clusters and single chambers) to help researchers, engineers and Fab's to manage actual but also future products and technologies. Based on innovative technologies like smart sensors, unique software architecture, including analytical methodology and sophisticated signal processing, this platform allows satisfying all the needs of in-situ plasma process control.

Besides Optical Emission Spectroscopy, as soon as plasma chamber has a top window, interferometric *LEM* camera gives local information on wafer etch or deposition rate and permits to obtain automatic endpoint detection on (remaining) thickness. Inside *LEM* camera, a CCD component allows simultaneous visualization to set the laser spot on the site to analyze. In addition to *LEM* classical 670 and 905 nm laser wavelengths, *DM1000* is dedicated to multi wavelengths interferometry using a white light source, typically from 300 to 700 nm.

After Process Control products introduction, our poster describes, first, *Recipe Designer 7* engineering flow and then results obtained in Fab's for Dry Etch Endpoint and chamber health monitoring applications. They describe misprocessing detection. Preventive maintenance setting, statistics and multi-run viewer for quality control in order to secure wafers during critical process.

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P2

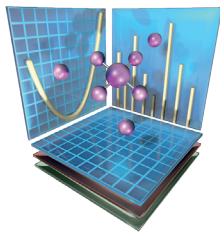
Bulk and Thin Films Standards for GDOES

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Authors proposed few technologies for manufacturing of standard samples with fixed concentration of gas, non-metal, or metal elements: pressing+sintering, hot-pressing, spark plasma sintering (bulk standards), deposition in different Ar+O+N₂+CH_x mixtures using industry-scale four magnetron PVD rig (thin film standards). Production of standard multilayer films with controlled layer thicknesses, periods, & Me/NMe ratio are discussed.

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GD Day 2014 Symposium

P3

Sample of Science: a peer-sharing platform for material scientists

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The strong development of Open Access in scientific publishing, claiming that research results should be freely accessible, followed by the emergence of the Open Data movement, stating that experimental or numerical research data should also be made accessible to the scientific community [1], shows that the revolution brought by Internet in how information can circulate, raises the essential issue of the access to scientific knowledge.

Research samples and scientific materials play a major role in many of original results obtained and in the design of new experiments. Their synthesis requires both scientific creativity and highly sophisticated equipment with highly-skilled specialized people to operate it. In this regards, they should be considered as «pieces of knowledge» just as scientific articles are [2]. Access to and circulation of these «pieces of knowledge» is fundamental for the advancement of science and sharing scientific samples needs to be promoted.

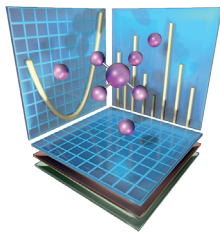
However, samples cannot be reproduced as easily as scientific articles or electronic data. While articles or data published online as a result of a research project can be accessed and reused as many time as needed, only a limited number of samples are produced in a research project. For this reason samples cannot be distributed like reprints; their authors shall decide whether to transfer some of their samples to a particular researcher. At some point, no sample may remain available for sharing. For that reason, a fully «Open» model for sharing scientific samples cannot be strictly derived from the Open Access or Open Data models. The Sample of Science web-platform [3] addresses this issue, proposing a model to foster the dissemination of scientific samples, allowing them to be more easily accessible while allowing scientists who share their samples to get recognition.

Sample of Science relies on a new peer validation process designed for scientific samples; each material transferred to a peer becomes a fully citable item, having its description published in a specifically created Open Access journal [4]. The authors of the transferred samples get the credit they can expect for providing “pieces or knowledge” to their peers, in terms of traceability, citability, visibility and accountability. Any researcher can propose her/his samples on the platform, allowing other researcher to contact her/him in order to discuss about a possible transfer of the sample, and then decide whether or not to send her/his samples available to that particular researcher. For both, Sample of Science is an efficient way of expanding their international scientific network, and maximizing the impact of their research [5]. Launched on spring 2013, Sample of Science is already used by researchers from all over the world and in various scientific communities.

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P4

Dedicated measurement test bench for study of RF discharge parameters of the GD-source in GD-TOFMS

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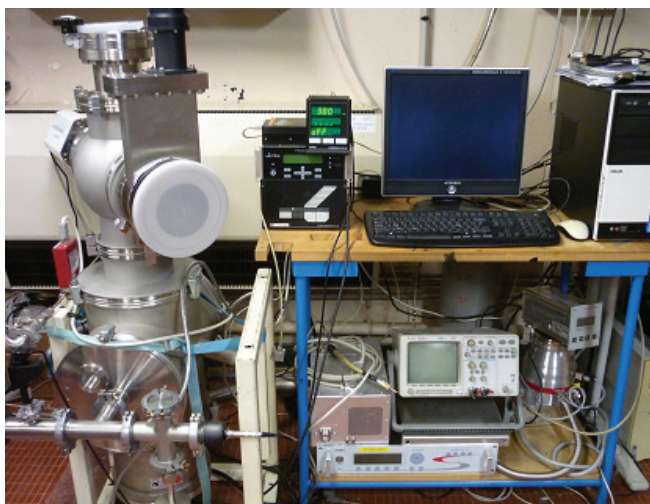
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The optimization of such complex analytical instrument, as Glow Discharge Time of Flight Mass Spectrometer require careful modeling and experimental verification on the specialized test station equipped with different sort of sensors that usually are not available on commercial instruments.

We have built a dedicated test bench for the experimental investigation of capacitively-coupled RF glow discharge source of GD-TOFMS system and started experiments for the validation and initial comparison with modeling results.

The test bench is built around standard high-vacuum DN200 cross and pumped with 1000 l/sec Leybold Vacuum turbomolecular pump backed by rotaty vane pump. Pumping rate can be varied with manual gate valve to reproduce pumping conditions in real instrument. Another pump provide necessary differential pumping for discharge volume and sampler stage. The system is equipped with pulse-capable 13.56 MHz RF generator Cito by Yxlon International.

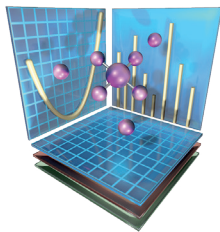


The analytics comprised of Maya 2000 Pro optical emission spectrometer from Ocean Optics, Prisma 100 quadrupole mass-spectrometer from Balzers, Langmuir probe, and the RF current/voltage sensor by Solayl. All is controlled via LabView software. First experimental results will be presented.

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GD Day 2014 Symposium

P5

Plasma and gas flow modeling for GD TOFMS instrument

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The GD source coupling to mass-spectrometric analysis instrument (in comparison with classical GD-OES system) requires accurate modeling of both, plasma in the source tube and ion transmission towards the MS interface. Large pressure differences (several Torr versus some 10^{-6} Torr) existing in the instrument demand combination of fluid modeling and DSMC. Our work is the step towards realization of such approach.

Plasma modeling of capacitively coupled RF-discharge in real-size GD cell is performed with axisymmetrical fluid code based on the model reported earlier [1]. The results are compared to published in the literature [2,3].

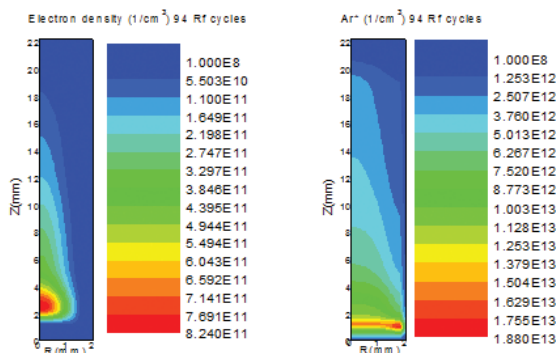


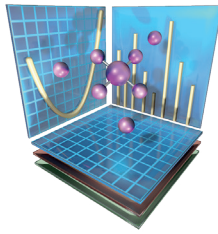
Fig. 1 Electron density (left) and Ar* metastables density (right) for RF voltage amplitude of 500 V and pressure 5 Torr.

It was shown that geometrical dimensions and material of the discharge tube, as well as discharge parameters all have influence on the performance of the glow discharge, such as Ar⁺ ion and Ar* metastables concentrations and ion currents, potential distribution across the discharge and power absorbed in the discharge. In Fig. 1 the electron density and the Ar* metastables density are plotted for a converged solution reached after 94 RF cycles. Typically the calculations, when done on a 3 GHz workstation, arrive to steady-state solution after several tens of hours. The work on the DSMC modeling of the gas flows beyond the sampler orifice and skimmer is ongoing. Higher pressure discharge volume calculations were already compared against experimental measurements and have shown good agreement.

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P6

New insights on the understanding of Cu(In,Ga)Se₂ /CBD-ZnS/ Windows interfaces for high efficiencies solar cells using advanced composition profiling techniques

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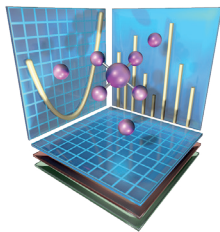
Unlike CIGSe based solar cells with a CBD-CdS buffer layer, CBD-ZnS based solar cells require light-soaking procedures to achieve optimal conversion efficiencies. However, for industrial applications, it is better to eliminate those post-treatment steps. In this work we have identified the role of oxygen during the deposition of ZnMgO or i-ZnO windows layers to highly improve the efficiency of solar cells and strongly reduce their transient behavior. However, so far the role of this window layer within the device structure is still not well understood. The purpose of this paper is to improve the understanding of the influence of the deposition conditions of both the CBD-ZnS buffer and the sputtered window layer, i.e. a better understanding of different interface formations in these cells using advanced composition profiling techniques such as glow discharge optical emission spectrometry (GDOES). The final goal remains the improvement of the CBD-ZnS based solar cell understanding and stabilization for future industrial applications.

The key results of this study are:

- i) the influence of the oxygen on the metastability of CIGSe cells and
- ii) the presence of Na at the CBD- ZnS/CIGSe interface. Moreover we have observed that the interfaces involving ZnS with absorbers and windows layers are strongly intermixed as compared to the one with CdS.

The influence of the interfaces composition will be discussed in relation with the ZnS-based solar cell properties.

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2014 Symposium

P7

Pulsed Radio Frequency Glow Discharge - Time of Flight Mass Spectrometry as new powerful tools for characterization of materials

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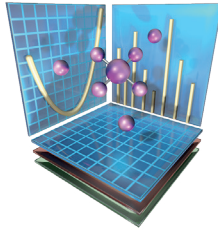
The coupling of pulsed radiofrequency glow discharges (RF-PGDs) to time of flight mass spectrometry (TOFMS) provides an amazing amount of data and analytical information because the TOFMS time-gated detection permits to collect complete mass spectra produced by different ionization mechanisms within each single glow discharge pulse cycle. This emerging technique makes possible to obtain multielemental depth-profiles with depth resolution in the nanometric range, good sensitivity, isotope ratio measurements, as well as the simultaneous production of elemental, structural and molecular information.

As a result, the use of RF-PGD-TOFMS allows the analytical characterization of a broad variety of sample types. Moreover, the analytical capabilities of the RF-PGD-TOFMS for some applications can be considered as really unique. Therefore, RF-PGD-TOFMS is expected to become a common tool for the characterization of innovative materials allowing for the fast quantitative multielemental (major, minor and trace elements) and isotopic depth-profile analysis of thin films and dopants distribution, as well as to investigate the presence of unexpected contaminants (including the sample surface), and to carry out molecular depth profile of polymeric materials.

On the frame of the European project EMPDA (2006-2009) and thanks to the loan of a RF-PGD-TOFMS prototype by Horiba Jobin Ivon, the University of Oviedo has got an acknowledged experience working with RF-PGD-TOFMS [1,2]. Moreover, by July 2014 the PLASMA PROFILING TOFMS instrument will be installed in our laboratories and will be ready to provide a service to any laboratory worldwide.

In this presentation, the present analytical potential of RF-PGD-TOFMS will be shown through an overview of recent applications including depth profiling of glass coated with films of a few nanometers thick, photovoltaic materials like thin film solar cells based on amorphous silicon, ultra low energy implants and even the elemental and molecular analysis of polymeric samples (e.g. screening of polymer-based coatings containing brominated flame retardants and identification of conductive polymeric coatings).

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GD Day 2014 Symposium

O8

Detection of hydrogen absorbed in Mg-based alloys using GD spectrometer

V. Knotek, P. Novák, D. Vojtěch

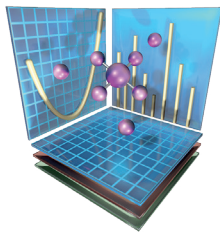
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The main task for using hydrogen as energy carrier is to develop its safe and efficient storage. Storing hydrogen in the form of light metals hydrides seems to be very prospective. Magnesium alloys, as efficient hydrogen storage materials, have attracted great attentions recently. Magnesium is light, inexpensive and non-toxic metal. The main advantage of magnesium for hydrogen storage is its ability to absorb up to 7.6 wt. % of hydrogen in the form of magnesium hydride (MgH_2). However, magnesium hydride suffers from high thermodynamic stability and slow hydriding kinetics, which limit its practical application. To improve thermodynamics and kinetics of magnesium hydride, the alloying of magnesium by transition and rare earth metals is often employed.

In this study, several as-cast Mg-based alloys alloyed by nickel and mischmetal (mixture of rare earth metals) were hydrided by an electrochemical hydriding method. The electrochemical hydriding was carried out in a 6 M KOH solution at 80 °C for 480 min and at 100 A/m². The microstructure of both as cast and hydrided alloys were investigated by optical and scanning electron microscopy and by X-ray diffraction. The real concentration of absorbed hydrogen in hydrided bulk samples of alloys is not easy to evaluate, because the hydrogen concentration is depth dependent. It means that a simple measurement of hydrogen content using hydrogen analyzer should be excluded. Therefore, we employed GD spectrometer in profiling mode. In this way, we obtained depth dependent signal of hydrogen (hydrogen profile) for each of investigated alloys. The real weight concentration of hydrogen was obtained by MgH_2 calibration.

The shape of hydrogen profile and its hydriding parameters such as maximum surface hydrogen concentration and the depth of hydrogen detection can serve as a guide for evaluating the influence of alloying metal on the ability of magnesium alloy to absorb hydrogen. Based on hydrogen profiles obtained for hydrided alloys, the most suitable alloy for electrochemical hydriding was determined. The influence of nickel and mischmetal on the hydriding kinetics was described. It was proved that GD spectrometer is useful instrument to study an electrochemical hydriding process.

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GD Day
2014 Symposium

O9

Depth Profiling Analysis of thin film composite membranes by Pulsed Glow Discharge Mass Spectrometry: Layer modifications due to oxidation in seawater

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R. Sandín², A. Sanz-Medel³.**

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Direct surface and depth profiling chemical analysis of multilayer materials demands a “multidimensional” knowledge, including simultaneous elemental and molecular information to characterize the new materials. Radiofrequency glow discharges allow obtaining direct chemical information with high depth resolution from a great variety of materials in a fast and easy way.

In addition, when radiofrequency glow discharges are powered in pulsed mode (rf-PGD) the technique gains new and interesting properties. In this powering mode, the discharge evolves according to the pulse frequency giving rise to three main regimes (prepeak, plateau and afterpeak) with different mechanisms of ionization. As a result, it is obtained a real possibility of measuring elemental and molecular ions when coupling the GD ion source to a fast mass spectrometer with time-resolved detection, such as a time-of-flight mass spectrometer (TOFMS). In this sense, RF-PGD-TOFMS can be an ideal technique for depth profile analysis of polymer based multilayers: the pulsed mode favoured the analysis of thermally sensitive materials and the capability of ion fragment detection allows distinguishing layers of similar elemental composition [1].

Thin film composite (TFC) membranes are semipermeable membranes used for water purification or desalinization. These membranes are typically made of a thin film of polyamide on top of a polysulfone porous layer deposited on a support sheet [2]. A limitation in the use of TFC membranes is the degradation through common oxidants employed in water treatment such as sodium hypochlorite (NaClO) and chlorine dioxide (ClO₂). Oxidation produces lower salt rejection in polyamide membranes. Traditionally Fujiwara test has been used to check if the membrane is affected by chlorine exposure (a small quantity of a dye solution is dropped on the membrane surface, the dye will adhere to the support material that has been oxidized, and these damaged areas will appear as bright pink spots) [3]. ATR-FTIR and X-ray photoelectron spectroscopy have also shown to be useful tools that can detect the oxidation of these membranes in the presence of NaClO [4].

In this work, the analytical potential of radiofrequency pulsed glow discharge time of flight mass spectrometry (RF-PGD-TOFMS) to analyse a commercial polyamide TFC membrane is investigated and the use of an Ar pre-chamber to avoid the air entrance in the discharge through the sample porous is evaluated. In a next step, the capability of RF-PGD-TOFMS to detect the oxidation suffered by these membranes after being immersed in seawater with different oxidant added (NaClO and ClO₂) is studied. The results are compared with those provided by other techniques.

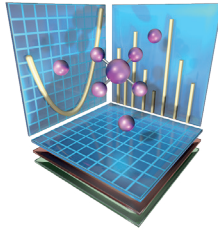
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GD Day 2014 Symposium

O10

Is GD sputtering modifying the composition of the material? An XPS study of the surface composition of GD craters

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Absorbers based on thin films technology and in particular CIGSe ($\text{Cu}(\text{In,Ga})\text{Se}_2$) are a good alternative to Silicon wafers for highly efficient photovoltaic cells. Currently, CIGSe record efficiencies reach 21% value in laboratory and 13% at the industrial scale. Cells' performances rely on the absorber's properties. In particular, the control of the chemical composition of the bulk and the presence of impurities is a crucial parameter, as well as the chemistry which occurs at the interface. Depth Profile characterization of the absorber layers can be carried out for instances by SIMS or by XPS, but analyses require long acquisition times. GDOES is an interesting way of analyzing CIGS, enabling to obtain quick and qualitative characterization but quantification of GD requires the use of complementary techniques or of reference samples.

Proper quantification also requires that the GD analysis does not drastically modify the material investigated. In this work, we have investigated interesting compositional changes of the bottom of the craters after GDOES analyses.

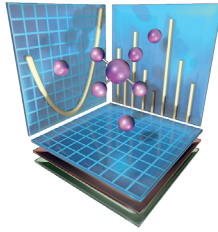
We have carried out depth profiles at different thicknesses and the sputtered surfaces have then been analyzed by XPS. Obtained results indicate a strong enrichment in Gallium.

An XPS depth profile done within the GDOES crater confirms the presence of gallium oxide and we could not reach the CIGS stoichiometry even after about 100 nm sputtered out.

SEM observations conducted in the GD crater show a pattern which tends to indicate that redeposition from the plasma has occurred. A Ne plasma has been used instead of Ar and confirms this plasma effect: with Ne a strong increase of both indium and Gallium at the surface are observed and correlations can be done with the plasma temperature

To finish, XPS analysis has been realized on a crater obtained by GD-TOFMS. The direction of the Ar flow in the GD-TOFMS is reverse compared to the standard one in GDOES allowing the melted particles present in the plasma to be flushed away from the surface when the plasma is stopped. Depth XPS profile on this crater confirmed this effect with a strong decrease of Gallium at the surface. Moreover, CIGSe stoichiometry was quickly obtained, indicating a very weak surface modification. A modification of the flow in GDOES at the end of analysis is therefore needed.

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GD Day 2014 Symposium

O11

Composition depth profile of electrodeposited alloy and multilayer films

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Electrodeposition is a widely used technique to produce various coating types. When the thickness of a coating is at least a few micrometers, the bulk composition is sufficient to describe the coating properties. However, the adhesion properties are determined by the initial atomic layers of a coating. This is why the study of the composition depth profile of a deposit is of high importance. In many cases, the thickness of the coating being grown achieves a few hundred nanometers until the steady-state deposition is achieved. Therefore, ultrathin deposits with an even in-depth composition is difficult to produce. In the last few years, our group developed a sample preparation method that makes it possible to detach the samples from their substrate and hence, to start the composition depth profile studies from the substrate side. This allowed us to learn the element distribution in the near-substrate zone with an unprecedented accuracy. The lecture will show this sample preparation technique in detail, which will be called as the reverse depth profile analysis.

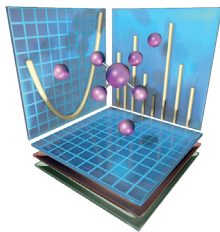
Among the composition depth profile methods, Secondary Neutral Mass Spectrometry (SNMS) is a new but very powerful method. Since SNMS was used for all composition depth profile studies to be shown, it will be described in comparison with other possible depth profile analysis methods, emphasizing its advantage concerning accuracy and quantitative sample characterization.

The electrodeposition of many binary and ternary alloys has been studied. It was found in all d.c. deposited samples that the component of highest deposition preference was accumulated in the near-substrate zone, regardless of the origin of the deposition preference and of the codeposition mode of the alloy components. When two alloy components were deposited preferentially, their accumulation sequence in the near-substrate zone was in accord with the order of the deposition preference. It has also been shown that the fluctuation in the local mole fraction of the preferentially deposited alloy components was strongly correlated when the deposition was performed in a stagnant solution.

The impact of pulse plating on the composition depth profile was studied in the Fe-Ni system. The smaller the duty cycle was, the more the steady-state alloy composition achieved the near-substrate composition. The duty cycle by which an even in-depth composition could be achieved was a function of the concentration of the reactants. The interrelation of the deposition parameters with the near-substrate composition change will be shown in detail.

The reverse depth profile analysis has also been applied to follow composition changes in two-pulse plated multilayer deposits. It has been shown that the evolution of the deposit surface roughness plays a crucial role in the quality of the depth profile analysis results. A method has been suggested for the calculation of the depth profile analysis results by using the mean surface roughness as a function of the deposit thickness. This method has been verified for electrodeposited Co/Cu multilayers.

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GD Day 2014 Symposium

P8

Development of method for preparation calibration samples of Titanium with Hydrogen for GDOES

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Keywords: hydrogen, sample preparation, GDOES

Main technological and operational characteristics of structural materials are determined by content of gas-forming impurities such as hydrogen, nitrogen, oxygen, carbon and sulfur. Calibration samples with certified composition and measurement error are required for most methods of gas-forming impurities determination. Currently there are not enough of calibration samples with certified values of hydrogen, and commercially available calibration samples are not suitable for the calibration of glow discharge optical emission spectrometers (GDOES), as it does not fulfill the necessary requirements for the shape and dimensions. Furthermore hydrogen content in such samples typically does not exceed 25 ppm. Preparation of samples with various geometrical dimensions and with a wide range of hydrogen concentration is possible using method of hydrogen saturation at gas atmosphere at high temperatures and pressures. The method for preparation calibration samples of titanium with hydrogen for GDOES was developed in the present work.

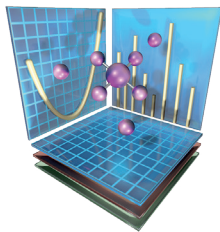
The cylindrical samples of commercially pure titanium alloy with sizes $\varnothing 20.5$ mm were prepared for investigation. Hydrogen saturation at gas atmosphere was carried out using automated complex Gas Reaction Controller LP [1] at a temperature 500 °C and a pressure 2 atm. Hydrogenation was performed in an automated mode until hydrogen concentration reached values 500, 1500 and 2500 ppm. Hydrogen concentration in the samples was determined in three ways: volumetric method during saturation, according to the mass difference before and after hydrogenation and by melting in an inert gas using a hydrogen analyzer RHEN602 by LECO. Annealing in a helium environment at a temperature 500 °C for 90 minutes was carried out in order to achieve a uniform hydrogen distribution in the samples volume. As a result, the samples with hydrogen concentration (507 ± 17), (1513 ± 21) and (2553 ± 31) ppm were prepared for calibration GDOES spectrometer Profiler-2 by HORIBA. Bulk-calibration for hydrogen in titanium was done using prepared samples. Hydrogen determination error in samples was 15 %.

This work was supported by RFBR project N°14-08-31033.

The authors gratefully thank P. Chapon from HORIBA for providing technical support in calibration procedure of GDOES Profiler-2.

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GD Day 2014 Symposium

P9

Profile Analysis of Magnetostrictive FeGa Thin Film using Rf GDOES

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Quantitative depth profile of $\text{Fe}_{1-x}\text{Ga}_x$ thin films coated on Si substrate using Radiofrequency Glow Discharge Optical Emission Spectrometer (RF GDOES) has been reported. The effect of power on the emission signals (& sputtering rate) of bulk Fe and FeGa alloy has been studied in detail and based on it 25 W power with pulse mode has been selected as ideal conditions for the depth profile analysis. Multi-matrix calibration was performed using certified reference materials and in-house standards. Crater depth of the sputtered films were measured using a profilometer and the data was input into the Quantum software of GD-Profilier 2 instrument to calculate the sputter rate. The relative sputtering rates were normalized with respect to the one of a low alloy steel. Measured thickness of the film coating is 225 nm with a broad interface region of 75 nm. Composition of the film in the uniform region is $\text{Fe}_{75.1}\text{Ga}_{24.6}$.

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P10

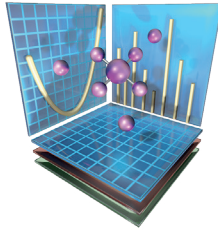
Elemental depth profile analysis of Co-Fe-Si thin films on Silicon substrate using RF GD-OES

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Magnetic thin films have become widespread with ever increasing demand for miniaturization of electronic data storage devices. In the present paper, the application of RF GDOES as an analytical tool for elemental depth profiling of as received Cobalt-Iron-Silicon thin films (Heusler class alloy) on Silicon substrate is discussed. A multi-matrix calibration was performed using a set of SRM's of cobalt, iron and silicon available from BCS, NBS and MBH. A bulk secondary standard of Co-Fe-Si prepared in-house and analyzed previously on ICP-OES is also used for calibration. The relative sputtering rates are normalized with respect to the global standard of low alloy steel (1) and concentration Vs depth, profiles of the Thin Films were recorded using GD Profiler-2 Quantum XP software.

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GD Day 2014 Symposium

P11

Development of a new GD micro-plasma for analysis of low sample volumes

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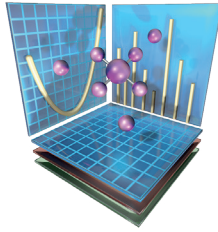
This study is based on a development of a new GD micro-plasma source allowing for analysis of very low sample volumes (about 10-20 μ L), that will further be coupled to an optical spectrometer (VS 140, HORIBA Scientific).

Such a device could lead to a very innovative analytical system such as a field analysis dedicated portable system. Moreover, the handling of very low sample quantities has become of major importance in the nuclear field, but also biological and environmental.

A continuous HT generator delivering a 10 to 100 mA current will produce the GD micro-plasma in the air, while the nebulization and polarization of the electrolyte containing the analyte will be possible with the use of metallic capillary tubing.

The determination of the source geometry parameters, such as the internal diameter, the anode-cathode gap, the flow and nature of plasma gas will constitute the bulk of the experimental work; whereas the determination of the current voltage/intensity parameters allowing for a sustainable plasma generation according to the solution brine content will be a major part of the parametrical study.

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GD Day
2014 Symposium

P12

RF-GDOES analyses of swelling and Ce migration, on ZrO₂ based sol gel coatings, after different immersion times in no-aggressive media

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The corrosion resistance of aluminum alloys is usually improved using a paint system, starting from surface, like: conversion coating, primer and top coat. Cr based conversion coatings have been widely used for aluminium alloys but these systems must be replaced due to health and environmental issues. The sol gel coatings could be a possible environmentally-friendly alternative for the replacement of chromate based coatings. Many studies are presenting, for aluminum substrates, the ZrO₂ based sol-gel coatings as an effective coating used to reduce the corrosion attack of aluminum alloys (AA 6060, AA2024, AA1050 etc..). In order to provide active corrosion protection to sol-gel coatings, Ce species can be incorporated in the sol gel solutions.

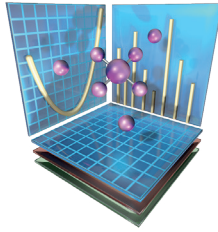
In this work, ZrO₂ based sol-gel coatings containing cerium nitrate were deposited on AA6060 aluminum alloy in order to evaluate the corrosion inhibition provided by the incorporated cerium ions. Cerium nitrate was added to the starting sol, based on zirconium alkoxide precursors. Three types of samples were produced: a non inhibited type consisting of 3 layers of ZrO₂, an inhibited system consisting of two layers of ZrO₂ with an intermediate layer doped with cerium nitrate and an inhibited system consisting of two layers containing cerium nitrate with a top layer of ZrO₂. Film thickness and composition were evaluated by means of Glow Discharge Optical Emission Spectroscopy (GDOES). Moreover, the GDOES was employed to prove cerium migration through the ZrO₂ coatings. The samples were immersed in diluted Harrison solution in order to promote the electrolyte ingress in the sol-gel coating. Each sample was analyzed by GDOES after an immersion time of 0, 1, 2, 3, 4, 5, 6, 7, 8, 24, 30 and 48 h.

The instrument, manufactured by HORIBA Jobin Yvon, is equipped with a standard 4 mm diameter anode, a polychromator with 28 acquiring channels, an RF generator and the Quantum XP software. The instrumental conditions were: 620 Pa Ar pressure and 35 W applied power. The calibration was performed with 20 samples selected among SUS (Setting Up Samples) and CRM's (Certified Reference Materials), grinded and polished before the use. The specimens were dried before the starting the test by using an hairdryer.

The obtained profiles were analysed in order to determine the coating thickness, the Ce dissolution and the diffusion of Ce species. To perform these measurements was used the Quantum XP software with the functions of: calculation of integral for each signal and peak detection. For the calculation of coating thickness was used a value obtained as an average of three data points: one point is the 0,5 wt% of substrate signal in coating, the second is the value where the main coating element signal (Zr) crossed the main substrate element signal (Al) and the third one where the main coating element reached a value < 0,5 wt% in the substrate region. The results were then plotted in order to obtain the graphs of the analysed parameters in function of the immersion time.

The results showed that with the RF-GDOES it is possible to follow the cerium migration within the coating. In particular it is observed that all coatings are subjected to swelling during immersion and that this phenomenon is more intense in Ce containing coatings. It is also proved that Ce tends to move toward the aluminum surface.

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GD Day 2014 Symposium

P13

Solutions to specific physical and chemical features of sample for analysis by RF-GDOES

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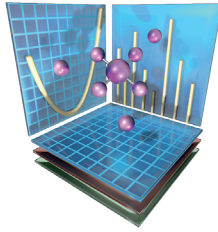
Radio Frequency Glow discharge Spectrometer is a versatile technique providing the compositional depth profile of conductive and non conductive solid materials, either bulk or coated.

The sample plays the role of the cathode and is placed along the ceramic to seal the source. RF-GDOES detects all elements including the light ones (as C, O, H and N) and is a comparative technique. As a matter of fact, the comparison of results can be done when they are obtained within the same applied source conditions.

Considering the standard geometry of the source, the ideal sample is flat, rigid enough to not be deformed by the applied low pressure in the lamp and with low surface roughness to not introduce any air in. BUT materials field deals with all sort of shape, and other kind of physical features such as roughness or porosity and can be also chemically sensitive to the atmosphere.

We will review here all these features and describe the possible solutions through two kind of strategy: mounting or/ and use of specific home designed accessories in order to deal with all sorts of samples and extend the applications field to embrace the whole materials world.

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GD Day 2014 Symposium

P14

Continuous Wave micro-plasma excited by microwaves in capillary tubes. Comparison between noble gas and molecular mixture operation

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Micro-discharges at atmospheric pressures have known a fast development over the last decade. However, most of them operate in impulse regimes and only very few works have presented confined microplasma in capillary tubes. Recently long lifetime continuous wave (CW) plasma in hollow optical fibers has been reported using microwave excitation for photonic applications [1,2]. Combining plasma properties and gas flowing conditions, this discharge is very interesting for microfluidics applications in capillaries [3]. This communication will give the principle of operation in CW and the main features of this particular micro-discharge.

Details of the experimental set-up and plasma operation are presented in [4]. Briefly, a surfatron microwave launcher was redesigned and adapted to ignite the plasma and to couple TM₀₀ surface waves (SW) which propagate between the plasma and the dielectric tube wall. Also, a very novel configuration using inner microstrip will be presented and compared to the surfatron one.

Here we compare the plasma parameters (electron density, gas temperature, etc.) in noble gas (Argon) and dry air (N₂ 80% + O₂ 20 %) over a large range of pressures and power injected (P_{in}) into the discharge, and for several tubes with different inner diameters (120, 320, 540, and 690 μ m).

Plasma diagnostic is performed by optical emission spectroscopy (OES) axially resolved along the tube axis (discharge length outside the surfatron extends up to 12 cm) and by mid-IR laser absorption was performed in a multi-pass cell to quantify the amount of NO produced by the discharge. The fraction of NO with respect to the amount of air molecules can exceed 10 ppm at atmospheric pressure. Kinetic modelling results extend the information of the active plasma species.

This plasma can operate at the tube edge producing a confined microplasma jet of few centimetres outside the capillary tube, in atmosphere, with a large plasma density ($> 10^{15}$ cm⁻³) and continuous production of localized active species, interesting for many applications.

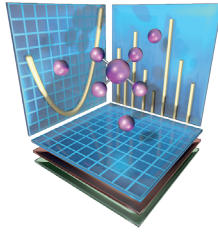
Acknowledgements

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GD Day 2014 Symposium

P15

RF GD-OES analyses of optical multilayers

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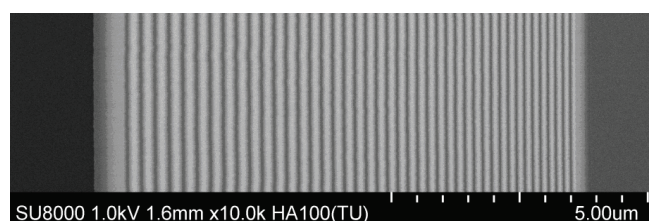
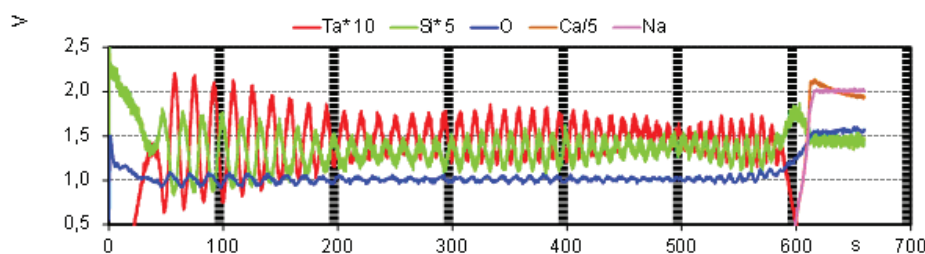
Optical multilayers with antireflective, highly reflective or solar-control properties are used on different substrates like glass or polymer films.

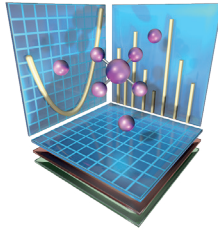
In the frame of our work we have tested the possibilities and limitations for the analyses of the chemical depth-profiles of different optical multilayers by RF glow discharge optical emissions spectrometry (RF GD-OES).

For the testing of the depth resolution a broad-band highly reflective optical Rugate filter with 46 periods of silicon oxide and tantalum oxide gradient layers with a total thickness of $9.65\ \mu\text{m}$ on 1 mm soda-lime was used. The optimization of a flat sputter crater was achieved by the variation of the total pressure, RF sputtering power and duty cycle. The flatness of the bottom of the sputter crater could be mainly affected by the sputtering pressure, whereas the steepness of the side walls could be drastically improved by optimization of sputtering power and duty cycle. The results show that with optimized sputter parameters the thinnest period of 140 nm could be still clearly resolved near to the bottom of the very deep sputter crater.

In addition the effect of spectral reflectivity on measured intensity of optical emission lines was tested using a 5 stack multilayer layer of silicon oxide and titanium oxide layers with a total about thickness 670 nm. This multilayer system exhibits a high reflectivity in the UV range and very low reflectivity in the visible range of spectrum. The effect of the changes in spectral reflectivity on the measured intensities of the optical emission lines were simulated as a function of the sputtering depth. The simulated results for the reflectivity of the used optical emission lines 365.35 nm for titanium and 288.158 nm for silicon versus sputtering depth are compared with the experimental results. It can be shown that for optimized crater profile the results corresponds very well to the simulated drastic changes in reflectivity.

Solar control layers for automotive applications are deposited on $50\ \mu\text{m}$ PET films. The multi-layer system with a total thickness of about 450 nm is composed of 5 periods with alternating thin silver and zinc-tin-oxide layers. For the RF GDOES analyses the coated PET films are glued on an aluminum substrate, which enables the production of flat sputter craters for the optimized sputtering pressure. On the other hand relative low sputtering powers and duty cycles must be used to avoid thermal damage of the sensitive substrates. The used relative low sputtering powers of 15 or 20 W restricts unfortunately a little bit the steepness of the sputter craters. Nevertheless all present 5 silver layers with a thickness of about 8 nm can be still clearly resolved.





GD Day 2014 Symposium

O12

Atom probe tomography: a mass spectrometry technique for 3D characterization of nanomaterials

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C. Perrin¹, M. Descoins¹, A. Portavoce¹, and X. Tan¹**

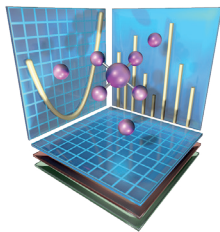
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The atom probe tomography has become an essential analysis to study materials at the nanometer scale. A typical example is the field of microelectronics in which the increase in complexity and the reduction of dimensions in devices make essential the development of new characterization tools with very high spatial resolution in order to analyze atomic composition at the nanoscale in devices. The atom probe is the only analytical microscope capable to produce 3D maps of the distribution of the chemical species with an atomic resolution inside a material. This technique has benefit from several instrumental improvements during last years. In particular, the use of laser for the analysis of semiconductors and insulating materials offers new perspectives for characterization. The capability of APT to map out elements at the atomic scale with high sensitivity meets the characterization requirements of semiconductor devices such as the determination of elemental distributions for each device region but also enable the chemical analysis of quantum dots, nanowires as well as the study of precipitation in steels and superalloys. This talk will be devoted to an introduction to the technique. The possibilities and performances of APT (chemical analysis of all the elements, atomic resolution, planes determination, crystallographic information...) will be described as well as some of its limitations (sample preparation, complex evaporation, detection limit, deformation...). Examples in the field of microelectronics [1-3], nanosciences [4, 5] and metallurgy [6] will be shown. In particular, APT sample preparation and analysis of transistors will be presented in order to illustrate how such analysis can be used to improve processes in microelectronics. A comparison with glow discharge spectrometry techniques will be done for thin film analysis.

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GD Day 2014 Symposium

O13

Ion-plasma modification of reed switch blades

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A reed switch is a small electromechanical device having two ferromagnetic blades (reeds) that are hermetically sealed inside a glass envelope. Generally, the protective coatings of gold or other noble metals are deposited on the contacting surface of reeds. As an alternative to this method, we proposed to produce nitride coatings on the surface of nickel-iron blades by ion-plasma treatment (IPT) directly in sealed reed switches. Our developments and research in this field are summarized in [1]. Here, we report the results of time-of-flight secondary ion mass spectrometry (TOF-SIMS) study on in-depth compositional changes in the near-surface layers of blades after ion nitriding.

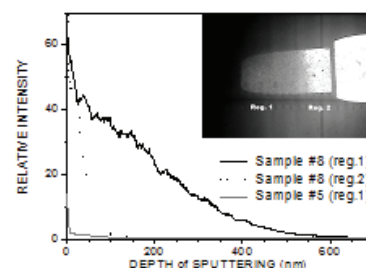
We studied two reed switches manufactured at RMCIP JSC (Ryazan). One of them (sample 5) was a blank sample. Another sample (sample 8) was subjected to ion-plasma treatment. For that, a pulsed DC potential (up to 2 kV) was applied between open contact blades with a gap of 27–30 μm . The polarity of the potential was changed with a frequency of 50 Hz. The glass envelope plays the role of working vacuum chamber, and the blades operate sequentially as anode and cathode. The duration of a single IPT cycle was chosen to be 30 s.

TOF-SIMS measurements were carried out at IPM RAS (Nizhniy Novgorod) using TOF.SIMS-5. The instrument operates in dual beam mode with pulsed 25 keV Bi^+ ions for analysis and 2 keV Cs^+ ions in DC mode for sputtering. Different atomic and molecular negatively charged secondary ions were registered. The craters depths were measured by an optical profiler Talysurf CCI-2000.

Two regions with different color were observed on the blade's surface of the sample 8 after thirty cycles of IPT (see the insert in figure). The reg. 1 is the working region, the contacting area of blades, where gas discharge was initiated by high-voltage pulses. This region turned dark after ion-plasma treatment. The reg. 2 is the nonworking region of blades; it continued to be of the same metallic color.

As characteristic ions for the nitride coatings, we selected intense molecular ions FeN^- , NiN^- , CN^- and NO^- .

The depth distributions of FeN^- ions are shown in figure.

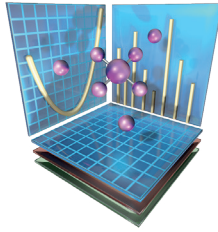


Depth distributions of FeN^- ions measured for the samples 5 (without IPT) and sample 8 (after IPT)

From the data presented in figure, we estimated the thickness of nitride coating (at the level of 10 % of maximum) within the range of 320 – 380 nm in the working and less than 75 nm in the nonworking regions of the sample 8 (after IPT). The slow decrease of FeN^- depth distributions in the working region of the treated blades can be explained by the combined influence of several factors: nitrogen diffusion, cathode sputtering and re-deposition of sputtered products, thermal decomposition of nitrides and the development of sputter-induced topographical relief in this region.

The formation of ca. 350 nm-thick oxynitride coating in the contacting region of the blades was observed. It was found that the origin of this coating cannot be explained just by nitrogen and oxygen diffusion inside the treated material. Rather, cathode sputtering and re-deposition of sputtered products, thermal decomposition of nitrides and oxides along with sputter-induced surface roughening can also contribute in the formation of the modified layers.

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<http://doi:10.3390/coatings2010008>



GD Day
2014 Symposium

O14

Morphological changes of tungsten surfaces by low-flux helium plasma treatment and helium incorporation via magnetron sputtering

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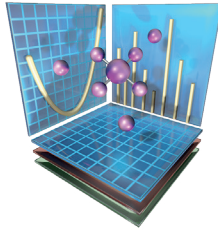
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The effect of helium on the tungsten microstructure was investigated firstly by exposure to a radio-frequency driven helium plasma with fluxes of the order of $10^{19} \text{ m}^{-2}\text{s}^{-1}$ and secondly by helium incorporation via magnetron sputtering. Roughening of the surface and the creation of pinholes were observed when exposing tungsten samples to low-flux plasma. A coating process using an excess of helium leads to a porous thin film.

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P16

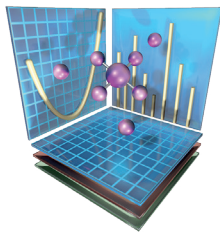
Raman Spectroscopy applied to thin layers analysis

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As the miniaturisation of electronic devices pushes the development of new nanomaterials, the analysis method should follow the same trend. Raman Spectroscopy proved its utility for bulk materials and adapts to the analysis of nanomaterials. The examples of applications on thin layers (MoS_2 , polymer, graphene) will be shown and explained.

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GD Day 2014 Symposium

P17

New developments in application of micro-wave discharges to surface treatments

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The use of high frequency (radiofrequency, RF, and microwave, MW) discharges has greatly expanded during the last decades, in different fields such as materials processing, thin film coatings or chemical analysis. Surface wave sustained discharges (SWD) are of particular interest, due to the possibility of generating long plasma columns by using an electrodeless configuration. They are flexible and versatile plasma sources, where a MW surface wave is propagated along the interface between the plasma and a surrounding dielectric tube. The created plasma acts at the same time as waveguide to assure wave propagation.

Surfatrons are effective plasma reactors designed to launch a surface electromagnetic wave [1], which can be used to generate reactive species inside small dielectric tubes over a wide pressure range (see Figure 1). The length of the plasma column can be controlled by modifying only the supplied MW power. In this work, a surfatron plasma source working at 2.45 GHz has been coupled to an ALD (Atomic Layer Deposition) reactor (see Figure 2). ALD is a deposition technique allowing for a precise control of layer growth, one atomic layer for each cycle. One cycle consists of two parts: during the first one the precursor (metal with ligands) is adsorbed; and during the second one a reactant gas (O_2 , H_2O , N_2 , NH_3 ...) reacts with the ligands leading usually to a binary compound film [2].

The plasma created within the surfatron tube is used to provide the reactive species needed for the second half of the ALD cycle (reactant step). The plasma distribution with respect to the substrate surface can be easily modified by varying the MW power. Therefore, the flux and nature of the plasma species arriving and interacting with the surface and reaction products can be tuned, a unique advantage of SWD with respect to other plasma sources.

Preliminary tests by using an Ar- O_2 plasma to deposit TiO_2 ultra-thin layers have been performed, and a further optimization of plasma parameters is currently in progress.

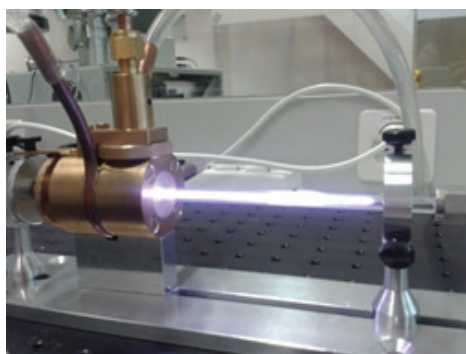


Figure 1: Ar plasma generated at low pressure (1 mbar) and 10 W

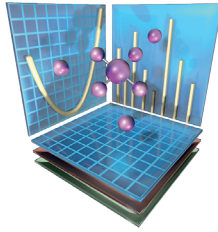


Figure 2: Surfatron plasma reactor coupled to ALD chamber

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GD Day
2014 Symposium

O15

Depth profile analysis on Cu(In,Ga)Se₂ solar cells by SIMS/SNMS and GDOES

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Depth profile analysis on Cu(In,Ga)Se₂ solar cells by SIMS/SNMS and GDOES Copper indium gallium diselenide (CIGS) is the thin film technology material with highest efficiency (20.8 %). This can be achieved by having a correct Ga profile and Na concentration. In my contribution I present the application of GDOES for measuring CIGS depth profiles and demonstrate the advantages and the problems of this technique compared to SNMS and SIMS. The main focus is on the gallium and sodium profile.

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O16

GDOES of Materials for Biomedical Applications

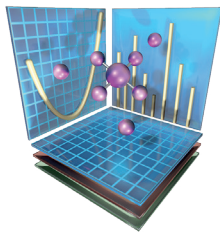
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The study is dedicated to the GDOES of different biomaterials contained components from alloys, polymers, & ceramics. Few groups of samples were measured:

- a) Bulk uncoated substrates (S) from Ti-based, Co- & Ni-based medical alloys, oxide ceramics, DP & DI bones, & polymers;
- b) S + functional coatings (FC) contained Ca, P, O, Si, Ag, Ti and deposited by PVD, ESA, MAO, ALD, SLS technologies;
- c) S+FC+ antibacterial top-layer with Ag or drugs

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GD Day
2014 Symposium

O17

Effect of annealing temperature on antibacterial activity of silver doped hydroxyapatite thin films

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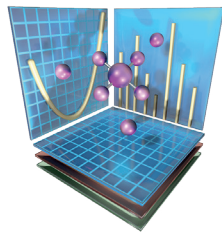
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In this study, we have investigated for the first time the influence of annealing temperature on the antimicrobial activity of Ag:HAp thin films deposited by thermal evaporation technique.

The Ag: HAp ($x_{Ag} = 0.5$) nanopowder dried at 80 °C for 72 hours has been deposited by thermal evaporation technique as solid layer on commercially pure Si disks substrate. By this technique the Ag:Hap nanoparticles, (source material) are evaporated in vacuum. The obtained Ag:HAp thin films were heat treated at 600 and 800 °C for 6 hours. Ag:HAp thin films were investigated by Scanning Electron Microscopy (SEM), energy dispersive X-ray analysis (EDX), Fourier Transformer Infrared Spectroscopy (FTIR), X-Ray Photoelectron Spectroscopy (XPS) and Glow Discharge Optical Emission Spectroscopy (GDOES). Furthermore, the antibacterial activity of the Ag:HAp thin films was evaluated against *Staphylococcus aureus* and *Pseudomonas aeruginosa* using the Luria-Bertani agar plate method.

The experimental results confirm a uniform deposition of an adherent layer. The size of Ag:HAp nanoclusters present in the layer increases with the annealing temperature. EDX and GDOES results have shown that the Ag:HAp deposited thin films consist of Ca, P, Si, O and Ag, all the elements being uniformly distributed. The presence of Ag on the surface of the Ag:HAp thin films was also observed. The antimicrobial activity of the Ag:HAp thin films varied depending on the temperature used during the heat treatment, which determined a difference in the Ag:HAp nanoclusters size present in the layers. Due to the annealing process, the Ag:HAp thin films exhibited an excellent antibacterial effect against both bacteria. This study demonstrated the effectiveness of Ag:HAp thin films as an antimicrobial agent for biomedical applications.

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O18

Characterization and antibacterial activity of samarium doped hydroxyapatite thin films

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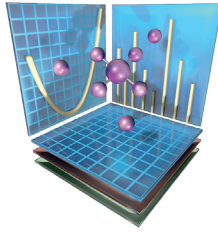
In this work, our research is focused on the elaboration and characterization of samarium doped hydroxyapatite (Sm:HAp) thin films, with potential applications in the biomedical field. The first study on the antimicrobial activity of Sm:HAp thin films published is also presented in this paper.

In order to investigate the influence of different χ_{Sm} concentrations on the properties of the Sm:HAp thin films, we have comparatively studied Sm:HAp thin films deposited with $\chi_{\text{Sm}} = 0$ and $\chi_{\text{Sm}} = 0.1$. Samarium doped hydroxyapatite (Sm:HAp) thin films was prepared on commercially pure Si disks substrate by sol-gel method. The samarium doped hydroxyapatite thin films were characterized by various techniques such as Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The elemental composition of the films was examined by X-EDS (Energy Dispersive X-ray) and GDOES (Glow Discharge Optical Emission Spectroscopy) methods. These techniques have facilitated the structural and chemical characterization of the samarium doped hydroxyapatite thin films. The antimicrobial activity of the samarium doped hydroxyapatite thin films was evaluated by the Luria-Bertani agar plate method.

The antimicrobial activity of Sm:HAp thin films was investigated in presence of Gram-negative and Gram-positive bacteria such as Staphylococcus aureus, Escherichia coli and Pseudomonas aeruginosa.

The results revealed the presence of a material composed mainly of calcium, phosphate, oxygen, hydrogen, and samarium ($\chi_{\text{Sm}} = 0.1$). The observation on the chemical composition of the coatings, obtained by GDOES measurements, gives information on the distribution of the elements throughout the film. The number of bacterial cells detected on the surface of Sm:HAp thin films was significantly lower compared with the results obtained for the HAp thin films.

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GD Day 2014 Symposium

O19

DBD atmospheric pressure plasma source coupled to OES and a MS

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Spatiotemporal characterization of a DBD atmospheric pressure plasma source. A DBD source has been developed for ambient air and surface analysis. The discharge is created in a dielectric cylindrical chamber ended with a capillary tube allowing the plasma jet development out of the source. Optical and ICCD diagnostics were used to get a better understanding of the excited species and plasma distributions. Results will be presented for neon and helium.

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P18

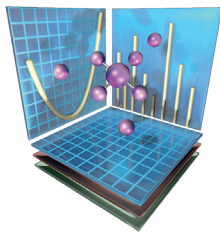
Spatiotemporal characterization of a DBD atmospheric pressure plasma source

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DBD atmospheric pressure plasma source coupled to OES and a MS. Atmospheric pressure sources are widely studied for ambient air and surface analysis. A DBD source has been developed to be coupled to a Time Of Flight Mass Spectrometer (TOFWERK). The discharge is created in a dielectric cylindrical chamber and a plasma jet is blown out of the capillary tube. In this study OES results as a function of He flow and applied voltage will be discussed. Preliminary TOFMS results will be also presented.

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GD Day 2014 Symposium

P19

Chemical analysis of CdTe solar cells by glow discharge techniques

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P. Chapon², J. Cooper^{2,**}**

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Thin film CdTe based photovoltaics (PV) is amongst the most promising technologies for solar electricity production worldwide. The current production cost of CdTe PV modules is well below \$1/Wp and hence can still compete with the recent surge of low-cost crystalline Si modules in the market. In order to maintain this competitiveness continuous efforts are needed to improve the conversion efficiency while maintaining or reducing the production cost. This may require the development of alternative fabrication methods for CdTe PV cells.

To this effect, atmospheric-pressure metalorganic chemical vapour deposition (AP-MOCVD) presents itself as a promising method of fabrication since it offers more degrees of freedom than conventional processes with the doping and alloying of the active layers used in today's CdTe PV devices, ranging from the p-n junction-forming semiconductors, CdS [1] and CdTe [2], transparent conducting oxide (TCO) [3] to high resistivity metal oxide buffer layers. Doping and alloying enables one to do away with the customary approaches of window layer (CdS) thinning and absorber layer (CdTe) (back surface) etching which are often considered risky due to pinholes formation which lead to micro-shorts.

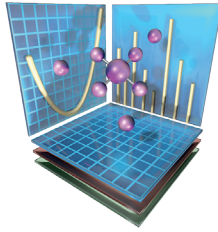
The control and run-to-run reproducibility of the various dopant concentrations and their depth-profile within the aforementioned materials are key to the inline production of CdTe PV cells and modules by the AP-MOCVD method. Even though conventional chemical analysis methods with high sensitivity such as Rutherford back scattering (RBS), secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS), etc. can successfully be used for this purpose, more rapid and cost-effective screening techniques could be highly advantageous for more frequent sampling which should allow tighter quality control, thereby reducing the associated material waste and costs.

In this study, glow discharge (GD) based techniques [5] GD Optical Emission Spectrometry (GD-OES) and Plasma Profiling Time-Of-Flight-Mass Spectrometry (PP-TOFMS) were assessed to investigate the chemical structure of high efficiency (> 10 %) CdS/CdTe and CdZnS/CdTe PV devices grown by AP-MOCVD [4]. These device layers were deposited onto indium-tin-oxide (ITO)/aluminosilicate superstrates and CdTe layers were doped with arsenic (10^{17} - 10^{20} atoms cm^{-3}) to achieve p-type character for the bulk and p+-type for the back surface for optimum performance. SIMS depth profiles were also obtained to determine the concentration profiles of main elements of interest within the p-n junction, namely Cd, Te, As, S, Zn, and Cl, which served as the reference to calibrate the data obtained by GD methods. It is shown that once optimised GD methods can be suited as an analytical tool in large scale production of CdTe PV and have the advantage of not requiring the high vacuum conditions of SIMS for more rapid turnaround.

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GD Day
2014 Symposium

P20

Characterisation of CZTSSe using Spectroscopic Ellipsometry and Pulsed RF Glow Discharge Optical Emission Spectrometry

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1) Context / Study motivation

CZTS compounds are interesting potential candidates for thin films solar cells as they are composed of only abundant and non-toxic elements.

Various analytical techniques are needed to understand the growth mechanisms, monitor and control the optical properties and the composition of the films, verify the thickness of the layers during deposition, profile the layers and see gradients.

2) Description of approach and techniques

Among the panel of techniques available, Spectroscopic Ellipsometry (SE) and Pulsed RF Glow Discharge Optical Emission Spectrometry (GD) come out due to their ease of use and the complementary information they provide – thickness, optical constants, bandgap energy for SE, elemental distribution as a function of the eroded depth for GD [1, 2].

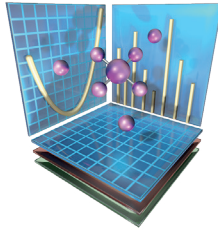
3) Results / Conclusions / Perspectives

From examples obtained on CZTSSe films, the discussion will show how SE data could be used for GD quantification and how GD controlled sputtering could be beneficial to reduce surface roughness or provide access to embedded layers prior to SE measurements.

References:

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Optical Characterization of CIGS by Spectroscopic Ellipsometry Poster presented at the JNPV 2012
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GD Day 2014 Symposium

P21

Optical characterization of CIGS using spectroscopic ellipsometry and Glow Discharge Optical Spectrometry

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Chalcopyrite based solar modules combine various layers deposited using thin film technologies. The absorber material is most often made of Copper Indium Gallium Selenide (CuInGaSe_2) realised by multisource evaporation and the contacts include sputtered Mo at the back and ZnO/CdS as window and buffer.

Various analytical techniques are applied to understand the growth mechanisms, to monitor and control the optical properties and the composition, to verify the thickness of the layers during deposition, to profile the layers and see gradients.

Among the panel of techniques available, Spectroscopic Ellipsometry and Glow Discharge Optical Emission Spectrometry come out due to their ease of use and the complementary information they provide. The presentation will illustrate on some examples the capabilities of the two techniques.

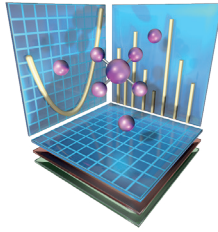
Spectroscopic Ellipsometry is a very powerful optical technique used to measure thin film thickness from 1 Å to tens of microns, optical constants, bandgap energy, surface and interface roughness, etc. It can be applied in situ or ex situ and it is ideally suited for the control of thin film photovoltaic structures.

Glow Discharge Optical Emission Spectrometry on the other hand is a destructive technique that relies on the controlled erosion of a representative part of a material (4 mm diameter craters) and provides the elemental distribution as a function of the penetration depth.

Ultra Fast Technique (one minute only is needed to sputter out all layers of a chalcopyrite solar cell and reach the glass substrate), it nevertheless offers nanometre depth resolution and is ideal to detect gradients,

The capability to measure all elements (including O, H, Ca, Na, C – simultaneously to Zn, Cd, S, Cu, Ga, Se, In, Te, Mo, In, Sn, Al, etc) allows near the line control of the full stack for a quick check up of each stage of the evaporation and deposition processes permitting to quickly react to identified problems.

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GD Day 2014 Symposium

P22

Quantitative Depth Profiling of Various Anodized Coatings by RF GDOES

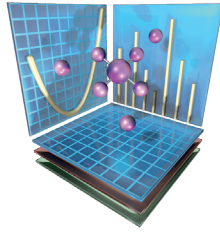
F. Li and S. Anderson

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RF GDOES has been used in our laboratory to quantitatively profile surface, near surface and interface of thick anodized coatings. These anodized coatings, typically $>40\ \mu\text{m}$ thick, are widely used in the semiconductor manufacturing process. Other industries that make use of such coatings include defense, aerospace, automotive, architectural, medical, marine, sporting goods, home appliances, and recreation. With the simultaneous multi-element profiling capability (a real-time profiling), RF GDOES was found to be very effective in examining coating composition, coating uniformity, interfacial contamination, and surface stoichiometry that can potentially have a profound effect on coatings' material properties such as corrosion resistance, wear resistance, surface hardness, lubricity, adhesion, dielectric strength, and aesthetic appearance. The RF GDOES profiling data was also found to be very valuable in optimizing anodization process, selecting base material (e.g. aluminum alloys), controlling surface and interfacial contamination, and ultimately preventing premature failure of an anodized coating.

RF GDOES uses a radio frequency plasma source for material sputtering, excitation or ionization. Many intrinsic limitations associated with traditional electron beam, ion beam and x-ray associated techniques (e.g. surface charging) are avoided in characterizing such a non-conductive anodic layer. Further signal intensities produced by RF GDOES were found to have a simple and well-defined mathematical (linear) relationship with elemental concentrations in a material. These encouraging analytical figures of merit coupled with the wide linear dynamic range possessed by RF GDOES and the availability of various material calibration standards developed in our laboratory have made a quantitative depth profiling possible.

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P23

Glow discharge optical emission spectroscopy to analyze thin electrodeposited polyaniline films

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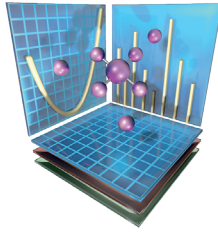
Glow Discharge Optical Emission Spectroscopy (GDOES) has been developed to perform depth profiles of thick metallic films, in tens of microns range. GDOES spectroscopy can also be used to analyze thin organic polymer films. Thin electrodeposited conducting polymer films remain an unexplored field of investigation for GDOES technique.

GDOES was used in this work to analyze electrodeposited polyaniline films, in addition to other techniques such as electron microscopy (SEM) and X-ray diffraction (XRD).

When polyaniline films were electrodeposited from HCl solutions, the presence of an anilinium chloride excess at the top surface of the polymer film was demonstrated using GDOES and XRD. Rinsing of these films with water led to the removal of this excess and to the partial dedoping of the polymer film due to the porous structure of polymer films.

When polyaniline thin films were electrodeposited from H₂SO₄ solutions, an anilinium hydrogen sulfate was incorporated into the polymer. After rinsing, hydrogen sulfate anions were not completely expelled from the polyaniline films as proved using GDOES.

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O20 **Reserved presentation**

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O21

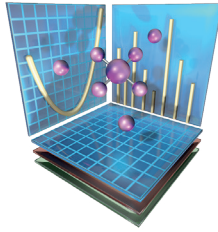
Dynamics of GDOES-induced surface roughening in metal interfaces

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The roughness induced during glow-discharge optical-emission spectroscopy (GDOES) measurements has been reported to cause a loss of resolution during GDOES depth-profiling analysis. In this paper, we undertake for the first time a study of the dynamics of the surface morphology of chromium and titanium thin films (designed in mono and multilayer structures) under the impinging of GDOES incoming ions. We performed this study under the theoretical framework of the dynamic scaling theory, by analysing surface morphology changes, as measured ex-situ by AFM, with irradiation time. For single metal layers it was found that, after an initial surface smoothing, the surface undergoes a rapid steep roughening for both systems, with quite similar quantitative dynamics. Once this roughening ends a second temporal scaling regime arises, operating for long length scales with dynamics depending on the sputtering rate of the material. For the chromium layer, with a very high sputtering rate of $5.5 \mu\text{m}\cdot\text{min}^{-1}$, this regime is consistent with the KPZ model, whereas for the titanium layer an EW scaling regime is indicated. These different scaling regimes are consistent with the development of larger surface slopes for the Cr system. In the multilayer systems, the initial roughness induced on the top Cr layer by GDOES has similar dynamics to that for single-layer Cr. However, a clear decrease in the roughness was observed once the underlying Ti layer, with a lower sputtering rate, was reached. This decrease in the induced roughness is maintained while the Ti layer is eroded. Therefore, choice of appropriate material (i.e. sputtering yield values) combinations and of their depth of location can enable tuning of GDOES-induced roughness and achieve substantial control over the depth profiling process.

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O22

The multiple facets of GD

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During the last 10 years I have been intensively working on the use of Glow Discharge Optical Emission Spectroscopy (GDOES) in the analysis of thin films and coatings. Most of my work has been presented in the different GD-days organized by HORIBA since 2004. In this talk I will make a brief summary of those results. In particular, I have been focused on the limits in depth resolution of GDOES down to the nanometer scale. The effects induced on the depth profiles during GDOES analysis of multilayer coatings were discussed in my talks of 2004 and 2006, while in the 5th GD-day of 2010 I presented a comparative study of depth profiling techniques such as RBS, SIMS, XPS and, of course GDOES (see Figure 1). Most of these techniques were applied to the study of the surface segregation of silver in complex coatings to be used for biomedical applications (See figure 2 from the 6th GD-day talk of 2012). Apart from the practical use of GDOES we have been interested on more fundamental aspects of the techniques as calibration, modelling and roughness induced effects. Therefore, in 2008 we proposed an alternative method for the quantification of nitrogen using homemade standards (Figure 3) while in 2010 we explained a simple model to describe the GDOES depth profiles (Figure 4). Finally this year we have presented a study of the dynamics of the surface morphology of metal thin films during the impinging of the GDOES incoming ions (Figure 5). All these works have pursued the main aim of placing GDOES as a well-established and recognized depth profiling technique within the material science field.

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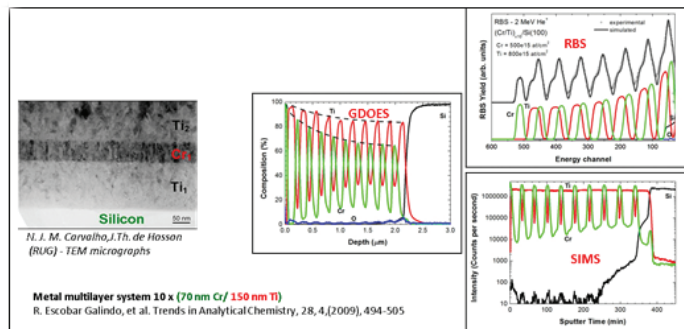


Figure 1

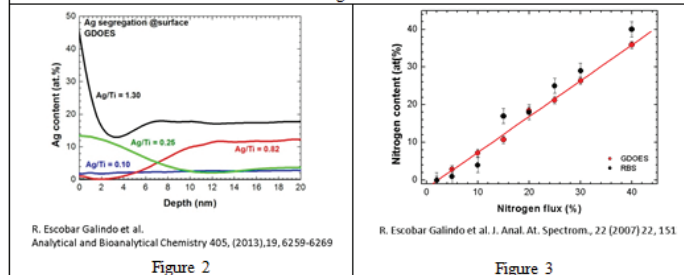


Figure 2

Figure 3

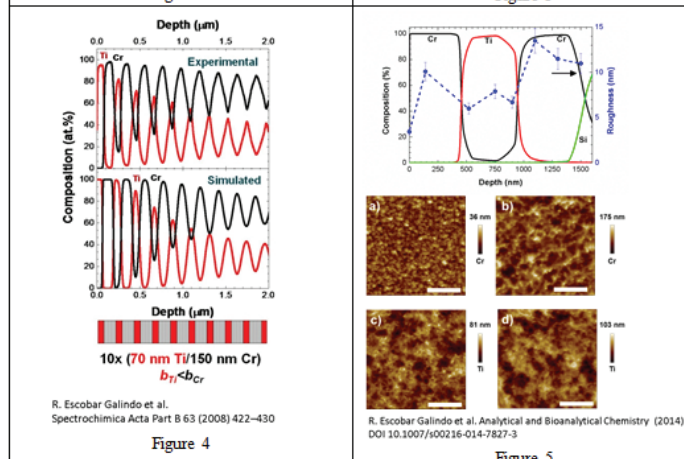
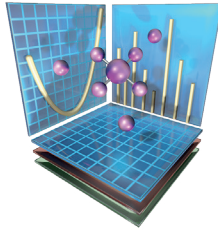


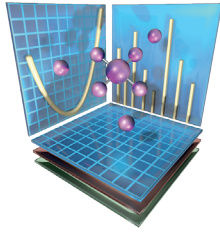
Figure 4

Figure 5



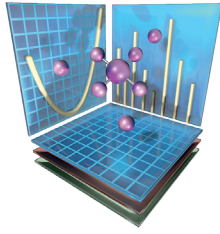
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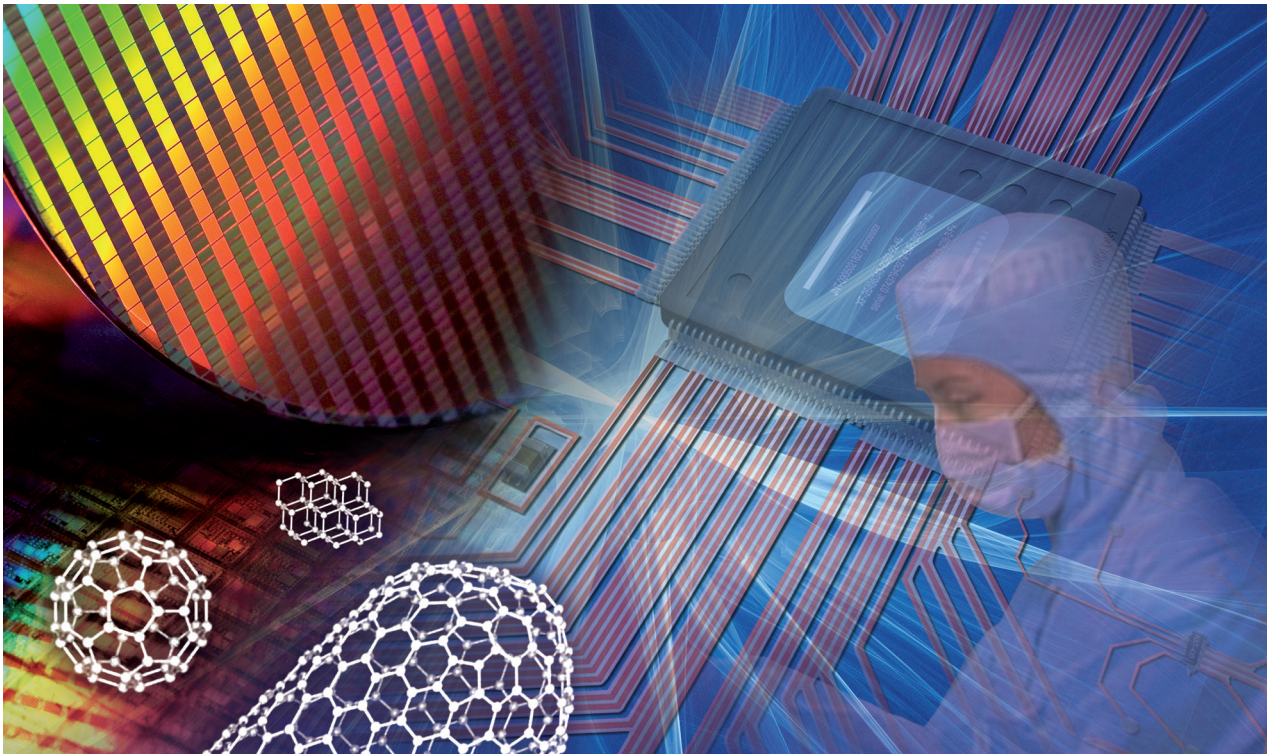
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