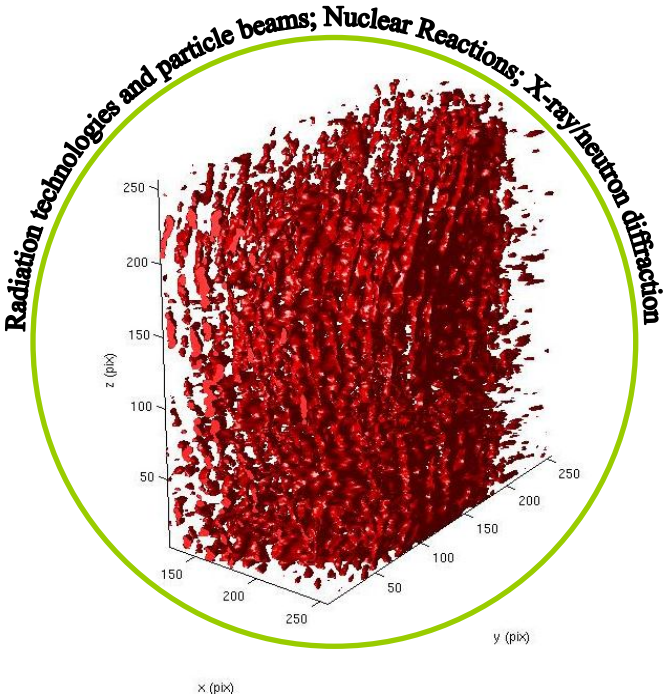
Physics and accelerators Unit



Physics and Accelerators Unit

Eduardo Alves

In 2010 the activities in the unit fostered its major goal: searching excellence biased by competence, innovation and creativity. The laboratories and new infrastructures installed under the re-equipment programme are fully operational.

The multidisciplinary approach of the research activities contributed to the reinforcement of competences in priority areas like Environment and Biomedical sciences as well as Advanced Materials and Nuclear sciences. Along with scientific achievements the post graduated formation was maintained through engagement of graduated students in the research activities, leading to M.Sc. and Ph.D. theses. The strategic collaborations with Institutions and Universities worldwide strengthened and were fundamental to maintain the high scientific production in the Unit.

The following laboratories and Groups are responsible for the R&D activity:

1 – Ion Beam Laboratory (IBL) equipped with a 2.5 MV Van de Graaff accelerator and an ion microprobe end-station, a 3 MV tandem accelerator with a micro-AMS system, and a 210 kV high fluence ion implanter. The laboratory is opened to external users, and the experimental studies cover the fields of Materials Science, Environment, Health, Biomedicine, Atomic and Nuclear Physics (cross-sections measurements). The research topics will appear in the next pages under the headings ***Advanced Materials Research Group, Materials Characterization with Nuclear Techniques, Elemental Characterization and Speciation Group, Group of Biomedical Studies and Nuclear Reactions Group.***

2 – High Temperature Materials Laboratory (MA^3T) equipped with one high-resolution, high-temperature diffractometer (*Hotbird*), particularly adapted to solve difficult problems in advanced materials and a high resolution diffractometer to study low dimensional single crystalline structures. The research activity in the laboratory is merged with the Advanced Materials Research Group.

3 – Ionising Radiation Laboratory is fitted with a Co-60 unit (UTR) with a semi-industrial dimension that has been running mainly to apply services for industrial purposes (under exploitation of CHIPionizing, S.A.). In order to develop R&D for new radiation technology applications, the upgrading and renewal of the equipment have been carried out by the *Radiation Technologies: Processes and Products Group*. The project implies new ionizing radiation equipment (e.g. electron accelerator and gamma experimental facilities), a multi-disciplinary laboratory with controlled environment, and use of automation-robotic systems in the facilities. The main R&D activities will appear under ***Radiation Technologies: Processes and Products Group.***

4 – Nuclear Instruments and Methods Laboratory activities are focussed in modelling radiation fields, calculating neutron physics parameters, measuring neutron cross-sections and application of electric discharges in analytical methods and environmental problems. The design of instrumentation for nuclear applications, and providing of specialized technical assistance in nuclear instrumentation is also part of the activities carried out. These will be presented under the title ***Nuclear Instruments and Methods.***

5 – Condensed Matter Group is focused in the processing of hybrid materials and the modification of new polymeric materials by gamma-irradiation using the ^{60}Co source of UTR as well as in their characterization using a wide range of techniques. The R&D work on these materials progress in collaboration with groups in Aveiro, Saclay and Budapest. The activities will be presented under ***Condensed Matter Physics.***

Staff

Researchers

E. ALVES, Princ.
F. MARGAÇA, Princ.
J.G.M. CORREIA, Princ.
R.C. da SILVA, Princ.
U. WAHL, Princ.
C. CRUZ, Aux.
I. GONÇALVES, Aux.
J. MANTEIGAS, Aux.
J. NEVES, Aux.
K. LORENZ, Aux. FCT
L.C. ALVES, Aux.
L.M. FERREIRA, Aux.
M.A. REIS, Aux.
M.L. BOTELHO, Aux.
M.T. PINHEIRO, Aux.
N.R. PINHÃO, Aux.
S. CABO VERDE, FCT
V. CORREGIDOR, FCT
V. DARAKCHIEVA, FCT
P.A. MIRANDA JAÑA Post-Doc. Fellow under the EU SPIRIT Project

Technicians

J. ROCHA
M. CABAÇA
M.F. BAPTISTA
N. INÁCIO
P. PEREIRA
R. PINHEIRO
T. JESUS

Administration and Informatics

A. FARIA
H. MARCOS
M.T. COSTA

Advanced Materials Research

Eduardo Alves

The Advanced Materials Research Group (GIMA) operates most of the experimental facilities at the Ion Beam Laboratory (IBL). The IBL is equipped with a 2.5 MV Van de Graaff accelerator with a nuclear microprobe and external beam facility; a 3 MV tandem accelerator with a 30 μm lateral resolution Accelerator Mass Spectrometry (AMS) system; a high flux Danfysik S1090 ion implanter.

The group explores and develop ion beam techniques to study advanced materials with high technological impact, e.g. wide band gap semi-conductors nanostructures, oxides and functional materials in collaboration with a long list of other groups. Among the wide band gap materials our major interests is focused on III-nitrides and ZnO. These alloys are the base of an emerging class of optoelectronic devices operating in the visible wavelength range of the electromagnetic spectrum being under intense research worldwide. Our work aims at the optimization of the implantation conditions of magnetic and optically active dopants in these materials. In addiction an intense research on the structural properties and Rare Earth doping of GaN/AlN QD layers continued in collaboration with Universities of Aveiro, Grenoble and Strathclyde.

The work in oxides aims at modification of the optical and structural properties of α-Al_2O_3 as well as the study of magnetic doping of ZnO by ion implantation. The potential of these materials for spintronics applications is being investigated with University of Aveiro and Faculty of Sciences of University of Lisboa.

Taking advantage of the versatility of ion beam techniques to study thin films and multilayers, important work continued on the characterisation of magnetic thin films for magnetic spin valves, tunnel junctions, and functional oxynitride coatings, in collaboration with INESC, University of Minho and New University of Lisbon.

The activities under the technology programme of the European Fusion Development Agreement (EFDA), in association with Instituto de Plasmas e Fusão Nuclear (IPFN) was focused on the study beryllium intermetallics and the study of surface erosion and redeposition processes as well as ^2H retention in JET tiles.

Training and Education continued as a major commitment of the group through the supervision of M.Sc. and Ph.D. thesis.

All the referred activities are funded by projects, either European or National (FCT), in collaboration with other Institutions. Of particular importance are the projects funded by the EC, *"FEMaS-Fusion Energy Material Science"*, EURATON 7th Framework Programme for Nuclear Research and Training, Grant agreement No 224752-CA, (2008-2011) and *"Support of Public and Industrial Research Using Ion Beam Technology (SPIRIT)"*, Grant agreement No 227012-CP-CSA-Intra (starting date 2009/03/01) and EFDA JET Technology Workprogramme JW10-FT-3.59.

The external collaborations allowed a continuous exchange of expertise and mobility of researchers, a key condition to keep the scientific activity of the group at the forefront of research and its international recognition in the field of processing and characterization of advanced materials with ion beams.

Publications (peer reviewed journals): 1 book chapter and 58 papers.
Conference and workshop contributions: 2 invited, 13 oral and 23 posters.
Running projects: 20

Research Team

Researchers(*)
E. ALVES, Principal (Group Leader)
R.C. SILVA, Principal
L.C. ALVES, Aux. (75%)
U.WAHL, Principal (85%)
K. LORENZ, Aux. (90%)
V.DARAKCHIEVA, Aux.
V. CORREGIDOR,, Aux.
A. R. RAMOS, Aux. (15%)
A. KLING, Aux. (15%)
N.P. BARRADAS, Aux. (15%)

A.C.MARQUES, Post-Doc, FCT grant
N. FRANCO, Post-Doc , FCT grant
R. MARTINS Post-Doc , FCT grant
P.A. MIRANDA JAÑA Post-Doc. Fellow under the EU SPIRIT Project

Students
B.M. NUNES,
I. FIALHO, M.Sc
L.M.PEREIRA, Ph.D. (FCT)
M.A.D. MERCIER, IST Student
M. XIE
N. CATARINO
S. MAGALHÃES, Ph.D. (FCT)
S. MIRANDA

Collaborators
A. RODRIGUES
C.P. MARQUES
J.V. PINTO
J.G. LOPES
M. VILARIGUES
R. MATEUS

Technical Personnel
J. ROCHA
F. BAPTISTA
P. PEREIRA

(*) Also members of CFNUL.

Lattice site location of optical centres in GaN:Eu light emitting diode material

K. Lorenz, E. Alves, I. S. Roqan[1], K. P. O'Donnell[1], A. Nishikawa[2], Y. Fujiwara[2], and M. Boćkowski[3]

Introduction

Europium doped GaN is a promising material for red light emitting diodes (LEDs) and lasers [1]. GaN:Eu was grown by organometallic vapour phase epitaxy (OMVPE) at temperatures (T_G) from 900 to 1100 ºC. Rutherford backscattering spectrometry/Channelling (RBS/C) was performed to investigate crystal quality, composition and Eu incorporation site [2]. Optical activity was assessed by photoluminescence.

Results

RBS/C minimum yields below 3% reveal the excellent crystal quality of all five investigated layers (Fig. 1). Eu incorporation is influenced by temperature with the highest concentration found for growth at 1000 ºC.

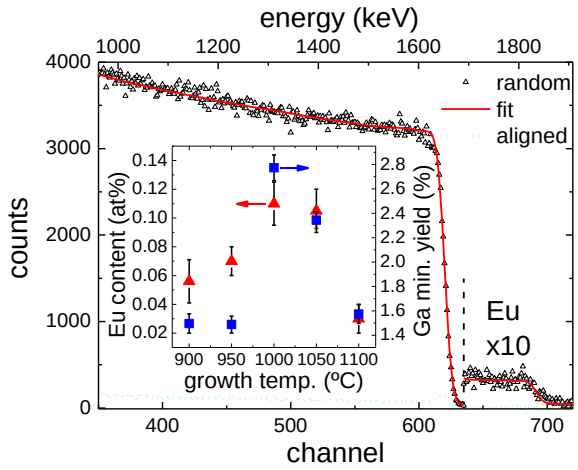


Fig. 1: RBS/C random and <0001> aligned spectra and the fit to the random spectrum of the sample grown at 1000 ºC. The inset shows Eu concentration and Ga minimum yield as a function of T_G for all in situ doped samples.

Fig. 2 shows full angular RBS/C scans across the <0001> and the <10 $\bar{1}$ 1> axes for two samples. In all samples, Eu is incorporated entirely on substitutional Ga sites with a slight displacement which is highest (~0.2 Å) in the sample grown at 900 ºC and mainly directed along the c-axis.

Photoluminescence (PL) measurements reveal that the dominant optical Eu^{3+} centres in samples grown at higher temperatures are identical to ion-implanted samples after high temperature and pressure annealing (Fig. 3). They are attributed to isolated, substitutional Eu [3]. The sample grown at 900 ºC, on the other hand, showed only a weak and broad red emission without the typical sharp lines. This, and the fact that Eu is found displaced from the substitutional site in this sample, was tentatively explained by the formation of Eu clusters promoted by a low diffusion length of adatoms at low growth temperatures. Finally, the red PL intensity of the best in situ doped sample is 20 times stronger than that of a low fluence implanted and fully annealed sample while the number of Eu ions is approximately 400 times larger, pointing to a significant potential for optimization of luminescence efficiency in future GaN:Eu based LEDs.

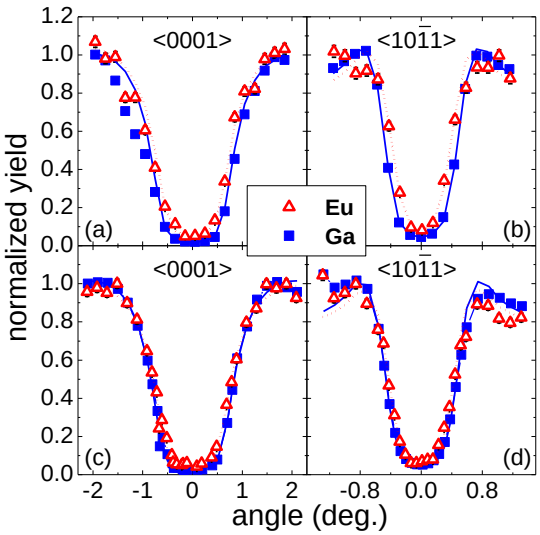


Fig. 2: Full angular scans (symbols) and fits (lines) for Eu and Ga across the <0001> and the <10 $\bar{1}$ 1> axes for samples grown at 900 ºC (a and b) and at 1000 ºC (c and d).

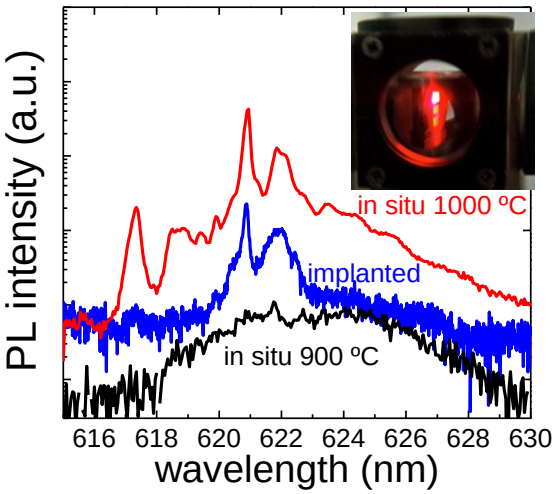


Fig. 3: PL spectra (λexc=348 nm) of samples grown at 900 and 1000 ºC compared to an Eu ion implanted sample. The inset photo shows the intense red Eu emission.

A. Nishikawa et al., Appl. Phys. Express 2, 071004 (2009).
K. Lorenz et al., Appl. Phys. Lett. 97, 111911 (2010).
I. S. Roqan et al., Phys. Rev. B 81, 085209 (2010).

[1] University of Strathclyde, Glasgow, U.K.
[2] Division of Materials and Manufacturing Science, Osaka University, Japan.
[3] Institute of High Pressure Physics, Polish Academy of Sciences Warsaw, Poland.

Lattice site location of optical centres in GaN:Eu light emitting diode material grown by OMVPE

K. Lorenz, E. Alves, I. S. Roqan[1], K. P. O'Donnell[1], A. Nishikawa[2], Y. Fujiwara[2], and M. Boćkowski[3]

Eu-doped GaN was grown by organometallic vapour phase epitaxy (OMVPE) at temperatures from 900 to 1100 ºC. Eu incorporation is influenced by temperature with the highest concentration found for growth at 1000 ºC. In all samples, Eu is incorporated entirely on substitutional Ga sites with a slight displacement which is highest (~0.2 Å) in the sample grown at 900 ºC and mainly directed along the c-axis. The dominant optical Eu^{3+} centres in samples grown at higher temperatures are identical to ion-implanted samples after high temperature and pressure annealing. They are attributed to isolated, substitutional Eu. The sample grown at 900 ºC, on the other hand, showed only a weak and broad red emission without the typical sharp lines. This and the fact that Eu is found displaced from the substitutional site in this sample was tentatively explained by the formation of Eu clusters promoted by a low diffusion length of adatoms at low growth temperatures. Finally, the red PL intensity of the best *in situ* doped sample is 20 times stronger than that of a low fluence implanted and fully annealed sample while the number of Eu ions is approximately 400 times larger, pointing to a significant potential for optimization of luminescence efficiency in future GaN:Eu based LEDs.

[1] Department of Physics, SUPA, University of Strathclyde, Glasgow, G4 0NG, U.K.
[2] Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Osaka, Japan.
[3] Institute of High Pressure Physics Polish Academy of Sciences 01-142 Warsaw, Poland.

Analysis of Rutherford Backscattering Spectrometry spectra for the determination of the InN content and its uncertainty of $Al_{1-x}In_xN$ films grown on GaN/sapphire templates

S. Magalhães, N. P. Barradas, N. Franco, E. Alves, I. M. Watson[1], K. Lorenz

Simulation softwares, such as NDF, RUMP or SIMNRA, are routinely used for the analysis of Rutherford Backscattering Spectrometry (RBS) spectra. In some cases, however, a manual analysis of RBS spectra may be more convenient and allows a more rigorous determination of the uncertainties in the derived sample composition. $Al_{1-x}In_xN$/GaN films represent such a case, in which the Al/In ratio, and therefore the InN molar fraction x, can be easily determined by integrating the areas in the spectrum corresponding to In and Al. In such an analysis, uncertainties in the charge, stopping powers and energy calibration are eliminated and the main sources of error are the counting statistics, background subtraction as well as uncertainties in beam energy and geometry of the measurements which can be easily taken into account. The main source of error in the RBS analysis of AlInN/GaN is the subtraction of the background below the Al-signal since it is superimposed to the Ga-signal of the GaN buffer layer. The necessity of a fast analysis gave the motivation of elaborating a data analysis program which automates the background subtraction and calculates the InN molar fraction and its uncertainty. The proposed method determines the Al-area using a third degree polynomial to fit the Ga-background which is then subtracted. A large number of different regions of interests are used in which the polynomial fit is performed and from which the error in the Al-area is estimated. A linear fit is used for subtracting the background below the In-signal which is mainly caused by pile-up. Various tests were performed to evaluate the method's validity. A manual analysis to a simulated "theoretical spectrum", using detector resolution and pile-up typical for the experiments, yields excellent agreement. The estimated errors in the InN molar fraction for samples with x~18% are around 0.5-1% absolute.

1. Institute of Photonics, SUPA, University of Strathclyde, G40NW Glasgow, U.K.

Structural and optical characterization of Europium implanted GaN quantum dots

S. Magalhães, M. Peres[1], V. Fellmann[2],B. Daudin[2], E. Alves A. J. Neves[1], T. Monteiro[1], K. Lorenz

Self-assembled GaN quantum dots (QDs) stacked in superlattices (SL) with AlN spacer layers were implanted with Europium ions to fluences of 10^{13}, 10^{14}, and 10^{15} cm^{-2}. Post-implant annealing was performed between 1000 ºC and 1200 ºC in nitrogen. The damage level introduced in the QDs by the implantation stays well below that of thick GaN epilayers. For the lowest fluence, the structural properties remain unchanged after implantation and annealing while for higher fluences the implantation damage causes an expansion of the SL in the [0001] direction which is only partly reversed after thermal annealing. Nevertheless, in all cases, the SL quality remains very good after implantation and annealing. Eu ions are incorporated preferentially into near-substitutional cation sites. Eu^{3+} luminescence was observed in all samples with the most intense emission assigned to the $^5D_0 \rightarrow {}^7F_2$ transition in the red spectral region. Optically active Eu centres in both GaN QD and AlN layers could be identified. For low implantation fluence the Eu centres inside GaN QD are dominant while for high fluences the emission arises from Eu in the AlN layers. The annealing temperature, on the other hand, does not cause any change in the local environment of the Eu-ions.

[1] Departamento de Física & I3N, Universidade de Aveiro, 3810-193 Aveiro, Portugal.
[2] CEA-CNRS Group "NanoPhysique et SemiConducteurs", CEA-Grenoble, France.

Structural and optical characterization of Eu-implanted non-polar and polar GaN

N. Catarino, E. Nogales[1], B. Méndez[1], E. Alves, K. Lorenz

Europium (Eu) ions were implanted into non-polar a-plane (11-20) gallium nitride (GaN) films grown on r-plane sapphire with fluences ranging from 1×10^{14} to 4×10^{15} cm^{-2} at room temperature (RT). Results are compared with similarly implanted polar c-plane (0001) GaN films. Structural and optical characterizations of the samples were performed using Rutherford backscattering spectrometry and channelling (RBS/C) and cathodoluminescence (CL) spectroscopy. RBS/C measurements for the as-implanted samples reveal similar damage formation for both materials with two different damage regions, one at the surface and one deeper in the crystal. For the highest fluences the channelling effect in the surface region is completely suppressed indicating amorphisation or nano-crystallization of this layer. The damage in the bulk stays well below the random level and is substantially lower for a-plane GaN, in particular for high fluences. In both cases, Eu is incorporated on near-substitutional Ga-sites. After annealing at 1000 ºC both materials show good recovery of the crystal quality and the Eu ions are optically activated. Both, *a*- and *c*-plane GaN films show similar behavior, the CL intensity is increasing steeply for implantation from 1×10^{14} to 2×10^{15} cm^{-2}; for the highest fluences the CL intensity is decreasing again due to the severe structural damage.

[1] Dpto. Física de Materiales, Universidad Complutense de Madrid, 28040 Madrid, Spain.

Optical doping of AlN micro- and nanorods by rare earth ions

V. Darakchieva, M.-Y. Xie,[1] R. Yazdi,[2] R. Yakimova,[1] J. Rodrigues, [2]T. Monteiro,[2] E. Alves, K. Lorenz

The doping of III-nitrides with optically active rare earth (RE) ions offers an attractive route to an all-nitride light emitting technology covering the entire wavelength range from UV to IR. The possibility to mix colours and achieve white light opens opportunities for efficient solid state lighting with high energy saving potential. The most challenging issue to solve on the way to produce RE doped devices is the efficiency, which is strongly dependent on the excitation cross-section. A promising approach may be the RE doping of nitride nanostructures where the carrier confinement can increase the excitation cross-section.

We performed RE doping of AlN microrods and nanorods in order to achieve emission in the visible. The AlN micro- and nanorods (Fig.1) were implanted with Eu (red), Tm (blue) and Er (green) RE ions and subsequently annealed in order to activate the ions and remove the crystal damage. The structural properties of the AlN rods have been studied before and after implantation and annealing. Cathodoluminescence measurements reveal strong emission lines from the RE ions at room temperature (Fig.1). The principal $^5D_0 \rightarrow {}^7F_2$ red transition is identified in the AlN rods implanted with Eu. A weak $^1G_4 \rightarrow {}^3H_6$ transition is detected in the blue spectral region of the Tm doped AlN sample, while the higher lying blue line ($^1D_2 \rightarrow {}^3F_4$), dominant in AlGaN alloys, is absent. The spectrum is dominated by the IR transition at around 800 nm. The Er doped AlN rods revealed very intense transitions in the red possibly due to an unintentional co-implantation with Eu. The visible green Er emission is seen only weakly in the 530 nm region. We are currently investigating the possibility of energy transfer from Er to Eu in these structures, as well as the RE ion incorporation and optically active centres.

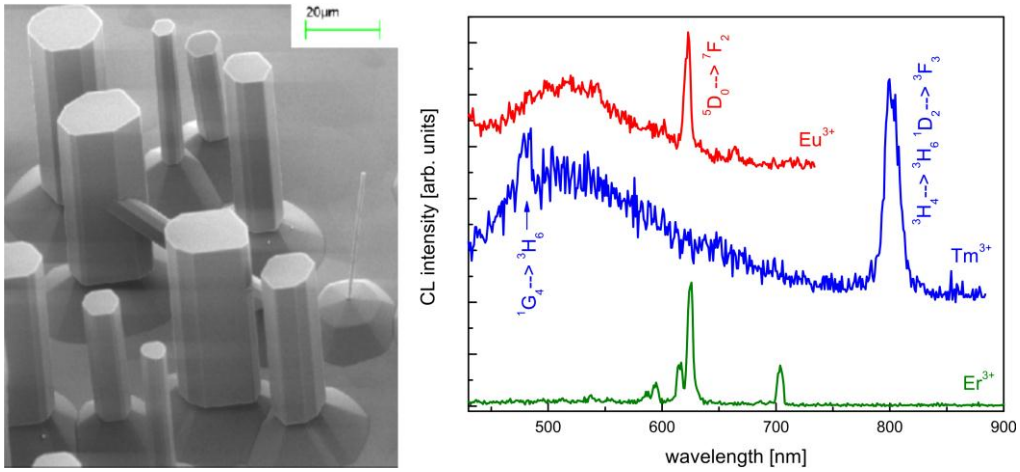


Fig. 1 - Scanning electron micrograph of the AlN micro- and nanorods implanted with different RE ions and their room temperature cathodoluminescence spectra.

[1] Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden.
[2] Departamento de Física, Universidade de Aveiro, 3810-193 Aveiro, Portugal.

Ion implantation of Cd and Ag into AlN and GaN

S. M. C. Miranda, E. Alves, K. Lorenz

Group III nitrides are promising and competitive materials for optoelectronic applications due to their wide and direct band gap. Although GaN and especially AlN show strong radiation damage resistance, the use of ion implantation in device processing still requires more knowledge on damage formation and appropriate post-implant annealing procedures. GaN and AlN thin films, grown by hydride vapor phase epitaxy on sapphire, were ion implanted at room temperature with cadmium (Cd) and silver (Ag), with fluences ranging from 1×10^{13} to 1.5×10^{15} cm^{-2} at 150 keV. The as-implanted samples were annealed at 950 ºC in a tube furnace under nitrogen (N) flow for 10 or 20 minutes, for Cd and Ag respectively. A proximity cap was used to prevent N from out-diffusing during the annealing. The samples were characterized by Rutherford Backscattering Spectrometry and Channelling and X-ray Diffraction measurements. The results indicate that implantation damage could be fully removed for the lowest fluences while for higher fluences the crystal quality was only partially recovered. Cd is found incorporated in substitutional cation sites (Al or Ga) while Ag is somewhat displaced from the substitutional position, probably due to the higher implantation damage. The substitutional fraction of Ag in AlN increases after annealing.

Unintentional incorporation of hydrogen in InN: diffusion kinetics and effect of surface orientation

V. Darakchieva[1], K. Lorenz, S.M.C. Miranda, N. P. Barradas, E. Alves, D. Rogala,[2] H.-W. Becker,[2] S. Ruffenach,[3] O. Briot,[3] W. J. Schaff,[4] C.L. Hsiao,[5] L.C. Chen,[5] L.W. Tu,[6] T. Yamaguchi,[7] Y. Nanishi[7]

Control of doping in InN and related alloys remains one of the most challenging issues on the way to develop the potential of these materials in new advanced photovoltaic and light emitting device applications. We studied InN films with (0001), (000-1), (10-11) and (11-20) surface orientations grown by molecular beam epitaxy (MBE) and metalorganic vapor phase epitaxy (MOVPE). The H depth profiles in the films are measured by elastic recoil detection analysis and nuclear reaction analysis. All films revealed enhanced H concentrations at their surfaces and significant H amounts in the bulk sufficient to explain the observed free electron concentrations in the films. We have established scaling between H and free electron concentrations in c-plane InN grown by MBE evidencing the major role of H for the unintentional n-type conductivity in this case. The bulk H concentration seems to be dependent on the polarity of the MBE films being lowest in the In-polar, intermediate in the N-polar and semipolar, and highest in the nonpolar InN films (Fig.1). We find similar H areal densities at the (0001), (000-1) and (1-101) surfaces, while nonpolar InN surfaces incorporate much higher amounts of H (Fig.1). Thermal annealing at 350°C in N_2 results in decrease of the H levels with comparable bulk/surface concentrations of H in the polar and semipolar MBE films. However, the H contents in the a-plane MBE films still remain significantly higher after the annealing. We also found a direct evidence for the major role H as a n-type dopant in MOVPE InN based on our annealing studies.

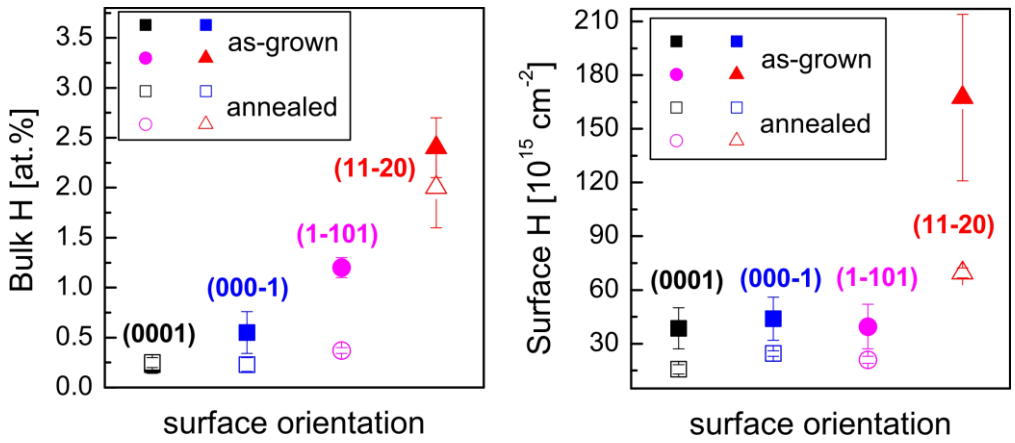


Fig. Bulk and surface H concentrations in four MBE InN films with different surface orientations grown in the same growth equipment.

[1] IFM, Linköping University, SE-581 83 Linkoping, Sweden.
[2] Ruhr-Universität Bochum, Germany.
[3] Groupe d'Etude des Semiconducteurs, CNRS, Université Montpellier II, 34095 Montpellier, France.
[4] Department of Electrical and Computer Engineering, Cornell University, Ithaca, NY 14853, USA.
[5] Center for Condensed Matter Sciences, National Taiwan University, Taipei 106, Taiwan, ROC.
[6] National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, ROC.
[7] Department of Photonics, Ritsumeikan University, Shiga 525-8577, Japan.

Structural anisotropy of nonpolar InN films

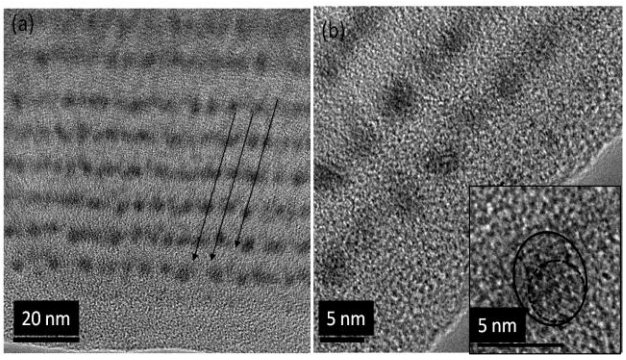
V. Darakchieva, M.-Y. Xie,[1] N. Franco, E. Alves, C. L. Hsiao,[3] L. C. Chen,[2] L. W. Tu,[3] Y. Takagi,[4] T. Yamaguchi,[4] Y. Nanishi[4]

We performed detailed study of the structural characteristics of molecular beam epitaxy grown nonpolar InN films with a- and m-plane surface orientations on r-plane sapphire and (100) γ-$LiAlO_2$, respectively, and semipolar (10-11) InN grown on r-plane sapphire. The on-axis rocking curve (RC) widths were found to exhibit anisotropic dependence on the azimuth angle with minima at InN [0001] for the a-plane films, and maxima at InN [0001] for the m-plane and semipolar films. The finite size of the crystallites and extended defects are suggested to be the dominant factors determining the RC anisotropy in a-plane InN, while surface roughness and curvature could not play a major role. We furthermore suggest strategy to reduce the anisotropy and magnitude of the tilt and minimize defect densities in a-plane InN films. In contrast to the nonpolar films, the semipolar InN was found to contain two domains nucleating on zinc-blende InN(111)A and InN(111)B faces. These two wurtzite domains develop with different growth rates, which was suggested to be a consequence of their different polarity. Both, a- and m-plane InN films have basal stacking fault densities similar or even lower compared to nonpolar InN grown on free-standing GaN substartes, indicating good prospects of heteroepitaxy on foreign substrates for the growth of InN-based devices.

[1] IFM, Linköping University, Sweden.
[2] Center for Condensed Matter Sciences, National Taiwan University, Taiwan.
[3] Department of Physics, National Sun Yat-Sen University, Taiwan.
[4] Department of Photonics, Ritsumeikan University, Japan.

Structural study of $Si_{1-x}Ge_x$ nanocrystals embedded in SiO_2 films

S.R.C. Pinto[1], R.J. Kashtiban[3], A.G. Rolo[1], M. Buljan[2], A. Chahboun[1,4], U. Bangert[3], N.P. Barradas, E. Alves and M.J.M. Gomes[1]



The structural properties of $Si_{1-x}Ge_x$ nanocrystals formed in an amorphous SiO_2 matrix by magnetron sputtering deposition were investigated. The influence of deposition parameters on nanocrystal size, shape, arrangement and internal structure was examined by X-ray diffraction, Raman spectroscopy, grazing incidence small angle X-ray scattering, high resolution transmission electron microscopy and ion beam analysis. We found conditions for the formation of spherical $Si_{1-x}Ge_x$ nanocrystals with average sizes between 3 and 13 nm, uniformly distributed in the matrix. In addition we have shown the influence of deposition parameters on average nanocrystal size and Ge content *x*.

[1] Physics Department, University of Minho, 4710 — 057 Braga, Portugal.
[2] Charles University in Prague, Ke Karlovu 5, 121 16 Prague, Czech Republic, Ruđer Bošković Institute, Bijenička cesta 54, Croatia.
[3] Nanostructured Materials Research Group, School of Materials, The University of Manchester, P.O. Box 88, Manchester, M1 7HS, UK.
[4] Physics Department, Dhar Mehraz Sciences Faculty, BP 1796, Fès, Morocco.

Effect of nitrogen on the $GaAs_{0.9-x}N_xSb_{0.1}$ dielectric function from the nir-infrared to the ultraviolet

N. Ben Sedrine, C. Bouhafs[1], J. C. Harmand[2], R. Chtourou[1] and V. Darakchieva[3]

We study the effect of nitrogen on the $GaAs_{0.9-x}N_xSb_{0.1}$ (x = 0.00, 0.65, 1.06, 1.45 and 1.90 %) alloy dielectric function by spectroscopic ellipsometry in the energy range from 0.73 to 4.75 eV. The compositional dependences of the critical points energies for the $GaAs_{0.9-x}N_xSb_{0.1}$ are obtained. In addition to the GaAs intrinsic transitions E_1, $E_1+\Delta_1$, and E_0', the nitrogen-induced Γ-point optical transitions E_0 and E_+, together with a third transition $E^{\#}$, are identified. We find that with increasing the N content, the E_0 transition shifts to lower energies while the E_+ and $E^{\#}$ transitions shift to higher energies. We suggest that the origin of the E_0, E_+ and $E^{\#}$ transitions may be explained by the double band anticrossing (BAC) model, consisting of a conduction BAC model and a valence BAC model.

[1] Laboratoire de Photovoltaïque de Semiconducteurs et de Nanostructures, Centre de Recherche et de Technologie de l'Energie, BP. 95, Hammam-Lif 2050, Tunisia.
[2] Laboratoire de Photonique et de Nanostructures, CNRS Route de Nozay, 91 460, Marcoussis, France.
[3] Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden.

Optical properties of InN/$In_{0.73}Ga_{0.27}N$ multiple quantum wells studied by spectroscopic ellipsometry

N. Ben Sedrine,[1] V. Darakchieva,[2] D. Lindgren[2], B. Monemar,[2] S.B. Che,[2] Y. Ishitani,[3] A. Yoshikawa[3]

The optical properties of two high quality fifty-periods of In-polarity InN/$In_{0.73}Ga_{0.27}N$ MQWs samples, grown by radio-frequency plasma-assisted molecular beam epitaxy, with different well (0.5-1nm) and barrier thicknesses (3-4nm) were studied. We employ spectroscopic ellipsometry at room temperature in the energy range from 0.6 to 6 eV, and incidence angles of 60 and 70°. Ellipsometric data were successfully modelled using the model dielectric function approach and a multilayer model assuming the MQWs as a homogeneous layer. The E_0, A and E_1 MQWs transition energies were determined and found to exhibit a blueshift with decreasing the well thickness.

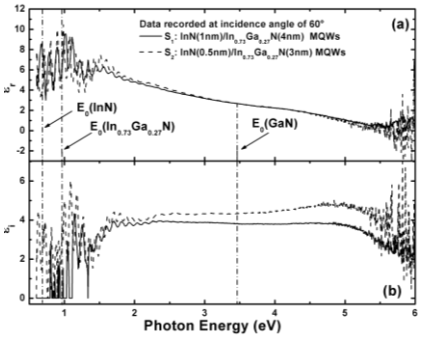


Fig. Pseudodielectric function real and imaginary parts for both samples.

[1] Laboratoire de Photovoltaïque de Semiconducteurs et de Nanostructures, Centre de Recherche et de Technologie de l'Energie, Tunisia.
[2] Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden.
[3] Graduate School of Electrical and Electronic Engineering, Chiba University, 263-8522 Chiba, Japan.

Optical active centres in ZnO samples

T. Monteiro[1], M.J. Soares[1], A. Neves[1], S. Pereira1[4], M.R. Correia[1], M. Peres[1], E. Alves, D. Rogers[2], F. Teherani[2], V. Munoz-SanJose[3], T. Trindade[4] and A. Pereira[4]

ZnO ($E_g \backsim$ 3.37 eV) is an semiconductor oxide with enahced properties for a wide range of opto-emitter applications spanning visible and short wavelengths. Bulk, thin films and nanomaterials obtained using different synthesis methods have been investigated for optoelectronic and biotechnological device applications. Nominally undoped bulk samples typically present a myriad-structured near-band-edge recombination, mainly due to free/bound excitons and donor–acceptor pair transitions. Furthermore, deep level emission due to intrinsic defects and extrinsic impurities, such as transition metal ions, are commonly observed in different grades of bulk ZnO samples. Undoped thin film and ZnO nanocrystal samples also present optically-active centres due to the presence of native and extrinsic defects. Continuing improvement in device performance hinges on improved understanding of the role of these defects present in ZnO samples. In this work a correlation between the optical centres was observed between nominally-undoped bulk, thin films and nanocrystal ZnO. We also observed a correlation between the structural properties and ion optical activation for single crystal samples which were intentionally-doped with rare earth ions (Tm, Er, Eu and Tb) either (a) by ion-implantation or (b) during synthesis. For the doped ZnO nanocrystals, intra-ionic recombination and XRD data suggest that the ions are in a crystalline environment.

[1] Departamento de Física, Universidade de Aveiro, 3810-193 Aveiro, Portugal.
[2] Nanovation, Orsay 91400, France.
[3] Departamento de Física Aplicada, Universidad Valência, Valência, Spain.
[4] Departamento de Química, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal.

Mn-doped ZnO nanocrystals embedded in Al_2O_3: structural and electrical properties

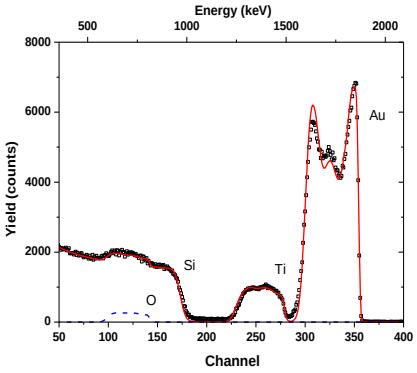
A Khodorov[1], S Levichev[1], A G Rolo[1], O Karzazi[2], A Chahboun[1,2], J Novak[3], A Vorobiev[3], C J Tavares[1], D Eyidi[4], J-P Rivière[4], M F Beaufort[4], N P Barradas, E Alves, L.C. Alves, D J Barber[5], S Lanceros-Mendez[1], M J M Gomes[1]

The structural and electrical properties of Mn-doped ZnO/Al2O3 nanostructures produced by the pulsed laser deposition technique were studied by grazing incidence small angle x-ray scattering (GISAXS), Rutherford backscattering spectrometry and capacitance–voltage measurements. The results revealed the multilayered structure in as-deposited samples and the annealing of the nanostructures at high temperatures was shown to promote the formation of nanocrystals embedded in the Al2O3 matrix, as was evidenced by GISAXS and high resolution transmission microscopy. Particle-induced x-ray emission analysis showed a doping of 8 at.% Mn in ZnO. Grazing incidence x-ray diffraction and Raman spectroscopy demonstrated that the nanocrystals have the pure wurtzite ZnMnO crystalline phase. Resonant Raman scattering displayed an increase of intensity of the 1LO mode as well as broadening of the 2LO mode related to the size effect. Capacitance–voltage measurements showed carrier retention with a voltage shift higher than those reported for similar systems.

[1] Centre of Physics and Physics Department, University of Minho, 4710-057 Braga, Portugal; [2] LPS, Physics Department, Faculty of Sciences, Fès, Morocco; [3] ESRF, Grenoble, France; [4] PhyMat, University of Poitiers, 86962 Futuroscope-Chasseneuil, France ; [5] Physics Centre, University of Essex, Colchester, CO4 3SQ, UK.

Functional and optical properties of Au:TiO_2 nanocomposite films: The influence of thermal annealing

M. Torrell[1], L. Cunha[1], A. Cavaleiro[2], E. Alves, N.P. Barradas and F. Vaz[1]



A set of nanocomposite thin films consisting of Au nanoclusters dispersed in a TiO_2 dielectric matrix was deposited by reactive magnetron sputtering, and subjected to thermal annealing in vacuum, at temperatures ranging from 200 to 800 °C. The obtained results show that the structure and the size of Au clusters, together with the matrix crystallinity, changed as a result of the annealing, and were shown to be able to change the optical properties of the films and keeping good mechanical properties, opening thus a wide number of possible applications. The crystallization of the gold nanoclusters induced by the annealing was followed by a systematic change in the overall coating behaviour, namely the appearance of surface plasmon resonance (SPR) behaviour. This effect enables to tailor the thin films reflectivity, absorbance and colour coordinates, contributing to the importance of this thin film system. The different attained optical characteristics associated with a reasonable mechanical resistance of the coatings induce the possibility to use this film system in a wide range of decorative applications.

[1] Universidade do Minho, Dept. Física, Campus de Azurém, 4800-058 Guimarães, Portugal.
[2] SEC-CEMUC–Universidade de Coimbra, Dept. Eng. Mecânica, Pólo II, 3030-788 Coimbra, Portugal.

Effects of Mg-ion implantation in α-Al_2O_3 and α-Al_2O_3:Mg crystals: Electrical conductivity and electronic structure changes

M. Tardío[1], I. Colera[1], R. Ramírez[1] and E. Alves

Undoped and Mg-doped α-Al_2O_3 single crystals were implanted with Mg ions, with an energy of 90 keV and a fluence of 10^{17} ions/cm^2. DC electrical measurements using the four-point probe method, between 295 and 428 K, were used to characterize the electrical conductivity of the implanted area. Measurements in this temperature range indicate that the electrical conductivity after implantation is thermally activated with an activation energy of about 0.03 eV both in undoped and in reduced Mg-doped α-Al_2O_3 crystals, whereas the activation energy in oxidized Mg-doped α-Al_2O_3 crystals remains close to that before implantation. The *I–V* characteristics of the latter samples reveal a blocking behavior of the electrical contacts on the implanted area in contrast to the ohmic contacts observed in α-Al_2O_3 single crystals with the *c*-axis perpendicular to the broad face, where the Mg ions were implanted. We conclude that the enhancement in conductivity observed in the implanted regions is related to the intrinsic defects created by the implantation, rather than to the implanted Mg ions. The relationship between the oxygen vacancy concentrations at different stages of etching and the changes in the electronic structure, the chemical bonding, and the Al^{3+}(2p)/O^{2-}(1s) and Mg^{2+}(1s)/O^{2-}(1s) relative intensities was studied by X-ray Photoemission Spectroscopy.

[1]Universidad Carlos III de Madrid, Departamento de Física, 28911 Leganés, Madrid, Spain.

Damage recovery and optical activity in europium implanted wide gap oxides

E. Alves, C. Marques, N. Franco, L.C. Alves, M. Peres[1], M.J. Soares[1] and T. Monteiro[1]

Defects play an important role on the optical behaviour of sapphire and magnesium oxide single crystals. We studied the optical properties of these oxides implanted at room temperature with different fluences (1×10^{15}–1×10^{16} cm^{-2}) of europium ions. Rutherford backscattering channelling shows that for fluences above 5×10^{15} cm^{-2} the surface disorder level in the Al-sublattice reaches the random level. Implantation damage recovers fast for annealing in oxidizing atmosphere but even for the highest fluence we recover almost completely all the damage after annealing at 1300 °C, independently of the annealing environment (reducing or oxidizing). Annealing above 1000 °C promotes the formation of Eu_2O_3 in the samples with higher concentration of Eu. The optical activation of the rare earth ions at room temperature was observed after annealing at 800 °C by photoluminescence and ionoluminescence. In Al_2O_3 lattice the highest intensity line of the Eu^{3+} ions corresponds to the forced electric dipole $^5D_0 \rightarrow {}^7F_2$ transition that occurs ~616 nm. For the MgO samples the Eu^{3+} optical activation was also achieved after implantation with different fluences. Here, the lanthanide recombination is dominated by the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition near by 590 nm commonly observed for samples were Eu^{3+} is placed in a high symmetry local site. The results clearly demonstrate the possibility to get Eu incorporated in optical active regular lattice sites in wide gap oxides.

[1] Departamento de Física e I3N, Universidade de Aveiro, 3810-193 Aveiro, Portugal.

Magnetic and transport properties of ZnO single crystals doped by ion implantation

C. Silva[1], A.R.G. Costa[1], R.P. Borges[1], M.M. Cruz[1], M. Godinho[1], R.C. da Silva

This research continued on two fronts, implantation doping with *i*) transition metals, and *ii*) non-magnetic gases.

i) *Magnetic and transport properties of transition metals doped ZnO*

Zinc oxide single crystals were implanted with Mn, Co and Ni ions with 200 keV energy and fluences between 1×10^{16} cm^{-2} and 1×10^{17} cm^{-2}, and analysed by RBS, RBS/channelling and XRD. Results showed that formation of nm sized particles occurred only in the case of 1×10^{17} cm^{-2} Ni. The nm sized Ni aggregates display super-paramagnetic behaviour, grow by annealing at 1073 K and oxidize: super-paramagnetism is retained in the oxidized state, but with lower T_B, indicating partial oxidation of Ni and formation of Ni/NiO core shell particles. On the contrary, with Mn super-paramagnetic behaviour was observed only upon 1073 K annealing of the highest implantation fluence, 1×10^{17} cm^{-2}. However, this was assigned to formation of $ZnMn_2O_4$ nanoparticles rather than Mn aggregation, as detected by XRD, consistently with a general dilution trend of Mn ions upon annealing. In the remaining cases – 1, 2 and 5×10^{17} cm^{-2} Ni and all but the lowest fluence of Co – annealing at 1073 K lead to aggregate formation and super-paramagnetic behaviour. Correlation with RBS/channelling measurements indicates that this is possibly driven by the dynamics of the annealing induced recovery of crystalline order. Damage and damage recovery as seen by RBS/channelling also correlate with the transport properties, as all the samples are insulating in the as implanted state and acquire measurable conductivities by annealing.

ii) *Magnetic and transport properties of nitrogen and argon doped ZnO*

Argon and nitrogen ions were implanted into ZnO single crystals with 200 keV energy and fluences of 1×10^{17} cm^{-2} and 2×10^{17} cm^{-2} in order to compare the influence of these non-magnetic elements in the magnetic and electrical behaviour of zinc oxide. RBS/channelling measurements showed that the high levels of disorder left in the implanted region are partially annealed only at and above 1073 K. As PIXE measurements show that there are no magnetic elements in the implanted samples, the ferromagnetic behaviour found by magnetic characterization of the as-implanted state, is certainly correlated with the implantation defects in the lattice. After annealing the ferromagnetic components decrease or completely disappear, in consistency with the defect origin of the recorded behaviour.

[1] Dep. Física da Universidade de Lisboa.

Single and polycrystalline mullite fibres grown by laser floating zone technique

R.G. Carvalho[1], A.J.S. Fernandes[1], F.J. Oliveira[2], E. Alves, N. Franco, C. Louro[3], R.F. Silva[2] and F.M. Costa[1,]

The laser floating zone technique was used to grow large $2Al_2O_3$–SiO_2 mullite fibres (up to 1.6 mm in diameter and 40 mm in length). The fibres grown at 10 mm/h are single crystalline in nature, while those pulled at higher rates (40 and 100 mm/h) are polycrystalline with a cellular microstructure. The crystals are highly [0 0 1] textured with respect to the fibre axis, as determined by X-ray diffraction analysis. The Raman spectra taken at different orientations corroborate the strong anisotropy observed by X-ray and SEM on both single crystalline and textured polycrystalline samples. Four point bending tests and ultramicroindentation Vickers experiments were performed at room temperature in order to characterize the mechanical properties. The presence of lamellar inclusions in the single crystalline fibres decreases the flexural strength (431 MPa) and the fracture toughness (1.2 MPa.m$^{1/2}$) compared to the polycrystalline ones (631 MPa and 1.6 MPa.m$^{1/2}$). However, the absence of grain boundaries in the single crystals leads to higher ultramicrohardness (H_V = 15.6 GPa) and Young's modulus (E = 170 GPa) than those of the polycrystalline fibres (14.2 and 145 GPa), where a glassy intergranular phase exists.

[1] I3N, Physics Department, University of Aveiro, 3810-193 Aveiro, Portugal.
[2] CICECO, Glass and Ceramic Engineering Department, University of Aveiro, 3810-193 Aveiro, Portugal.
[3] CEMUC, Mechanical Engineering Department, University of Coimbra, 3030-788 Coimbra, Portugal.

Transition metals nitrides for magnetic applications

R.C. da Silva, A.R.G. Costa[1], M.M. Cruz[1], M. Godinho[1]

New research has been started in transition metals nitrides aiming at magnetic applications.

Synthesis of Fe, Co and Ni nitrides at the nm scale for magnetic applications has been achieved in various forms, thin films deposited by RPLAD, powders by nitridation of metal oxide particles, and embedded nitride particles made by N ion implantation. Deposition parameters of the thin films were studied, RBS analysis showing that in *e.g.* Co-nitride a stoichiometric layer is readily obtained from a low pressure pure N_2 atmosphere. As for the implanted metals, RBS and XRD measurements showed that N ions were successfully retained to fluences of 1-2×10^{17} cm^{-2} and that nitrides did form in Fe and Ni – as Fe_2N and Ni_3N – but not in Co.

[1] Dep. Física da Universidade de Lisboa.

Stoichiometry changes of BFO in the thin film form

R.C. da Silva, B. Ribeiro[1], *R.P. Borges*[1]

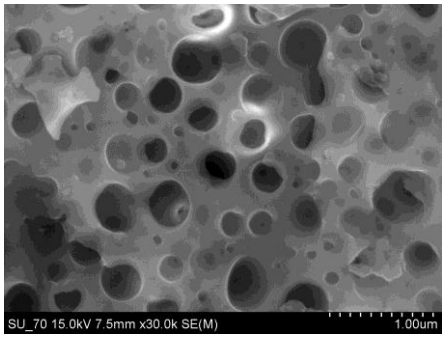
A number of $BaFe_{1-x}O_3$ thin films (BFO) of thicknesses in the range 50 nm to 120 nm were deposited onto $SrTiO_3$ (STO) substrates and its compositions analysed by RBS in order to ascertain the cations ratios [Ba]:[Fe]. Detailed analysis was performed by assigning initial compositions and thicknesses for the films and allowing the RUMP© code to simulate the expected RBS spectra. In each case the theoretically simulated spectrum was compared with the corresponding experimental spectrum and the compositions reworked to reach convergence. By using the PERT module of the RUMP© package the layers compositions and/or thicknesses were left free to be varied over intervals from ±5% up to of as much as ±20% of the nominal values, in a fitting procedure by a non-linear least squares method. From these analyses a number of conclusions are extracted:

– The cation compositions are slightly Ba-rich, with an average [Fe]:[Ba] smaller than but close to unity;
– The overall compositions are O-rich (*i.e*. cation deficient) in relation with the nominal composition, with an anion to cation ratio above 1.5 by less than 5%.

[1] Dep. Física da Universidade de Lisboa.

Structural and thermal characterization of SiO_2–P_2O_5 sol–gel powders upon annealing at high temperatures

M. Elisa[1], *B.A. Sava*[2], *A. Volceanov*[3], *R.C.C. Monteiro*[4], *E. Alves, N. Franco, F.A. Costa Oliveira*[5], *H. Fernandes*[6] *and M.C. Ferro*[6]



This study deals with SiO_2–P_2O_5 powders obtained by sol–gel process, starting from tetraethoxysilane (TEOS) as precursor for SiO_2 and either triethylphosphate (TEP) or phosphoric acid (H_3PO_4) as precursors for P_2O_5. In the case of samples prepared with H_3PO_4, TG–DTA data showed an accentuated weight loss associated to an endothermic effect up to about 140 °C, specific for the evaporation of water and ethylic alcohol from structural pores, and also due to alkyl-amines evaporation. Sol–gel samples prepared with TEP exhibited different thermal effects, depending on the type of atmosphere used in the experiments, i.e. argon or air. XRD analysis revealed that annealed sol–gel samples prepared with H_3PO_4 showed specific peaks for silicophosphate compounds such as $Si_3(PO_4)_4$, $Si_2P_2O_9$, and SiP_2O_7. XRD results for annealed sol–gel samples prepared with TEP indicated mainly the presence of a vitreous (amorphous) phase, which could be correlated with SEM images. The presence of SiO_2 in the sample might be expected. Thus, we have searched for any SiO_2 polymorph possible to crystallize. Only potential peaks of cristobalite were identified but some of them are overlapping with peaks of other crystalline phosphates. SEM analysis indicated a decrease of the amount of crystalline phases with the increase in the annealing temperature.

[1] National Institute of Optoelectronics-INOE 2000, 1, Atomistilor Str., P.O. Box MG-5, 77125, Bucharest-Magurele, Romania.
[2] National Institute of Glass S.A., 47th Pallady Bvd, Bucharest 032258, Romania.
[3] Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, P.O. Box 12-134, Bucharest, Romania.
[4] New University of Lisbon, Department of Materials Sciences, CENIMAT/I3N, 2829-516 Caparica, Portugal.
[5] Laboratório Nacional de Energia e Geologia I.P., Product Engineering Unit, Estrada de Paço de Lumiar-1649-038, Lisboa, Portugal.
[6] University of Aveiro, University Campus of Santiago, 3810-193 Aveiro, Portugal.

Study of double layer metal contacts on CdZnTe for radiation detectors.

Q. Zheng[1], *F. Dierre*[1], *R. Fernández-Ruiz*[2], *V. Corregidor, J. Crocco*[1], *H. Bensalah*[1], *E. Alves, E. Diéguez*[1]

Cd(Zn)Te is a II-VI semiconductor with a wide range of room temperature nuclear applications, used for medical, industrial and safety systems. To take in advantage the electronic properties of the Cd(Zn)Te, ohmic contacts are classically deposited to obtain detectors with low leakage current, extended electrical field profile and higher detector efficiency. Nanometric double layers of different metal-semiconductor-metal (MSM) depositions on CdZnTe substrates were deposited at Crystal Growth Laboratory (Madrid) by electroless method. At ITN, RBS was used to determine the thickness, depth profiles and the composition of the layers deposited at the surface. The results have contributed to a better knowledge of the mechanisms involved during the deposition, where the Cd ions are rejected into the solution and tellurium oxide is incorporated during the contacts growth. Among the different metals used (Pt, Ru, Rh, Au, Pd), Pt contacts have shown a linear ohmic behaviour and a good gamma response by ^{57}Co source. On the other hand, Ru and Rh contacts have a poor gamma response, indicating that the process have to be optimized.

[1] CGL, Physics Department, Autónoma University of Madrid, Spain.
[2] SiDI, Autónoma University of Madrid, Spain.

Study of alternative substrates for the deposition of Si nanowires

A.Kling, A. Rodríguez[1], T.Rodríguez[1]

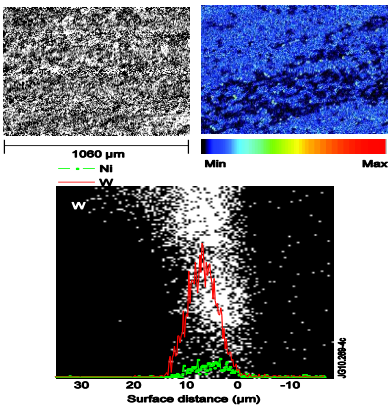
Although the first synthesis of Si nanowires dates back to 1957 interest in them revived recently due to their unique physical properties, e.g. light emission, field emission, and quantum confinement effects. Among the various known methods for the production of Si nanowires chemical vapor deposition using Au-coated Si substrates is one of the most frequently used where the gold acts as a catalyst. Despite its innumerous advantages gold is not compatible with present state CMOS technology production standards and therefore alternative catalyst materials are procured. Sn and Au-Ga alloy layers where deposited on Si wafers and their thickness and composition studied by RBS using 2 MeV He^+ ions for as-deposited and annealed samples. It was found that in the case of Sn even at room temperature oxidation occurs that affects also the underlying Si. On the other hand, Au-Ga alloys show only a minimal oxidation on the surface but react strongly with the silicon during annealing at 500ºC. He-RBS spectra could only be fit assuming a small but in the spectra virtually invisible carbon contamination of the Au-Ga alloy. Additional studies using the strong $^{12}C(p,p)^{12}C$ scattering resonance at about 1.75 MeV were performed to corroborate the presence of carbon and quantify it. The origin of this contamination is presently under investigation.

[1] Dpto. Tecnología Electrónica, E.T.S.I. de Telecomunicación, Universidad Politécnica de Madrid, 28040 Madrid, Spain.

Surface composition and morphology changes of materials for fusion reactors

L.C. Alves, E. Alves, N P Barradas, R. Mateus[1], P. Carvalho[1], J.P.Coad[2], A. M. Widdowson[2], J. Likonen[3], S. Koivuranta[3], V. Chakin[4], A. Moeslang[4], P. Kurinskiy[4], R. Rolli[4], H.-C. Schneider[4], JET-EFDA Contributors#

The use of ion beams for the study of materials for fusion reactors has been centered in the characterization of:
i) - Beryllium pebbles and V/Ti beryllides degree and extent of oxidized surface layer after air annealing at temperatures of 600 ºC, 800 ºC and 1100 ºC; ii) - Erosion and redeposition processes at the JET first-wall carbon tiles during plasma operations;
i) The beryllium pebbles annealed at 600 ºC and 800 ºC present an oxidized layer extending from 0.15 µm up to 0.25 µm. At 1100 ºC, some of the pebbles have a strong oxidation reaction leading to the alteration of surface morphology and even to the detachment of Be oxide. In what concerns beryllides, the formed oxide layer after air annealing at 800 ºC during 1 h, is larger in the case of the V beryllide (~0.7 µm) than for the Ti beryllide (~0.3 µm).
ii) Marker tiles containing a thin W layer were mounted in the JET vessel in order to study erosion-deposition processes in differente areas of the reaction chamber during JET plasma operations. Broad and microbeam ion techniques allowed determining surface and/or depth profile distribution of several elements such as W (the used marker) Ni, Cr, Fe (Inconel structural material) and Be (plasma impurity), contributing for predicting the lifetime of components for future devices such as ITER.
Still related with fusion materials, the study of surface alterations of beryllium pebbles and V/Ti beryllides under high–fluence neutron irradiation is beeing carried out.



[1] EURATOM/IST Portugal; [2] EURATOM/CCFE UK; [3] EURATOM/TEKES Finland, [4]KIT Germany.

Hydrogen retention in gallium samples exposed to ISTTOK plasmas

R.B. Gomes[1], R. Mateus[1], E. Alves, H. Fernandes[1], C. Silva[1], P. Duarte[1]

The use of liquid metals such as lithium and gallium have been pointed out as a suitable solution to solve problems related to the use of solid walls submitted to high power loads. A proper use of liquid materials in fusion reactors depends on their affinity to retain hydrogenic isotopes. While retention in lithium has been studied in detail, less is known for gallium. Taking into account the deep influence of this property on plasma behavior it is deemed relevant to perform such studies in tokamak plasmas. An experimental setup has been developed to produce high purity gallium samples which were exposed to ISTTOK plasmas on both liquid and solid phases. Hydrogen retention and in-depth profiles were simultaneously measured by ERDA and RBS analytical techniques. Experimental data proved that most of the retention takes place in a thin layer near the surface. Liquid samples present higher retention values which may be understood if higher hydrogen diffusivity is assumed. Retained fraction ($H_{retained}/H_{incident}$) around 0.3 and 1 % were obtained for solid and liquid samples, respectively.

[1] Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, 1049-001 Lisboa, Portugal.

Carbon deposition on beryllium substrates and subsequent delamination

R. Mateus[1], N. Franco, L.C. Alves, M. Fonseca[2], P.A. Carvalho[1,3], E. Alves

Beryllium and carbon are foreseen as materials for plasma facing components of future fusion devices. Erosion, re-deposition and annealing arising from heat-load events during reactor operation will produce mixed material layers and compounds on the plasma facing surfaces, leading to changes in local melting point, sputtering behaviour, hydrogenic species retention and dust formation due to delamination.
In order to mimic the erosion/deposition processes, carbon layers have been evaporated onto beryllium plates and annealed in the 373 to 1073 K range for 90 min. Ion beam measurements revealed a smooth beryllium and carbon interdiffusion at the samples surface up to 773 K. A carbide formation reaction front became apparent for higher temperatures in scanning electron microscopy observations, with the volume fraction of Be_2C crystals resulting also evident in X-ray diffraction patterns. The annealing treatments induced delamination of large surface areas through telephone cords blistering attributed to strain energy release. At 1073 K cracking occurred preferentially along blister boundaries. This fracture behaviour seems caused by the different thermal expansion coefficients of the phases. The results show that delamination of re-deposited layers in PFCs is a natural mechanism of dust formation.

[1] Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, 1049-001 Lisboa, Portugal.
[2] Centro de Física Nuclear, Universidade de Lisboa, 1649-003 Lisboa, Portugal.
[3] ICEMS, Departamento de Engenharia de Materiais, Instituto Superior Técnico, 1049-001 Lisboa, Portugal.

Ni-Ti alloy surface modified by plasma immersion ion implantation of nitrogen

R.M.S. Martins, N. Barradas, E. Alves, D. Henke [1], H. Reuther [1], J.C.S. Fernandes [2]

The wide spectrum of applications in implantology imposes special requirements on the biocompatibility of Ni-Ti. The use of coatings in order to modify the surface characteristics of a material is a widely used approach. However, in the case of medical devices whose shape or size is modified during the procedure of insertion or due to the working conditions, metallic or metal oxide coatings may crack. In the frame of project SPIRIT-77, plasma-immersion ion implantation (PIII) has been employed in order to overcome these limitations. This technique was used to modify and improve the superficial region of a superelastic (at body temperature) Ni-Ti alloy. The working plan comprised ion implantation of nitrogen. The experiments were performed in a HV chamber, with a base pressure of 3×10^{-4} Pa and a working pressure of 0.2 Pa, equipped with an RF plasma source operating at a power of 350 W. High voltage pulses of either 20 or 40 kV and length of 5 µs were applied to the samples using a frequency of 400 Hz. The sample holder was not intentional heated (T < 125°C). The depth profiles of the elemental distribution in the alloy surface region, obtained by Auger electron spectroscopy, clearly show a Ni-depleted fraction for experiments performed with 40 keV (Figure 1) due to the formation of titanium oxynitride (TiN_xO_y). Furthermore, the PIII technique leads to a graded interface between the modified surface and the bulk Ni-Ti alloy, which is a plus for improving adhesion.

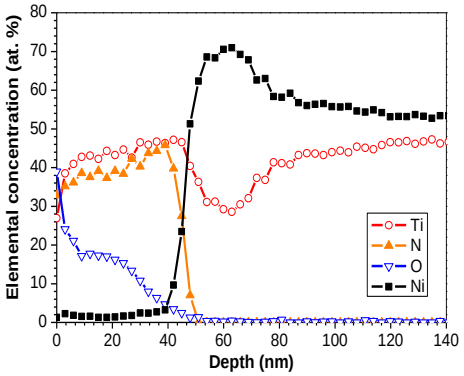


Figure 1: Results obtained for a Ni-Ti sample implanted with nitrogen (40 keV; 1 hour).

[1] Institute of Ion Beam Physics & Materials Research, Forschungszentrum Dresden-Rossendorf, P.O.Box 510119, 01314 Dresden, Germany.
[2] ICEMS/DEQB, Instituto Superior Técnico, TULisbon, 1049-001 Lisboa, Portugal.

Corrosion in XV and XVI century stained glasses

M. Vilarigues[1,2], A. Ruivo[2,3], P. Redol[1,4], A. Machado[1], P.A. Rodrigues[1], V. Corregidor, L.C. Alves, R.C. da Silva

The study of corrosion in two stained glass panels from the south aisle of St[a]. Maria da Vitória Monastery, at Batalha (Portugal), was also carried out. These panels exhibit extensive corrosion with darkening phenomena. By using external µPIXE and µPIGE, the elemental compositions of large fragments were obtained, enabling the selection of representative corroded areas, from which elemental distribution maps were produced. Calcium and potassium rich structures were found – at the surface and inside cavities in the glass – that were identified as oxalates and carbonates, by Raman microscopy and µFTIR. The dark spots in the glass surfaces were found to be Zn and Pb rich. These findings indicate that the corrosion observed was due not only to reactions with atmospheric water and CO_2 but also with the oxalic acid secreted by micro-organisms. Furthermore, it did not result from reactions with atmospheric SO_2 or acid rain.

[1] DCR/FCT-UNL; [2] VICARTE/FCT-UNL; [3] REQUINTE/FCT-UNL; [4] Mosteiro da Batalha.

Medieval Yellow silver staining – Convento de Cristo, Tomar

M. Vilarigues[1,2], J. Delgado[1], A. Ruivo[2,3], H. Marçal[1], V. Corregidor, L.C. Alves, R.C. da Silva

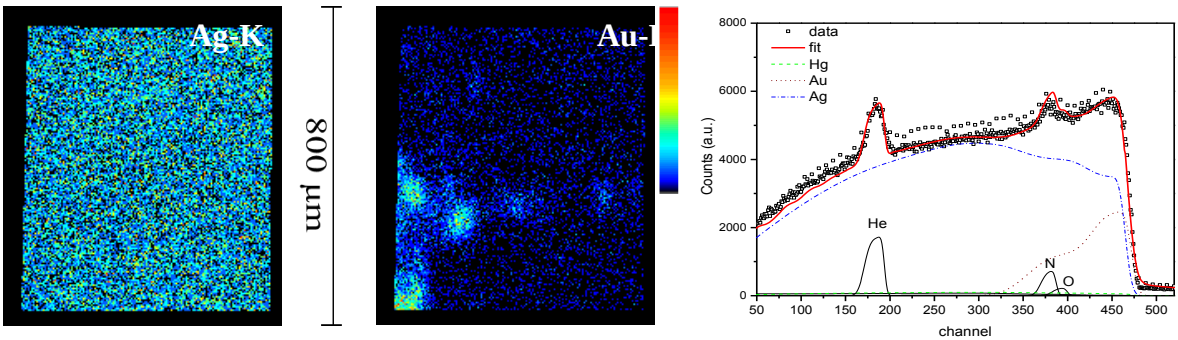
The technique of yellow silver staining consists on applying a diluted Ag salt at the glass surface which is then fired at temperatures between 500 ºC and 650 ºC. However, the yellow silver stained glass fragments recently discovered in Convento de Cristo, contain an Ag-Cu mixture. In order to understand the role of Cu and the influence of the firing temperature and glass type on the resulting colours, several soda and potash glasses were produced, stained with Ag or with a Ag-Cu mixtures and characterised using µXRF, µPIXE and optical spectroscopy in the UV-Vis range. Three of the fragments display a single absorption band in their UV-Vis spectra, each centred at 418 nm wavelength which is consistent with the formation of a colloidal dispersion of spherical Ag nanoparticles with dimensions of ~10 nm. The fragments with more vivid colours, on the other hand, present a two band absorption spectra, that may indicate the formation of either non-spherical nanometer-sized particles, or a bimodal distribution of particles sizes. Although the finest yellow colours were observed in the soda laboratory glasses, either stained with Ag or with a Ag-Cu mixture, the ones with Ag-Cu staining were obtained at lower firing temperatures. The role played by Cu in this process could not be attributed to the formation of Cu nanoparticles, since the surface plasmon resonance at ~565 nm could not be found in the UV-Vis spectra. For all the laboratory samples stained with a Ag-Cu compound mixture or in the historical fragments, the corresponding concentration depth profiles obtained by µPIXE show that Ag penetrates into the glass during the annealing, leaving Cu behind and closer to the surface. It can also be noticed that the Ag diffusion extent on these laboratory glasses is significantly smaller than the one observed when only the Ag solution is used. The obtained experimental results can be understood consistently, if the transit time, i.e. the time available for atom-metal cluster interaction by diffusion, is the key parameter for the growth of the Ag nanoparticles and their final dimensions at a given firing temperature. Cu seems to play an important role in the increment of the transit time.

[1] DCR/FCT-UNL; [2] VICARTE/FCT-UNL; [3] REQUINTE/FCT-UNL.

Characterization of Mercury Gilding Art Objects by External Proton Beam

V. Corregidor, L.C. Alves, N.P. Barradas, M.A. Reis, M.T. Marques[1,2], J.A. Ribeiro[1,2]

The fire gilding is one of the methods used by the ancient goldsmiths to obtain a rich, metallic glow and durable golden appearance in ornamental objects. This layer is characterized, among others, by its thickness (several microns) a diffusion profile and a Hg content (between 0–21 wt%) depending on the temperatures achieved during the process. Gilded sacred art objects dated from the XVI to the XVIII centuries, belonging to the Casa-Museu Dr. Anastácio Gonçalves Collection (Lisbon) were analysed using the external ion microprobe at Nuclear and Technological Institute, Lisbon. The average concentrations of homogeneous areas were calculated with GUPIX, DATTPIXE and NDF codes showing very similar results. Efforts related with finer detector efficiency calibration, stability of the He flow control and data base consistency issues should be done to overcome the registered differences. Generally speaking, and comparing the composition extracted for several points on two of the pieces which are totally gilded, the ostensorium, from the mid-XVIII century, has an average Hg content (12 %) which is larger than the one observed for the reliquary, from the XVI century, (10 %). About two centuries separate the goldsmiths responsible for these objects and probably different production locations and sources of the materials explain the differences between them. In some particular cases the simultaneous fitting of the RBS and the PIXE experimental data reveals that the inhomogeneous composition observed in the PIXE maps are mainly due to superficial inclusions which are Au rich with a diffusion profile into the silver object. (Figure 1)

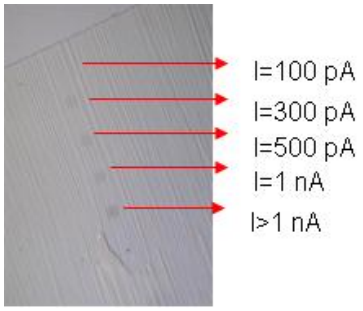


[1] Casa-Museu Anastácio Gonçalves, Av. 5 de Outubro, 6-8 1050-055 Lisboa, Portugal.
[2] IMC, Palácio Nacional da Ajuda, 1349 – 021 Lisboa, Portugal.

Induced defects by an external proton beam on pigments used on easel paintings

V. Corregidor, L.C. Alves, N.P. Barradas, M.A. Reis

IBA techniques using an external proton beam can be applied to Cultural Heritage objects, giving information about the elemental composition of a punctual or a determined area. One of the applications is the easel paintings, to determine the composition of the pigments used by the painters. In some cases, this information can help to assign the painter, date the paint or discover later conservation process. Although the techniques are considered as non-destructives, in some cases some defects can be created if carbonate minerals are involved, with the appearance of dark brownish regions that eventually disappear along the time. To avoid the presence of this induced defects, the experimental conditions (beam current, time of measurement, etc.) should be optimized. In this work white colours from Michael Harding chart colour were analysed as a function of beam current, varying from 0.1 nA to 1.5 nA. On the "Titanium White N.2", made of zinc oxide and titanium oxide, weak visible marks were observed after the measurements when higher currents were used but they disappear after few hours. On the other hand, the "Cremnitz White", made of lead carbonate, visible marks were detected even using low current values (figure 1). The marks fade out along the weeks, and after five months the marks made using the higher current values are still visible. Efforts should be done to reduce the marks, not only optimizing the experimental conditions but also the post-treatments to accelerate the fade out process. These treatments have to guarantee the integrity of the art objects, so no heat treatments or aggressive one should be considered.



Micheal Harding - Oil Colours Cremnitz White

Synchrotron-radiation based micro-computed tomography applied to the characterization of dinosaur eggshells

Rui M.S. Martins [1], Octávio Mateus [1,2], Felix Beckmann [3], Philipp Klaus Pranzas [3]

The study of fossilized eggshells is a very important topic for the Museum of Lourinhã. Although the eggshell fragments are subject to diagenetic processes unique features can be preserved. The histostructure of the eggshell provides information with biological and paleoenvironmental implications. For example, the eggshell pore pattern is associated with gas exchange ratios between nest environment and embryo. Therefore, the study of the porosity of the shell can provide valuable information about the level of humidity of the area where the egg was laid. The synchrotron radiation based micro-computed tomography (SRμCT) studies have been performed at the beamline HARWI II at the storage ring DORIS III located at DESY in Hamburg, Germany. The eggshell fragments have been collected in three different sites of the Lourinhã formation, namely: Peralta, Paimogo and Porto de Barcas (Figure 1a). The first data recorded for eggshells is shown in the figure below. The effective pixel size corresponds to 6.4 μm, which allows a direct, non-destructive visualization of the morphology of the pores and their connectivity in the eggshell fragments, providing information that is either exceedingly difficult or impossible to obtain by traditional methods based on section cutting.

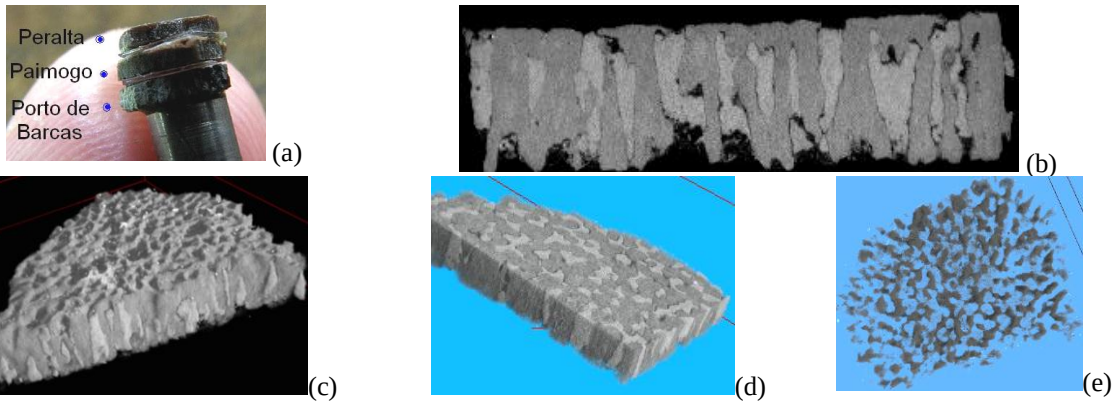


Fig. Eggshell fragments collected in three different localities of the Lourinhã Formation (Peralta, Paimogo and Porto de Barcas): (a) photograph of the eggshell pieces mounted on the sample holder used for SRμCT; (b) a microtomographic slice through the eggshell type of the locality of Porto de Barcas; (c) a three-dimensional image of the complete sample of the locality of Porto de Barcas; (d) sectioning of the three-dimensional image of the sample of figure 1c providing information about pore connectivity in the eggshells; (e) pore canals run through the shell which permit gas exchange between the embryo and atmosphere.

[1] Museu da Lourinhã, Rua João Luis de Moura, 2530-157 Lourinhã, Portugal.
[2] CICEGe, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.
[3] Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck-Str. 1, 21502 Geesthacht, Germany.

Study of dinosaur eggshells from the Lourinhã Formation by x-ray diffraction

Rui M. S. Martins [1], Norbert Schell [2]

X-ray powder diffraction has proven itself to be a valuable tool in geochemistry and mineralogy. However, although this technique can be useful to determine if eggshells had undergone diagenetic alteration, a detailed study of their structure from the external surface to the internal surface is required in order to "map" mineralogical alterations. The eggshell fragments selected for the experiments at the High Energy Materials Science beamline HEMS side station at PETRA III have been collected in two different sites of the Lourinhã Formation, namely: Paimogo and Peralta. The eggshell type detected in Paimogo, of thickness of about 0.92 mm, is ascribed to the theropod *Lourinhanosaurus antunesi*. The external morphology and the size of the eggshells of Paimogo and Peralta sites are comparable. They can be from the same species or a closely related taxon. However, more details are required to draw final conclusions. X-ray diffraction data was acquired in transmission mode (image plate MAR345) using a beam spot of 0.1 mm in vertical with 87 keV energy. The measurement carried out at the topmost zone of the eggshell shows that although the main mineral content of the samples was found to be calcite there is also quartz in the sample from Paimogo. The presence of very weak diffraction peaks associated with quartz is still noticeable in the data obtained at the central zone of the eggshell fragment collected at Paimogo site. On the other hand, the intensities of the diffraction peaks related to calcite are quite similar for both samples. It is suggested that in either case, the original shell material was composed of calcite. The internal surface of the shell from Peralta shows as well the presence of quartz and apparently a higher content of this phase is available in this sample zone when compared to the sample from Paimogo. Furthermore, the presence of fluorapatite was identified. This study provides information that helps us to create models about the diagenetic processes. It will be more accurate the comparison between eggshell fragments collected at different sites which is done aiming the identification of species.

[1] Museu da Lourinhã, Rua João Luis de Moura, 2530-157 Lourinhã, Portugal.
[2] Helmholtz-Zentrum Geesthacht, Max-Planck-Str. 1, 21502 Geesthacht, Germany.

Stopping power of ^{11}B in Si and TiO_2 measured with a bulk sample method and Bayesian inference data analysis

Z. Siketić[1], I. Bogdanović Radović[1], E. Alves and N.P. Barradas

The popular stopping power interpolative schemes require experimental data to be developed. Where the data bases are sparse, with few experiments available, interpolations can be more inaccurate. This is the case for the stopping of heavy ions, where even for important targets such as Si there is a need for more measurements. For compounds, the situation is even worse with very few measurements available. In particular, the stopping in oxides and nitrides often deviates significantly from what would be expected using the Bragg's rule. We apply a method that uses bulk or thick film samples to determine the stopping power of ^{11}B in Si and TiO_2. The method, which relies on Bayesian inference analysis of RBS spectra obtained at different energies, has been previously validated by verifying the results obtained in the well-known system ^{4}He in Si.

[1] Ruđer Bošković Institute, P.O. Box 180, Zagreb 10002, Croatia.

Data analysis software and Pitfalls in Ion Beam Analysis

N. P. Barradas, *C. Jeynes[1]*, E. Rauhala[2]

The 2nd Edition of the Handbook of Modern Ion Beam Analysis (IBA) was published in 2010, and included a chapter dedicated to data analysis software for ion beam analysis and another one about the pitfalls of IBA. The data analysis software in ion beam methods are computer programs designed to extract information about the sample from the measured ion beam spectra. The desired information includes identification of sample elements, their concentrations, areal densities and thicknesses of layers. At best, one spectrum can be converted to concentration depth distributions of all elements in the sample. Often, however, such a full description of the sample based on a single experiment is not possible. The analyst can then perform additional experiments with different experimental parameters such as ion energies, different measurement geometry, use another ion beam technique, or include information from other complementary techniques. The chapter deals mainly with the data analysis software of particle-particle ion beam analysis techniques, RBS, ERDA and NRA. Short sections on PIXE and other techniques such as NRP and channelling were also included. The chapter on pitfalls showed how to avoid many problems when determining elemental depth profiles accurately with light-ion Rutherford backscattering spectrometry (RBS) using MeV ion beams. IBA can, of course, use various other beams and related techniques and use these for a variety of other purposes, including profiling of crystalline defects. The discussion presented therefore also covered pitfalls in a number of other important examples

[1] University of Surrey Ion Beam Centre, Guildford, England.
[2] Accelerator Laboratory, University of Helsinki, Finland.

Development and deployment of a micro-tomography system at the ITN nuclear microprobe

A.C. Marques, R.C. da Silva, L.C. Alves

Ion beam tomography offers an essentially non-destructive way of obtaining 3D information at a microscopic level. A new project aiming at developing and deploying a micro-tomography system at the ITN nuclear microprobe started this year. First sets of Scanning Transmission Ion Microscopy (STIM) 2D maps obtained by irradiation under different angles and also of Particle Induced X-ray Emission (PIXE) 2D maps obtained by irradiating at closely spaced energies (and constant angle) successfully served three main purposes: *i*) demonstrating the feasibility of tomographic experiments with the existing equipment, as is, or with only minor changes; *ii*) identifying and solving experimental difficulties, *e.g.* rotational misalignment artefacts, implying new mechanical setup and/or *a posteriori* correction strategies; *iii*) testing and selecting methodologies and programs for manipulation and conversion of 2-D projection maps to tomograms and 3-D image rendering, as well as devising technique-specific issues for reconstruction algorithms to operate on the measured projection data. One difficulty of paramount importance is the lack of accurate rotational positioning of the existing goniometer. This is being solved by design and installation of a more precise and mechanically stable rotation system and a new sample holder fitting to the rotation rod. Sets of synthetic projection maps were generated and successfully used to test and adapt freeware reconstruction software [Tomography, Florida State Univ.]. Using this software, the projection data obtained by STIM was successfully reconstructed with a filtered back projection algorithm (BFP): a test STIM tomography experiment was performed on a butterfly wing by irradiating it with 2 MeV protons at equally spaced tilts, between –60° and +60°, yielding a set of 17 projection maps, 256×256 pixels across (corresponding to a scanned area of 1320×1320 μm^2). A Hamamatsu S1223-01 PIN diode detector was used for data collection, in an off-axis geometry arrangement. The collection times were around 5 minutes per STIM map. The 3-D reconstruction of the scanned wing volume, obtained by means of the BFP algorithm is shown in Fig.1, along with one 2-D projection map as obtained in the STIM experiment. Although only a first test, the reconstruction already reveals structural details *e.g.* sets of approximately equidistant longitudinal ribs. A test PIXE tomography experiment was also performed on a geological sample of a pyrite. The collection times were around 5 minutes per PIXE map. The reconstruction achieved using the same software was based in a set of 9+8 256×256 pixels Ni-distribution maps (1060×1060 μm^2) and is shown in Fig.2: the Ni inclusion 3-D pattern becomes clearly visible.

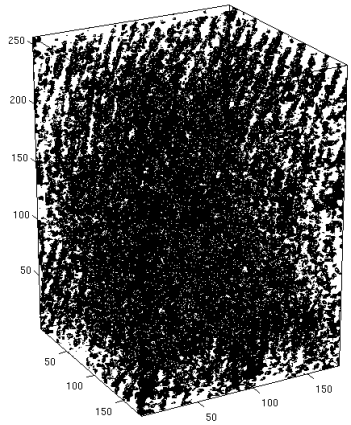
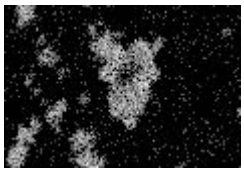


Fig.1: STIM-T reconstruction of a volume section of a butterfly wing: longitudinal ribs are perceived between outer and inner wing foils.



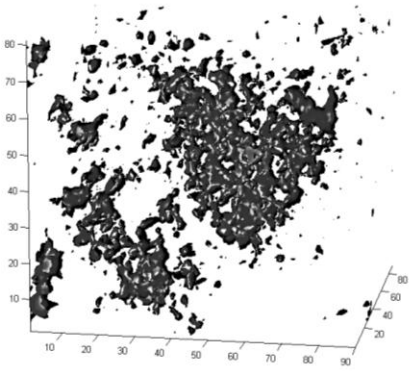


Fig.2: one of the Ni 2-D maps obtained by PIXE, and the resulting reconstruction showing the Ni inclusion 3-D pattern.

Finally to run the reconstruction algorithm in a more user friendly way, a simple and practical single window interface was developed, that considerably simplifies the data visualization after each reconstruction step.

As reconstruction quality and therefore the ability to distinguish such small structures are affected by the number of projection maps available, and this number also depends on time, use of interpolation between projection maps (acquired at consecutive angular positions) was attempted as a time saving tool. This expedient solution allowed some improvement of reconstruction based on fewer (approximately half) projection maps.

Biomedical Studies

Teresa Pinheiro

The aims of the Biomedical Studies group are the study of putative biomarkers in order to characterize exposure, diseases and therapy efficacy and to identify potential targets for novel therapies.

Efforts were developed in the translation of basic biomedical research into novel diagnostics and therapies for the benefit of human populations exposed to metals, and of patients with chronic diseases.

Undertaken research is an end product of intense and interactive collaborative work among researchers in Cardiology, Pneumology, Dermatology, Biology, Biochemistry, Chemistry and Environmental Sciences.

Current projects join different groups from three ITN Units, Reactor, UCQR and UFA, which are working in consortium with other research institutes, academia and hospitals.

Major research areas focused:

1) Environmental health research establishing new biomarkers of exposure;

2) Clinical outcomes research establishing disease progression and clinical response to therapy;

Recently an interdisciplinary project has been initiated in collaboration with the Universidad Autónoma, Madrid and University of Singapore that will explore safety issues related to nanoparticles. Stem cells will be used as a model, and different techniques will be applied to locate nanoparticles in cells and evaluate the biological response.

Other issues such as bio-availability of metals in aquatic environment are recently being explored under collaboration with the Instituto Nacional de Recursos Biológicos, illustrating the continuous potential of microbeam techniques in life science research.

A variety of scientific and technical skills developed in Biomedical Studies group of ITN, involving proton microscopy, inductively coupled plasma mass spectrometry (ICP-MS), flow cytometry and other cell function evaluation techniques, helped consolidating the scientific niche and launching new areas of research.

Continued funding in the areas of environmental and biomedical sciences during the last years had strengthened existing skills and promoted advanced training of Ph.D. and M.Sc. students.

The main achievements of 2010 are summarised in the following pages.

Research Team
Researchers

T. PINHEIRO, Aux., Group Leader
L.C. ALVES, Aux. (25%)
R. VELOSO, Post-Doctoral, FCT grant

Students

P. NAPOLEÃO, Ph.D., BI grant
B. BATISTA, M.Sc., QREN grant
C. FRANCO, M.Sc., BI grant
C. RAMOS, M.Sc., BI grant
P. FÉLIX, M.Sc. BI, ITN
S. ANDRADE, M.Sc. Student, FC-UL
S. VELOSO, M.Sc. Student, FC-UL

Technical Personnel

R. PINHEIRO

Collaborators

A.B. ALMEIDA, Full Prof., FM-UL/Hospital Sta. Maria
A. BARREIROS, Aux. Resarcher, LNEG
A.M. VIEGAS-CRESPO, Princ. Researcher, FC-UL
F. ARAÚJO, Princ. Researcher, UCQR, ITN
M.C. MONTEIRO, Ass. Prof., CESPU, Porto
M. MOTA CARMO, Ass. Prof., FCM-UNL
M. SELAS, Nurse, CHLC/EPE, Hospital Sta. Marta
P. FILIPE, Aux. Prof., FM-UL/Hospital Sta. Maria
R. CRUZ FERREIRA, M.D., CHLC/EPE, Hospital Sta. Marta
M.D. YNSA, Researcher, CMAM, Univ. Autónoma Madrid, Spain

Exhaled Breath Condensate – a new biomarker of exposure to metals

P. Félix, C. Franco, L.C. Alves, T. Pinheiro, S.M. Almeida, M.C. Freitas, F. Araújo, M. Santos, A. Barreiros[1], A. Bugalho de Almeida[2], S. Garcia[3],

Objectives: The aim of the project is to investigate whether Exhaled breath Condensate (EBC) can be employed for a better risk assessment of human exposure to metals.
The project is a joint initiative of ITN units *Reactor and Nuclear Safety* and *Physics and Accelerators*. The project was carried also in tight collaboration with the *Environmental and Analytical Chemistry Group* of the UCQR/ITN.

Methods: Approximately 100 workers have been enrolled in the study, working at two Pb processing industries located in the Lisbon geographical area. A group of non-exposed voluntaries working in offices was also constituted for baseline interpretation of EBC data. The EBC was collected under tidal breathing conditions using commercial equipment (EcoScreen, Jaeger, Germany) and the elemental concentrations measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) installed at UCQR/ITN.
The particulate matter (PM) in the work place and in offices was evaluated by INAA (URSN/ITN and TUDelft, NL) and PIXE (UFA/ITN). PM was collected in stacked filter units that allowed PM fractioning: 2.5-10 µm in the first stage (PM_{10}) and < 2.5 µm ($PM_{2.5}$) in the second stage.

Results: Implementing standard procedures of EBC collection and analysis for metal exposure assessments was one of the milestones of this project. This objective involved EBC matrix characterization, traceability of the analytical method and EBC collection time optimization. EBC contained a miscellaneous of particles in a variety of dimensions, as can be depicted in Fig 1.

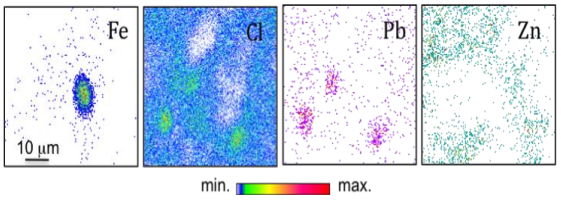


Fig. 1 – Images of the dry deposit of exhaled breath condensate of workers obtained by Proton Microscopy installed at UFA. Particles of varied composition can be identified.

These features influence metal content determination. The study of analytical reliability of EBC showed that acidification was required to obtain sample homogenization. The quantitative results obtained with ICP-MS were validated by comparison to those obtained with Total Reflection X-ray Fluorescence (TXRF).
The EBC collection methodology was examined by studying the variations in EBC metal contents along the working week. In Fig. 2, the Pb levels in EBC are shown. Levels were relatively steady during the working period in Industry 1 and significantly higher than in Industry 2. In the later Pb levels increase in the end of the working week. The EBC of workers showed concentrations well above non-exposed individuals (controls).

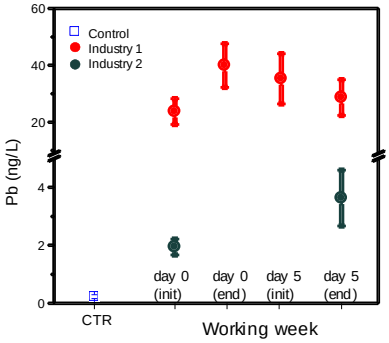


Fig. 2 – Pb concentration in EBC of controls and workers along the working week.

The levels of Pb in airborne particulate matter (PM) in the workplace and in offices compare to Pb contents measured in EBC (Fig. 3).

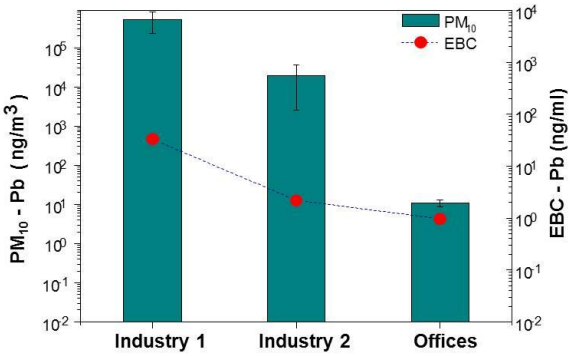


Fig. 3 - Concentration of Pb in PM_{10} collected at each studied site followed Pb concentration in EBC.

Conclusions: 1) It was confirmed that EBC analysis was valid and within limits of confidence <5 % for Cr, Mn, Sb and Pb. **2)** The most representative collection times were at the beginning and at the end of the week-working period. **3)** The elemental concentrations in EBC can be associated to exposure.

Publications

S.M. Almeida, T. Pinheiro, P.M. Felix, C. Franco, M.C. Freitas, L. Alves, A. Barreiros, S.M. Garcia, Int. J. Environ and Health, 4 (2010) 293-304
S.M. Almeida SM, P.M. Felix, C. Franco, et al., Nucl. Instrum Methods A 622 (2010) 453-455
T. Pinheiro, M.A. Barreiros, L.C. Alves et al., Nucl Instrum and Methods B (in press).

[1] LNEG, Lisboa
[2] Hospital de Sta Maria, Serv. Pneumologia/FM-UL
[3] Instituto de Soldadura e Qualidade

New biomarkers for Coronary Artery Disease

P. Napoleão, C. Ramos*, R. Cruz Ferreira [1], M. Mota Carmo[2], M. Selas [1], M.C. Monteiro[3], M.B. Criado[2], A.M. Viegas-Crespo [4], F. Caeiro [4], A. Turkman[5], V. Andreozzi [5], A.S. Andrade*[4], S. Veloso*[4], T. Pinheiro**

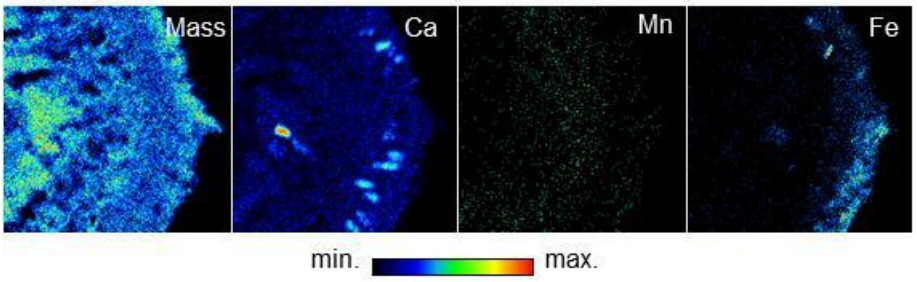
The main goals are the identification and characterization of the vulnerable plaque in hopes of identifying morphologic and physiological features that predict plaque rupture in coronary syndromes. The study is longitudinal, assessing patients to 180 days after intervention. Several molecules, inflammatory cells, and endothelial progenitor cells (EPCs) are been studied. These cells and molecules may have relevant roles in endothelial dysfunction and in the processes involved in plaque rupture as confirmed by the angiographic detection of luminal obstructions and virtual histology intravascular ultrasound (VH-IVUS)-derived measurements of the atherosclerotic plaque. Results obtained so far suggest that variations of several markers (e.g., vascular endothelial growth factor, oxidized lipoproteins, lymphocytes and EPCs) may express the evolution of disease. During 2010 two M.Sc. thesis were carried out under the current projects.

Project funding: FCT/PIC/IC/82734/2007; LAHSM/2010 - Liga de Amigos do Hospital de Sta. Marta.

Metal bio-availability in water-sediment interfaces – a micro-distribution evaluation.

R. Veloso[6], C. Vale[6], T. Pinheiro**

The main objectives are to understand the micro-distribution of trace elements across the interfaces between salt marsh sediments and inhabitant organisms and between sediment and water in natural environment. The micro-distribution of trace elements in sediment profiles were carried out by Proton Microscopy to assess the concentration gradients and infer metal fluxes, specially Mn and Fe, from sediment to the overlying water. Also the elemental profiles between sediments and benthic organisms are being investigated to elucidate whether metals are sorbed on the cellular or tissue wall or uptake by the organism. In the figure below the distribution of Ca, Mn and Fe can be seen in a transversal section of a root. The most external region of the section corresponding to the sediment-water interface is marked by a sharp decrease of Mn and increase of Fe.

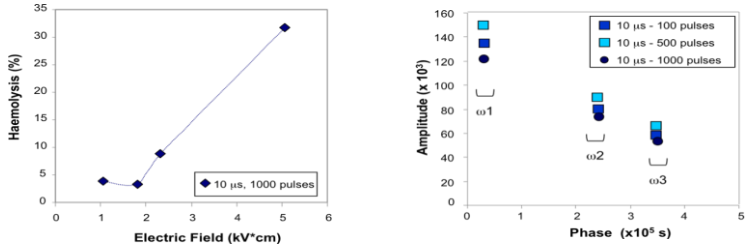


Funding: SFRH/BPD/47473/2008

Effect of Electric Pulsed Field in Human Blood Cells

B. Baptista, V. Dores*, T. Pinheiro*, H. Canacsinh[7], L. Redondo[7]*

The effect of ultra-short pulses (few μs) of high intensity in the permeability of living cell membrane was studied. Human erythrocytes were used to study the electrical model of the cell and calculate the resistivity of the cell membrane. Haemolysis was measured after pulse application. A theoretical mathematical model was developed based on Fast Fourier Transform to extract the amplitude and frequency components of current signals. The graph in the left shows the increase of haemolysis with electric field; the right graph shows the frequency components (ω), which differ according to exposure conditions, illustrating the adequacy of the theoretical model to the cell study. (Collaborative work under the contract QREN -1600-A2P2).



[1] Serv. Cardiologia, Hospital Sta. Marta; [2] Faculdade de Ciências Médicas, UNL; [3] CESPU, Porto; [4] CESAM, FC-UL; [5] CEA, FC-UL; [6] INRB-IPIMAR; [7] ISEL; * ITN – UFA

Elemental Characterization and Speciation
CEEFI

Miguel A. Reis

The Elemental Characterization and Speciation work line of ITN Ion Beam Laboratory (CEEFI/LFI), carries out R&D work on ion beam based nuclear analytical techniques aiming at elemental composition characterization and instrumental speciation methods. Focusing being on applications to small mass samples (self-supported thin films, micro and nanoparticles) and/or small mass structures (deposited and deep laying thin films, embedded micro and nanostructures).
The main issue being originally, particle induced x-ray emission (PIXE) applied to the characterization of airborne material and its impacts, lead to the installation of an aerosol characterization set-up, which includes a DOAS system (operational since June 2007), a meteorological station (operational since January 2008), on-line in the Portuguese Meteorological Institute Urban Stations Network, and a PM10 and PM2.5 sampling station.

The installation, in 2008, of the High Resolution High Energy PIXE (HRHE-PIXE) set-up at ITN, the world first cryogenic microcalorimeter high resolution EDS X-ray detector based PIXE system, lead to very important results showing the advantages of these detectors use for both fundamental research as well as applications.

As a consequence of this a revision of the objectives of the CEEFI main work line was carried out, and the emphasis was shifted towards fundamental, technical and software development for PIXE, as well as frontier applications of the technique.

Within the organics of the Ion Beam Laboratory (LFI), CEEFI is the responsible for the maintenance and improvement of PIXE facilities.

In respect to 2010 developments, it was possible to show that the details put in evidence in the PIXE spectra by using the microcalorimeter detector do contain information related to the electronic environment of the x-ray emitting ion, which results were presented and discussed at the International Conference on PIXE and its Analytical Applications held in Guildford U.K.

Regarding frontier applications, nanoparticles, thin films, and chemical or electronics environment mapping are presently the main scope of CEEFI work line.

Within this context, during 2010, important results on thin film analysis, spot scans of a polished agate stone and analysis of Gd nanoparticles were published and accepted for publication.

In respect to airborne particulate matter, an one month training program for an IAEA fellow was carried out, and PIXE services were provided to the scientific community

Research Team

Researchers

M.A. REIS, Aux., Group Leader
R.B. Yadav, Post-Doc. Fellow under the EU SPIRITproject.

Students

P.C. CHAVES, Ph.D. student, FCT grant
A. TABORDA, Ph.D. Student, FCT grant

Technical Personnel

R. PINHEIRO

Collaborators

N.P. BARRADAS, ITN
A. CARVALHO, CFMC-UL
L. CARVALHO, Ass. Prof., CFA-UL, FC-UL
A. FERRAZ, Aux. Prof., CFMC-UL, IST

Fundamental Developments and Solid State Effects in PIXE

M.A. Reis, P.C. Chaves, A. Taborda, N. Barradas, A. Carvalho[1], L. Carvalho[2], A. Ferraz[3]

Objectives

Elemental and speciation characterization methodologies for small mass samples, like airborne particles are nowadays a more and more important issue, needed for both a better monitoring of airborne particulate matter and its impacts, including nano particulate matter hazards, as well as for technical and industrial developments niches associated to particulate matter engineering. During 2010 most of the line activities were focused on the single subject of "Fundamentals Developments and Solid State Effects in PIXE", mainly as consequence of two ongoing PhD thesis on the subject, but also due to the overlap between this subject and that of Key task 15 of the 7th FP project "Support of Public and Industrial Research Using Ion Beam Technology (SPIRIT)", Grant agreement No 227012-CP-CSA-Intra (starting date of 2009/03/01), in which the team is involved.

Results

In respect to results during 2010, and as a consequence of a significant amount of effort put in the exploitation of the spectra from the energy dispersive high resolution microcalorimeter x-ray detector POLARIS, installed in 2008, a few major outcomes were reached, two of which (presently in press) are illustrated in fig. 1.

Two supporting by products necessary to achieve these results were also established during 2010, namely: (1) the robustness of the Python code P2HA.py, specially developed by the team for the conversion of POLARIS detector pulses data onto histogram spectral data, and (2) a set of important developments carried out in the PIXE spectra fitting Fortran 2003 code DT2fit.for, presently under development by the team.

The major final outcomes reached in 2010 all share, a common base result that was only possible due to the high resolution, large energy window, low background and purity characteristics of the spectra from the POLARIS microcalorimeter.

Making use of this properties it was possible within the ongoing PhD thesis of P.C. Chaves, to infer the importance of X-rays low energy satellites upon the experimentally measured values of main lines intensity when determine using standard Si(Li) detectors.

In parallel to this, the studies of silicon oxide material (of a polished agate sample) and those of the corresponding reference, a pure Si single crystal slab, showed an highly probable presence of plasmon satellites accompanying both the main line as well as Radiative Auger Emission (RAE) satellites (the KL23L1 RAE line is shown in grey in fig.1 (left)).

These results also lead to a better interpretation of data determined on the analysis of Gd2O3 nanoparticles, which when irradiated by 750 keV show a spectrum too much different from that of a Gd2O3 powder pellet irradiated in the same conditions (fig.1 (right)). These differences are interpreted as due to differences in the plasmon and RAE satellites structure.

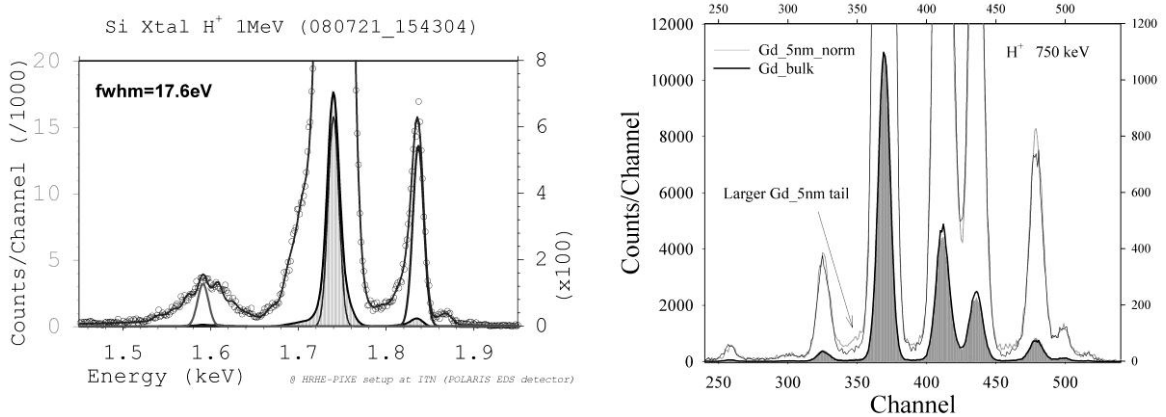


Fig.1 (Left) High Resolution PIXE spectrum of a pure Si single crystal sample irradiated with a 1.0 MeV proton beam provided by the ITN 3.0 MV Tandetron and collected using the POLARIS microcalorimeter X-ray detector. Open dots being a vertical zoom of the full spectra shown in grey, allow the clear identification of Radiative Auger Emission (RAE) KL23L1 satellite as well as plasmon satellites of both the main KL23 (Lα1) and of the RAE transition (in: M.A. Reis et al. *X-ray Spectrometry* (2011), in press). (Right) Gadolinium Lα low energy tail structure, being higher for a spectrum of Gd2O3 5nm particles than for a pellet of pressed Gd2O3, irradiated in the same experimental conditions, clearly reflects a solid state effects signatures originated in satellite contributions such as those shown in the Si spectrum in the left. (in: A. Taborda et al., Physics Research International, (2011) in press).

[1] Centro de Física da Matéria Condensada da Univ. de Lisboa, Fac. Ciências da Univ. de Lisboa, Portugal.
[2] Centro de Física Atómica da Univ. de Lisboa, Fac. Ciências da Univ. de Lisboa, Portugal.
[3] Inst. Superior Técnico, Univ. Técnica de Lisboa, Portugal

Radiative Auger Satellites Influence Upon Relative Line Ratios in PIXE
P.C. Chaves, M.A. Reis, A. Taborda, N. Barradas, M. Kavcic

The study of relative line intensities for transitions to the same sub-shell,was initiated in 2003 after a strange results was found, which pointed to a significant and unexplainable result showing that when measured using Si(Li) detectors these ratios were apparently changing with the change of the energy of the irradiation beam. A result not compatible to the established knowledge in the field. Results were then presented to the international community in 2004 and a PhD program, which included studies within this context was initiated in 2005. In 2010, after 5 years of data gathering, discussions within the international community about possible origins for the observations, the use of the very high resolution wave length dispersion systems from the Institute Josef Stefan, the development of specific fitting software and finally the analysis of high resolution spectra from the POLARIS detector, a very important conclusion was reached. Radiative Auger Emission satellites, first proposed by Bloch on 1935 to be associated to magnetic quadrupolar transitions, and first observed by Aberg and Utriamen in 1969 associated to electric dipolar transitions, were recognised as a major contribution for low energy tails of main lines. Since the detector response functions are fixed structures, variations in main lines yield will affect the intensity measured for close by transitions due to the lack of accountability of associated RAE transitions, when Si(Li) detectors are used.

[1] Institute Josef Stefan, Ljubljana, Slovenia .

Eu L3 sub-shell alignment by proton impact and Lα2/Lα1 relative yield ion energy dependence
M.A. Reis, R. Yadav, E. Alves, S. Fazinic[1]

Polish pure graphite targets were implanted with ~5 x 10^{16} at/cm^2 of ^{152}Eu isotopes accelerated to 150 keV on the ITN Danphysic Ion Beam Implanter. A thin Eu target was then irradiated by proton beams of 1.25, 1.5, 1.75 and 2.0 MeV at the Ruder Boskovic Institute (RBI) in Zagreb, Crotia, in order that high resolution PIXE spectra could be obtained using the RBI wave length dispersive (WDS) detector, under the scope of the Joint Research Activities of the Key Task 15 of the project "Support of Public and Industrial Research Using Ion Beam Technology (SPIRIT)", Grant agreement No 227012-CP-CSA-Intra (starting date 2009/03/01). Spectra covering two different energy regions were obtained at different irradiation times, and simultaneous Si(Li) spectra were used to normalize WDS spectra relative to different collection times. The experiment complexity makes that so far only the Lα2/Lα1 spectra and ratio could be dealt with. Still the comparison of experimental line ratios and theoretical line ratios determined after correction to L3 sub-shell alignment, show that even in the case of the Lα2/Lα1 , oscillations are observed, which are not explained by theory. Spectral data for the determination of Lβ2/Lα1 ratios and its variation with proton beam energy is also being processed, but collected data requires a more complex calculation because corrections are necessary to compensate for small variations on the WDS unit observed during the long run irradiations needed to obtain good spectral data.

[1] Ruder Buskovic Institute, Zagreb, Croatia .

Materials Characterization with Radioactive Nuclear Techniques

João Guilherme Martins Correia

A **laboratory infrastructure** on materials characterization is maintained and developed at ISOLDE-CERN by the Nuclear Solid State Physics group of ITN and CFNUL. ISOLDE is a European Large Scale Facility where more than 1000 isotopes and isobars of 80 elements are produced and delivered as ion beams of high elemental and isotopic purity, which is a unique feature in the world. In this context nuclear techniques such as Emission Channeling (EC) and Perturbed Angular Correlations (PAC) provide complementary atomic scale information to the material analysis capabilities available at ion beam laboratories. This infrastructure and projects are refereed and reevaluated each year within the scope of FCT-supported CERN projects. In 2010 the scientific work was centered in the following research subjects approved by the ISOLDE Scientific Committee:

a) IS453 (U.Wahl) "Emission Channeling Lattice Location Experiments with Short-Lived Isotopes". The lattice sites of dopants and impurities in scientifically and technologically relevant semiconductors are studied with the emission channeling technique at highly diluted concentrations. During 2010, ^{56}Mn (2.58 h) was used to study the lattice site of the transition metal Mn implanted into ZnO, Si, Ge, GaAs, $SrTiO_3$ and AlN. The ^{24}Na (14.95h) alkaline isotope was used to study p- and n-Si doping. Being Mg an essential p-type dopant in semiconductors, we have pursued lattice location studies on GaN, AlN and InN using ^{27}Mg (9.45m). Looking forward for lattice site location of Be a first demonstrative experiment was performed in GaN with the short lived isotope ^{11}Be (13.8s).

b) IS487 (V. Amaral) "Study of Local Correlations of Magnetic and Multiferroic Compounds". PAC is used to study a large variety of multiferroic $RMnO_3$ (R= rare-earth) manganites and cromites $ACrO_2$ (A=Ag,Cu) as a function of the elements R, A, and of temperature. By combining PAC data with first principle simulations (f.p.s.) of charge density distributions on these materials, local phenomena that correlate the coexistence of ferroelectricity, ferromagnetism and ferroelasticity are studied. During 2010 PAC experiments were performed in several multiferroic oxides (manganite, nickelite, chromite) pnictides and chalcogenides. The experimental studies are accompanied by the theoretical analysis and calculation of the hyperfine parameters using *ab initio* methods for determining the electronic structure as well as the modeling of the relevant physical properties.

c) IS481 (K. Lorenz) "The role of In in III-nitride ternary semiconductors", have combined γ–γ with e^--γ PAC using the ^{111m}Cd/^{111}Cd and the ^{117}Cd/^{117}In isotopes. Results obtained in 2010 have confirmed the role of the In dopant, as being predominantly stabilizing defects in GaN, InN and AlN.

In what R&D projects are concerned, first alpha particle detection tests were successfully done with a highly pixelated 256x256 14×14mm^2 Si detector (TimePix). This setup will be mounted at the ITN accelerator to be tested on RBS/Channeling experiments using H^+ and He^{2+} beams. In parallel, the new high-resolution goniometer from Panmure, dedicated to on-line electron EC experiments with short-lived isotopes, has been mounted on a (very) special sustaining cradle to be commissioned on-line at the ISOLDE GHM-beam line in 2011.

Of interdisciplinary nature, these activities integrate and initiate students from different backgrounds and universities, in applied nuclear physics. With shared work between the different environments of ITN, CFNUL and ISOLDE – CERN, there participate students and senior researchers from the universities of Lisbon, Aveiro, Porto, Braga as well as from Leuven (Belgium) and Bonn(Germany). During 2010 one MSc student defended his thesis; five Portuguese and one German PhD students performed work for their thesis and one new PhD student is about to start work, using this infrastructure within the scientific proposals and R&D projects.

Research Team

Researchers

J.G.M. CORREIA, Princ.
U. WAHL, Princ. (15%)
K. LORENZ, Aux. (10%)

Students

T. MENDONCA, PhD student, FCT Grant
J.N. GONÇALVES, PhD student, FCT Grant
L. PEREIRA, PhD student, FCT Grant
C. SOUSA, PhD student, FCT Grant
L. AMORIM, PhD student, IKS-Leuven Grant
D. Silva, (new) PhD student, FCT Grant
M. BARBOSA, (new) PhD Student FCT projects
G. OLIVEIRA, (new) PhD Student FCT projects
J. Belo, (new) PhD Student FCT projects
P. KEßLER, PhD Student HISKP Bonn Grant (e-γ PAC)

Collaborators

V. AMARAL, Ass. Prof., U. Aveiro
J.P.E. ARAÚJO, Aux. Prof., U. Porto
M.R. SILVA, Ass. Prof., IST, Lisboa
J.C. SOARES, Prof. Emeritus, U. Lisboa
L. REDONDO, Ass. Prof., ISEL, Lisboa
H. HAAS, Emeritus Researcher, ITN
A. VANTOMME, Prof., IKS Leuven
R. Vianden, Prof., HISKP Bonn

S. DECOSTER, Post-Doc, IKS Leuven
A. L. LOPES, Post-Doc, FCT Grant

IS453 experiment: Emission channeling lattice location studies

U. Wahl, J.G. Correia, E. Alves,
S. Decoster[1], L. Amorim[1], A. Vantomme[1], M.R. da Silva[1,2] , L. Pereira[1,4], J.P. Araújo[4] ,
and the ISOLDE collaboration[5]

Results

1. Lattice location of Mn in GaAs

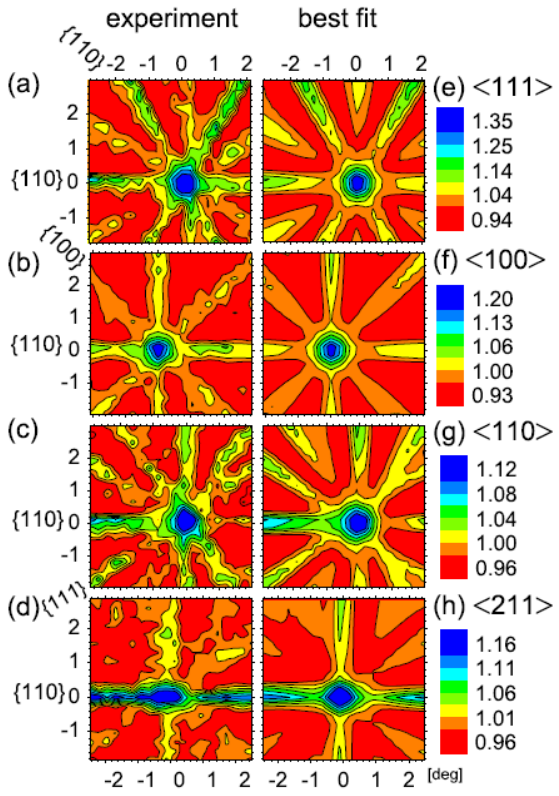


Fig. 1: (a)-(d) Angular emission patterns of β^- particles from ^{56}Mn in GaAs in the vicinity of <111>, <100>, <110> and <211> crystallographic directions following annealing at 300 °C. (e)-(h) best fits of theoretical patterns for a combination of 71% of ^{56}Mn on substitutional S_{Ga} and 29% on interstitial T_{As} sites.

The ternary compound $Ga_{1-x}Mn_xAs$ represents the best understood dilute magnetic semiconductor system which exhibits ferromagnetism, although the maximum Curie temperature T_C realized (around 200 K) is currently still considerably below room temperature. Whereas it is well-known that T_C in $Ga_{1-x}Mn_xAs$ increases with increasing Mn fraction x and that Mn mostly replaces Ga atoms, it was suggested in the literature that there is a limit imposed on T_c by the amount of Mn atoms that are incorporated interstitially. However, the exact location of interstitial Mn was unknown and its thermal stability and diffusion behaviour were uncertain as well. We have studied the lattice location of ^{56}Mn implanted into p^+-GaAs:Zn. Fig. 1 compares the normalized experimental ^{56}Mn β^- emission yields along the four major directions with the best fits of theoretical patterns, which were obtained for a combination of 71% of ^{56}Mn on substitutional S_{Ga} and 29% on tetrahedral interstitial T_{As} sites. Measuring the emission channeling effects as a function of annealing temperature showed that the interstitial Mn fraction of ~30% was converted to substitutional Mn only for annealing temperatures above 400 °C, which is contrary to the claim reported in the literature that Mn interstitials anneal by means of outdiffusion from the sample at temperatures around 200 °C.

2. Emission channeling with short-lived isotopes

Using our emission channeling on-line setup at the ISOLDE GHM beamline, we participated in three beam times using short-lived radioactive isotopes in 2010. During the Mg beam time we determined the lattice location of the potential acceptor ^{27}Mg (9.5 min) in InN, and Mg was found mainly on substitutional In sites. Due to beam sharing with a nuclear physics experiment, exceptionally 10 days were available for emission channeling experiments with Mn isotopes, and lattice location data was obtained for ^{56}Mn in $SrTiO_3$, InN, *si*-GaAs, n^+-GaAs, $Ga_{0.99}Mn_{0.01}As$, $Ga_{0.95}Mn_{0.05}As$, Ge, *p*-Si, p^+-Si, ^{59}Mn in p^+-GaAs and 3C-SiC , as well as a high angular resolution measurement of ^{56}Mn in ZnO. The bulk of this data is currently being analyzed and the results can therefore not yet be entirely included in this report. However, the *si*-GaAs, n^+-GaAs and GaMnAs experiments confirmed the results described above for ^{56}Mn in p^+-GaAs. First test for the use of ^{11}Be (13.8 s) in β^- emission channeling experiments in GaN were undertaken during a Be beam time, showing that this isotope can be used for lattice location purposes, however, however that it suffers from some background problems due to its high β^- endpoint energy of 11.5 MeV.

[1] Instituut voor Kern- en Stralingsfysica (IKS), Katholieke Universiteit Leuven, 3001 Leuven, Belgium
[2] Centro de Física Nuclear da Universidade de Lisboa (CFNUL), Av. Prof. Gama Pinto 2, 1649-003 Lisboa
[3] Instituto Superior Técnico, 1049-001 Lisboa
[4] Departamento de Física, Universidade do Porto, 4169-007 Porto
[5] CERN, 1211 Geneva 23, Switzerland

IS487 experiment – Hyperfine Interactions in MnAs studied by Perturbed Angular Correlations of γ-Rays using the probe 77Br→77Se and first principles calculations for MnAs and other Mn pnictides.

J.N. Gonçalves[1], V.S. Amara1[1], J.G. Correia, A.M.L. Lopes[2]

New systems that exhibit simultaneous magnetocaloric, magnetoelastic and magnetoresistance effects are particularly challenging, looking forward to understand their properties for immediate applications. Hyperfine techniques offer unique tools, which the Perturbed Angular Correlation (PAC) Technique is particularly appropriate to probe at a nanoscopic scale, in the surroundings of highly diluted impurity elements, microscopic phase transitions involved in these materials phenomenology. The case study here presented resumes the use of radioactive ^{77}Br/^{77}Se PAC probe to study MnAs phase transitions, which work has just been accepted by Physical Review B, i.e., the MnAs compound shows a first-order transition at $T_C \approx 42$ ºC, and a second-order transition at $T_t \approx 120$ ºC. The first-order transition, with structural (hexagonal-orthorhombic), magnetic (FM-PM) and electrical conductivity changes, is associated to magnetocaloric, magnetoelastic, and magnetoresistance effects. We report a study in a large temperature range from −196 up to 140 ºC, using the γ−γ perturbed angular correlations method with the radioactive probe ^{77}Br→^{77}Se, produced at the ISOLDE-CERN facility. The electric field gradients and magnetic hyperfine fields are determined across the first- and second-order phase transitions encompassing the pure and mixed phase regimes in cooling and heating cycles. The temperature irreversibility of the 1st order phase transition is seen locally, at the nanoscopic scale sensitivity of the hyperfine field, by its hysteresis, detailing and complementing information obtained with macroscopic measurements (magnetization and X-ray powder diffraction). To interpret the results, hyperfine parameters were obtained with first-principles spin-polarized density functional calculations using the generalized gradient approximation with the full potential (L)APW+lo method (WIEN2K code) by considering the Se probe at both Mn and As sites. A clear assignment of the probe location at the As site is made and complemented with the calculated densities of states and local magnetic moments. We model electronic and magnetic properties of the chemically similar MnSb and MnBi compounds, complementing previous calculations.

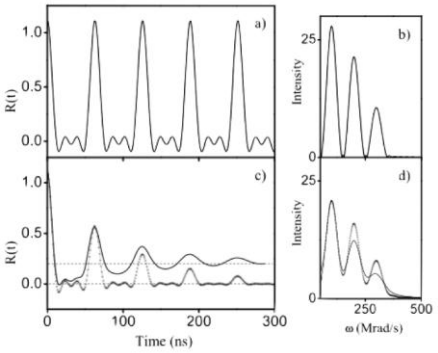
[1] Department of Physics and CICECO, Aveiro University, Aveiro, Portugal.
[2] CFNUL, Lisbon University, Portugal.

Implementation of "ab initio" Perturbed Angular Correlation Observables for Analysis of Fluctuating Quadrupole Interactions

M.B. Barbosa[1,2], J.G. Correia. J.P.E. Araújo[2]

The PAC technique offers a privileged way to look at time transient phenomena involving changes of electronic density at the nanosecond time scale, among which polarons and charge ordering could be featured within a certain temperature range. Still, a proper analysis modeling was missing due to the difficult formalism and heavy computer power required. This year M. Barbosa presented his M.Sc. thesis on the development and implementation of a ab-initio simulation program based on stochastic Hamiltonians that reproduce electronic density fluctuations during the measurement time, allowing data analysis to polycrystalline and single-crystalline systems with dynamic interactions. This program was briefly tested on the experimental case of ^{181}Hf:GaN. In the near future we aim to adapt the code to parallel computing and three transition stochastic states, necessary to interpret some physical problems.

1 Department of Physics and IFIMUP, Porto University, Portugal.



Legend: (a) Schematic representation of R(t) with no attenuation, η = 0, with the correspondent Fourier transform on (b). (c) Representation of R(t) for the same frequency as in (a) with EFG static distribution attenuation (top curve) and, with attenuation due to fast EFG fluctuations (bottom curve), with the correspondent Fourier transform represented on (d). In in the case of damping due to dynamic interactions the ω1, ω2, ω3 amplitudes decrease by the same factor while for a damping originated by static-like frequency distribution the attenuation is proportional to the frequency itself. The R(t) additionally shows an exponentially-like vanishing a_0, as a function of time, for dynamic interactions.

IS481 experiment – An In-defect complex as a possible explanation for high luminous efficacy of InGaN and AlInN based devices

P. Kessler[1], K. Lorenz, S.M.C. Miranda, J. G. Correia, K. Johnston[2], R. Vianden[1] and the ISOLDE collaboration

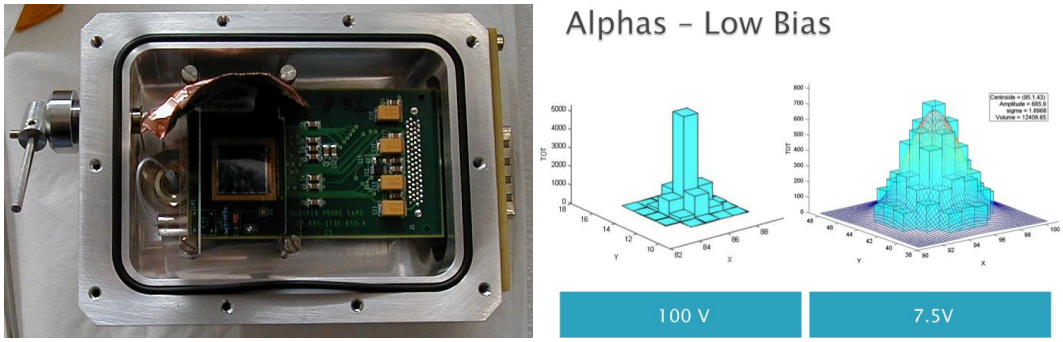
The role of indium in GaN and AlN films was investigated with the γ– γ and e-γ perturbed angular correlation (PAC) methods. Using the PAC probe ^{111}In/^{111}Cd, in addition to indium on substitutional cation sites a large fraction of probes is found in a distinctly different microscopic environment, which was attributed to the formation of an indium nitrogen-vacancy (V_N) complex. The influence of electron capture induced *after-effects* was ruled out by additional measurements with the PAC probes ^{111m}Cd and ^{117}Cd on differently doped GaN samples. It is further shown that V_N is not bound to substitutional Cd impurities, suggesting that the In- V_N complex formation is a particularity of In in GaN and AlN. In fact, after the decay of ^{111}In to ^{111}Cd, below a critical temperature, VN remains nearby to the probe atom during the measurement, since VN has not enough energy to leave the cadmium within the lifetime of the initial excited state of ^{111}Cd. This originates a specific EFG with a temperature dependent attenuation that allowed developing a preliminary model to interpret the trapping and release of V_N in In doped AlN and GaN.

[1] Helmholtz–Institut für Strahlen- und Kernphysik, Universität Bonn, 53115 Bonn, Germany
[2] Technische Physik, Universität des Saarlandes, 66041 Saarbrücken, Germany

R&D development –TimePix detectors for emission channeling and / or He^{2+} RBS/Channeling studies

E. Bosne[1], M.R. Silva[2], U. Wahl, J.G. Correia, M. Campbell[3], L. Tlustos[3], X. Ll. Cudie[3]

Looking forward to the future, where short-lived isotopes with high beta energies require improved position detection resolution, since December 2007 that we are working with the MEDIPIX CERN collaboration at CERN (http://medipix.web.cern.ch/MEDIPIX/). In 2010 we have developed the mounting and tested one of such detectors with 256x256 pixels covering ~15x15mm2, with alpha particle emitters aiming emission-channeling experiments. The system, which is shown in the figure below (left), is now ready to be tested on-line at a He^{2+} beam line of the Rutherford Back-Scattering Channeling (RBS/C) ITN - accelerator. The figure further shows on the right, the pixel response to single impacts of 5.6MeV alpha particles from a ^{241}Am source for two bias voltages. With the detector biased at 100 V, the charge generated by an alpha particle hit is confined to a few pixels only, while it spreads over a considerable number of pixels at the lower detector bias of 7.5 V. However, this effect is actually beneficial: since the charge spread is exactly Gaussian, a Gaussian fit to the charge distribution at low bias provides sub-pixel position resolution, being the integral used for energy determination.



Legend: (left) timepix detector implemented on the special housing developed by us, to be mounted at the ITN-Sacavém accelerator beam line. (righ) Alpha particle event taken as a function of bias voltage; the spectra show on z the energy deposition (TOT) signal deposited per pixel on a single event. Fitting the spectra with a pure 2D Gaussian, provides the full energy (integral) and the precise (x,y) event hit coordinates (centroid of the Gaussian).

[1] Department of Physics and CICECO, Aveiro University, Aveiro, Portugal.
[2] CFNUL, Lisbon University, Portugal.
[3] MEDIPIX, CERN, 1211 Geneva 23, Switzerland.

.

Nuclear Reactions

Adelaide Pedro de Jesus

This group has been involved in the experimental study of nuclear reactions relevant to nuclear astrophysics and also to ion beam analytical techniques.

The on-going work is related to the development of the AMS line to study reactions relevant to nuclear astrophysics.

Also a new line has been installed in the new Tandem 3MV accelerator, for nuclear reaction studies both for fundamental nuclear physics and nuclear astrophysics and for applied PIGE work.

Research Team

Researchers

A.P. JESUS, Full Professor (FCT/UNL), Group Leader
J.P. RIBEIRO, Associate Professor (FCUL)
J. CRUZ, Assistant Professor (FCT/UNL)
D. GALAVIZ, Pos-Doc (CFNUL)

Students

M. FONSECA, Ph.D. Student, (FCT/UNL)
H. LUÍS, Ph.D. Student, (FCT/UNL)

Experimental Study of Nuclear Reactions for Astrophysics

H. Luis, J. Cruz, D. Galaviz, A.P. Jesus, M. Fonseca, J.P. Ribeiro

Objectives

Following its experimental work in nuclear reactions relevant for primordial and stellar nucleosynthesis (hydrogen burning), the group is focusing now in later stages of stellar nucleosynthesis, namely alpha, carbon and oxygen burning and p-process. Some of the studies will proceed within international collaborations, making use of facilities such as ERNA, FAIR, ISOLDE. Other studies will be conducted at ITN, taking advantage of the heavy ion beams available at the 3 MV Tandem accelerator and of the accelerator mass spectrometry (AMS) line.

Results

During this year, the optimization of the AMS line for detection and quantification of ^{36}Cl was initiated. ^{36}Cl is one of several short to medium lived isotopes (as compared to the earth age) whose abundances at the earlier solar system may help to clarify its formation process. There are two generally accepted possible models for the production of this radionuclide: it originated from the ejecta of a nearby supernova (where ^{36}Cl was most probably produced in the s-process by neutron irradiation of ^{35}Cl) and/or it was produced by in-situ irradiation of nebular dust by energetic particles (mostly, p, α, ^{3}He -X-wind irradiation model).

The Accelerator Mass Spectrometry (AMS) technique has gained international reputation as the technique to detect and quantify rare isotopes as ^{14}C, ^{10}Be, ^{26}Al, ^{36}Cl and many others, that are continuously being produced by cosmic radiation, being very useful as geochronometers, as probes of production and evolution of geological formations and of environment and climate changes, also useful for dating and model cosmic radiation and solar activities.

Future Work

During 2011, cross sections of neutron capture by ^{35}Cl and (p,d) and (d,p) reactions on ^{37}Cl and ^{35}Cl will be obtained.

Development of a PIGE Set-up

M. Fonseca, J. Cruz, D. Galaviz, A. P. Jesus, H. Luis, J. P. Ribeiro

Objectives

The aim of this work is the extension to all light elements of previous work, in order to install an analytical set-up for light element analysis, based on the detection of the gamma radiation induced by low energy protons, PIGE.

This technique will open new perspectives of applied work in environment and health problems.

Results

A precise method based on a code [1] that integrates the nuclear reaction excitation function along the depth of the sample was implemented for thick and intermediate samples. For that purpose some reaction excitation functions were measured in the same analytical conditions. The energy steps needed to define accurately the excitation function were used as energy intervals for the integration procedure.

Previous results obtained at the Van de Graaff accelerator on ^{25}Mg(p,p'gamma)^{25}Mg with proton energies up to 2.4 MeV and ^{9}Be(p, gamma)^{10}B were analysed and published [2].

The nuclear reactions ^{10}B(p,alpha gamma)^{7}Be, ^{23}Na (p,p'gamma)^{23}Na, ^{19}F(p,p'gamma)^{19}F, ^{7}Li(p,p'gamma)^{7}Li and ^{25}Mg(p,p'gamma)^{25}Mg were measured up to 4.0 MeV at the 3 MV Tandem accelerator at ITN. Also some applications of PIGE were performed, namely for studying ceramic glazes [3].

Future work

The group has submitted a three year project within a IAEA Co-ordinated Research Project (CRP) on "Assessment of Nuclear Data Needs for Particle Induced Gamma Ray Emission (PIGE)", that has been accepted.

References

[1] R. Mateus, A. P. Jesus, J. P. Ribeiro, Nucl. Inst. and Meth. B229, 302-308 (2005)
[2] M. Fonseca, A. P. Jesus, H. Luís, R. Mateus, J. Cruz, L. Gasques, D. Galaviz, J. P. Ribeiro, Nucl. Instr. & Meth. B 268, 1806-08 (2010)
[3] M. Fonseca, H. Luís, N. Franco, M. A. Reis, P. C. Chaves, A. Taborda, J. Cruz, D. Galaviz, N. Fernandes, P. Vieira, J.P. Ribeiro, A.P. Jesus; Accepted to Nucl. Instr.& Meth. B

Condensed Matter Physics

Fernanda Margaça

The Group's main field of research is the development and characterisation of materials with new or improved properties. For this purpose, radiation is used as a tool to investigate the structure and to induce structural modifications in particular samples.

Special polymeric materials have been investigated in collaboration with groups from the Universidade de Aveiro, Umiversidade de Coimbra and Universidade Nova de Lisboa, Laboratoire Léon Brillouin (CEA-CNRS-Saclay) in France, Paul Scherrer Institute, Villigen in Switerzand and the Budapest Neutron Centre in KFKI, Hungary.

The main effort has been made to characterise the hybrid materials as well as the co-polymers, both prepared by gamma irradiation using the ^{60}Co source of UTR, to optimize the processing protocol in order to improve the properties of the obtained materials.

The systems studied involve the development of new copolymers (HEMA grafted on LPDE thin films) suitable for bioapplications and hybrid materials prepared from mixtures of a polymer (PDMS) and different metallic alkoxides.

During 2010 progress continued in the copolymers development. A new methodology for determination of the grafting yield in gamma induced grafted copolymers, based on thermal analysis data, was developed. A report for registration of a National Patent for the new polymeric material and its method of preparation is being elaborated.

The project entitled *Hybrid materials for biomedical applications*, with funding from the Foundation for Science and Technology, was started in May 2010.

Hybrid materials for biomedical applications were prepared by the sol-gel process with the addition of a new alkoxide (calcium nitrate). Some selected samples of these new materials were measured by small angle neutron scattering in the Paul Scherrer Institute, in Switzerland. They have also been characterised by other more conventional techniques, most of them available at ITN.

In collaboration with researchers from Universidade Nova de Lisboa, the synthesis and characterization of novel γ-induced porous HEMA-IL composites is being investigated. Work is also progressing towards the development of catalytic membranes of poly (vinyl alcohol) containing sulfonic acid groups.

A project entitled *Preparation of polymeric materials catalytically actives on biodiesel production by vegetable oils methanolysis*, was approved and obtained funding from the Foundation for Science and Technology. It is due to start in February 2011.

Research Team
Researchers

F.G. CARVALHO, Senior, (retired)
F.M.A. MARGAÇA, Princ, Group Leader
A.N. FALCÃO, Princ.
L.M.M. FERREIRA, Aux.
C.M.M. CRUZ, Aux. (20%)
J.S.NEVES, Aux. (20%)

Collaborators

I.M.M. SALVADO, Dep. of Glass and Ceramics Engineering UIMC, University of Aveiro
M.H. CASIMIRO, Dep. de Química, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa
M.H. GIL, Dep. of Chemical Engineering, Faculty of Sciences and Technology, Coimbra University

A new methodology for the determination of the grafting yield on γ- induced grafted copolymers

L.M. Ferreira, J.P. Leal and A.N. Falcão

Objectives

The development of an expeditious and consistent experimental and mathematical methodology for the determination of the grafting yield in gamma induced grafted copolymers, based on thermal analysis data.

Results

Polymer crystallinity can be determined by thermal analysis techniques, namely by *Differential Scanning Calorimetry (DSC)*, which has become a fundamental tool in the study of phase transition temperatures, providing precious data about the structural organization of the matter. The melting enthalpy of a material is related to the energy required to break the intermolecular bonds, and it can be used to evaluate its crystallinity. Thus, polymer chains more ordered, i.e., more crystalline, have stronger intermolecular bonds and in greater number, and therefore, higher temperatures and enthalpies of fusion. The degree of crystallinity of a polymer (X_c) can be calculated from its enthalpy of fusion, according to the relation:

$$X_c = \frac{\Delta_f H}{\Delta_0 H} \times 100$$

where $\Delta_f H$ represents the melting enthalpy of the polymer sample measured by DSC and $\Delta_o H$ is the melting enthalpy of the polymer in "completely" crystalline form.

In PE-g-HEMA films, a polyethylene based copolymer grafted with methacrylate 2-hydroxyethyl, we observed the existence of a consistent correlation between the grafting degree and the crystallinity of the copolymers (Figure 1).

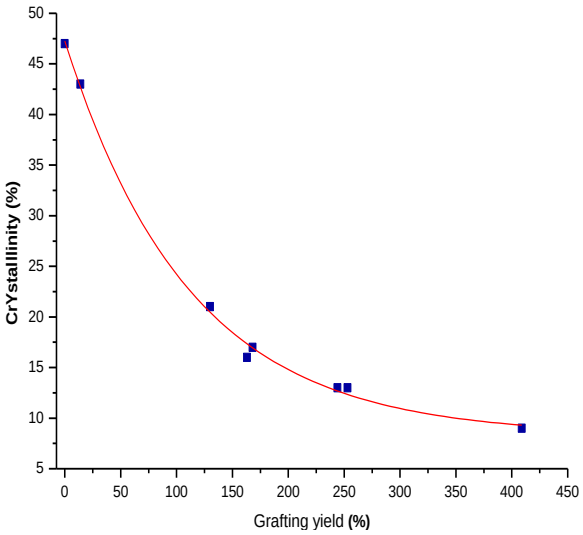
The data are fitted by a first order exponential decay function of the type:

$$y = y_o + A_1 \cdot e^{(-x/t_1)}$$

which in this case takes the form:

$$X_c = 8{,}30 + 38{,}96 \cdot e^{(-x/111{,}60)} \qquad (R^2 = 0{,}998)$$

The good agreement between experimental data and the mathematical fit function (R^2= 0,998), is a good evidence that the structural damages induced in polyethylene backbone depend strongly on the graft of poly(HEMA).
Moreover, this fact also allows to considerer DSC analysis as an alternative to the gravimetric method, to determine the grafting yield in copolymers. A DSC assay makes possible to determine, promptly and accurately, the melting enthalpy and the degree of crystallinity of a sample, and thereby to obtain its graft degree.



Evolution of the crystallinity degree of the PE-g-HEMA films with its yield of graft.

For our PE-g-HEMA copolymeric films, the above equation can be rewritten as follows:

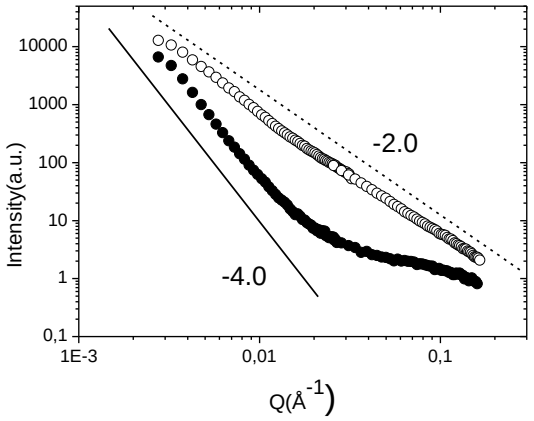
$$\textit{Yield of graft (\%)} = \ln\left(\frac{X_c - 8{,}30}{38{,}96}\right) \times (-111{,}60)$$

This provides a new way to quickly calculate the copolymers grafting yield, from its degree of crystallinity.

Hybrid Materials for Biomedical applications

F.M.A. Margaça, I.M.Miranda Salvado[1], J.J.H. Lancastre, L.M. Ferreira, A.N. Falcão, L. Almásy[2]

Hybrid materials PDMS-modified $CaO\text{-}SiO_2\text{-}ZrO_2$ were prepared and studied as to the bioactivity behaviour after immersion in SBF for different periods of time. It was found that both the addition of ZrO_2 and the thermal treatment promoted the deposition of a hydroxyapatite surface layer on the synthesised materials [1]. They were characterised by TG, DTA, XRD and small angle neutron scattering (SANS). Figure 1 shows the SANS spectra for the sample prepared with no zirconia, before heat treatment (full circle) and after (open circle). The results showed that in the material prepared without Zr the oxide network evolved by RLMC aggregation, resulting in smooth interfaces at the nanometric scale. The oxide network of samples with PrZr grew by RLCC aggregation presenting a mass fractal structure, at the nanometric scale. The observed correlation between nanoscale structure and bioactivity should be further investigated in order to improve the processing conditions of materials for biomedical applications.



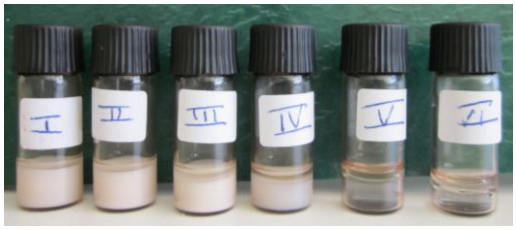
[1] Portela Marques MM, Miranda Salvado IM, Margaça FMA, Ferreira LM., *J. Therm. Anal. Calorim.* **100** (2010) 557–561

[1]Dep. Glass and Ceramics Engineering, CICECO, Aveiro University, 3810-193 Aveiro, Portugal
[2]Lab. for Neutron Scattering, PSI, CH-5232 Villigen, Switzerland

Synthesis and characterization of novel γ-induced porous HEMA-IL composites

M.H. Casimiro[1], M.C. Corvo[1], A.M. Ramos[1], L.M. Ferreira, F.M.A. Margaça

In collaboration with researchers from REQUIMTE-DQ/FCTUNL we have synthesized and characterized a novel polymer-ionic liquid composite with poly(2-hydroxyethyl methacrylate), PHEMA, and 1-buthyl-3-methylimidazolium hexafluorophosphate, $BMIPF_6$, obtained by γ-irradiation at room temperature. The ionic liquid has a porogenic role during the γ-induced polymerization. The resulting composites can be converted into an organogel by addition of DMSO, and converted back to a porous composite by immersion in water. These properties turn the obtained composites suitable for diverse biomedical and green industrial technology applications.



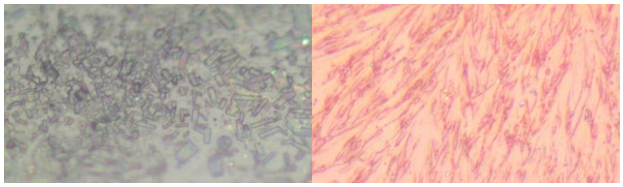
HEMA-IL composites (after irradiation)

[1]REQUIMTE, CQFB, Dep. de Química, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Caparica

Development of catalytic membranes of poly(vinyl alcohol) containing sulfonic acid groups

M.H. Casimiro[1], A.G. Silva[1], A.M. Ramos[1], J. Vital[1], L.M. Ferreira

We have developed solid acid catalysts consisting in membranes of poly(vinyl alcohol) functionalized with sulphonic groups. These groups are introduced into the polymer matrix by gamma irradiation anchoring of methanesulfonic acid. These membranes show good catalytic activity in the reaction of isoamyl acetate production. Although, due to the formation of complex structures during irradiation, these membranes are still being object of a more exhaustive characterization.



(Before catalytic reaction) (After catalytic reaction)
Functionalized PVA membranes

[1]REQUIMTE, CQFB, Dep. de Química, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Caparica

Laboratory of Polymers Characterization
L.M. Ferreira, F.M.A. Margaça

In 2010 the *Laboratory of Polymers Characterization* changed its location to a new and better suited place, in the ground floor, in the extension of the UFA main building. It also changed name to *Laboratory of Macromolecular Materials (LMC)*. It consists of two main parts. One dedicated to the chemical and physical manipulations of samples and the other to the mechanical and other physical analysis. This change was necessary in order to improve the working conditions, namely allowing the use of all our experimental and analytical resources in a safer and more efficient way. The significant development of activities requiring manipulation and characterization of macromolecular materials was the other important reason for this move.

Photographs of the facilities of the LMC in its final stage of installation at the new location.

Radiation Technologies: Processes and Products

M. Luísa Botelho

Radiation Technologies: Processes and Products is an interdisciplinary group that uses the holistic approach as the key to conceptualize a research or a service. This interdisciplinarity, using Biology, Chemistry and Physics science, allows the study of a subject from various angles and methods unified by a common goal: the validation of methodologies to understand the subject of study, which core is ionizing radiation.

The group *modus operandi* permits a constant connection with Industries, Universities and other Research groups applying its "way of knowing" in response to requested services, as a collaborator in a research project or in the transmission of knowledge.

The group activities focus on the delineation, development, validation and application of technologies and processes in various fields, such as Environment, Food and Pharmaceutics. As a fundamental part of the validation studies, Risk Analysis is being applied as a process management tool either in production lines of studied products (*e.g.*: food, devices and pharmaceuticals) or in environmental control (*e.g.* hospitals rooms, pharmaceutical industries and buildings energetic certification).

In the scope of ITN mission the group is requested by the authorities or private industries to undertake a consultant role on sterilization and decontamination procedures mainly applying ionising radiation. The group also develops work with the National and International normalization, standardization and certification bodies (IPQ, CEN and ISO).

The Group's main R&D activities are focused at employing ionising radiation technologies to new processes and applications in Agriculture, Food, Pharmaceutical, Wastewater Treatment, Art and other areas. In order to improve our understanding of the Radiation effects in products integrated methodologies composed by Analytical Methods of Biology, Microbiology, Chemistry and Physics are being used. Molecular Biology new trends based on PCR technique are being developed as a diagnostic tool (*e. g.:* potential pathogenic micro-organisms) and as well as fingerprinting methods to assess the biodiversity profile of environmental samples. Furthermore, R&D in environmental virology is being carried on, namely the inactivation of enteric viruses (e.g. norovirus and adenovirus) by ionizing radiation for disinfection purposes.

In 2010 two FCT projects were initiated both focusing ionizing radiation applications taking advantage of IRIS and LETAL infrastructures. One (Pulse Radiolysis - PTDC/QUI-QUI/104229/2008) is related with the implementation of a pulse radiolysis system at the LINAC Accelerator to study the mechanistic details of the degradation of chemicals compounds. The other project (RADIART - PTDC/HIS-HEC/101756/2008) deals with art objects and the potentiality of gamma radiation as a decontamination tool. An ionizing process treatment with gamma and electrons radiation is being studied for food preservation (e.g. chestnuts) in the scope of a collaboration project (CHESTNUTSRAD - QREN nº 13198/2010) with School of Agriculture of IPB.

Training and "know-how" diffusion are one of the main issues of this Group reflecting in the attainment of academic degrees (Graduation, M.Sc. and Ph.D.) and in the dissemination of obtained results in the scientific community (publications, workshops and conferences).

The financial support of the group is based on projects, sponsored by National (e.g. FCT, AdI) and International (e.g IAEA) science foundations and expertise services to Industrial Companies.

Research Team

M.L. BOTELHO, Aux., Group Leader
S. CABO VERDE, Aux.
P. SANTOS, Post-Doc, FCT Grant

Students

R. MELO, Ph.D. student, FCT Grant
A. ANTÓNIO, PhD student FCT Grant
J. REIS, PhD student from UE
C. FRIAS PhD student from UP
T. SILVA, FCT/UNL, Master student
I. NUNES, FCUL Master student
V. DORES, QREN/ISEL Grant
N. MESQUITA, PhD student from UC
M. OLIVEIRA, graduation student from ESAS

Technical Personnel

H. MARCOS, system operator, ITN

Collaborators

C. CANTO E CASTRO, ITN Network Manager
J.P.LEAL, UCQR., ITN Researcher
P. MATOS, Technical Director of CHIP,S.A
J. TRIGO, INIAP Researcher
P. MAZARELO and S. XISTO, LM Researchers
R. TRINDADE, UPSR Researcher
I. PAIVA, UPSR Researcher
R. TENREIRO, DBV-FCUL Professor/ICAT
A. PORTUGAL, U.C., Professor
S. J. NASCIMENTO, F.F./ U P, Professor
A. VIEIRA, FCT-UNL, Professor
L. REDONDO, ISEL, Professor
H.CANACSINH, ISEL, Professor

IRIS up to date

P.M.P. Santos, A. A. Amílcar[1], R. Melo, S. Cabo Verde, T. Silva, H. Marcos, I. Nunes, M. Oliveira, V. Dores and M. L. Botelho

Objectives

Dosimetric studies are being carried out in the ionizing radiation facility IRIS, using the radiation equipments: ^{60}Co experimental source Precisa22 and the Linear Accelerator (Linac). These studies intended to dose map both equipments for further ionizing radiation treatment processes optimizations.

Results

The difficulty in obtaining agreement between simulations and experimental results has been a permanent stimulus to achieve optimal conditions for radiation treatment processes. A model based in the Monte Carlo simulation using the irradiation equipments available at IRIS – an experimental gamma irradiation chamber (Precisa22, Graviner Ltd, UK) and a Linac – will be applied in this study. A dosimeter mapping of Precisa22 and preliminary dosimeter measures in the Linac were performed.

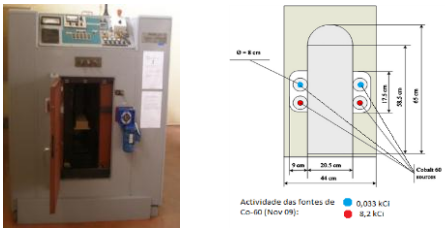


Fig. 1 – Precisa22 irradiation chamber: activity of sources and dimensions.

The ^{60}Co irradiation facility (Fig. 1) consists of a 65 cm x 50 cm x 20 cm (h x d x w) rectangular cavity surrounded by a lead protection barrier. Four ^{60}Co sources, with an activity of 305 TBq (8.233 kCi) in November 2009, are positioned in stainless-steel tubes located in the lateral walls of the chamber, in positions directly facing each other, about 30 cm above the chamber floor. The movement of the sources in the 50 cm long tubes is controlled by an automatic mechanism. The dosimetric study was performed using Fricke solution as reference dosimeter, within the range of 40 to 400 Gy. The irradiation geometry is composed by a four level steel frame that delimitates the irradiation chamber and supports four wood racks with 27 positions each. The higher estimated dose rate was 4 kGy/h obtained in the level 2 of the irradiation geometry (second upper level near the sources). In opposition, the lower dose rate achieved was 0.080 kGy/h at the bottom level 4, close to outside door.

The Linac (Fig. 2) can operate both in electron and in photon mode and deliver an energy comprised between 4 and 12 MeV. A magnetron working at a frequency of about 3 GHz and triggered between 10 and 300 Hz delivers pulses of several ms.

Fig. 2 – Linac: bunker; modulator; accelerating structure and electron/photon beam exit (270° loop).

A preliminary dosimetric study was conducted in the Linac using Fricke dosimeter. The accelerator set up was 10 MeV; 50 mA; 2.28 μs in the electron mode. Fricke solution amilon bags (9.5 x 3.5 cm; n = 3) were placed in the irradiation tray (28.5 cm x 9.5 cm) and irradiated at a distance of 30 cm of irradiation head. For the selected irradiation geometry and Linac configurations, the higher obtained dose rate was 1.12 ± 0.03 kGy/h in the center position (bellow irradiation head), and the lower was 0.48 ± 0.06 kGy/h in the left side of the tray.

The dose mapping for both equipments is being accomplished and further evaluated by simulation and routine dosimetry.

This R&D work is the theme of a PhD Thesis (FCT SFRH/PROTEC/67398/2010).

Influence of gamma radiation on the antioxidant properties of edible chestnuts – In food irradiation the dose distribution inside the chamber and the dose uniformity ratio must be well characterized to control the irradiation process. An estimation of dose was performed using Fricke chemical dosimeter solution, obtaining a dose rate of 0.27 ± 0.04 kGy, for the selected geometry inside the irradiation chamber. The dose uniformity ratio obtained was similar to one (D_{max}/D_{min} = 1.3). The dose uniformity ratio obtained is in conformity with the good practices for food irradiation that should be less than 3. In this preliminary study the results suggested that a variation of 0.27 kGy affected the skin and fruit properties in different ways, maybe due to different chemical composition of these parts. However, along storage time the control and irradiated samples follow the same tendency. Further studies will be done in order to elucidate the influence of irradiation in chemical composition and nutritional value of chestnuts fruits. This R&D work is under a Protocol between several entities and is supported by "ON.2 - Programa Operacional Regional do Norte" with the Project CHESTNUTSRAD - QREN nº 13198/2010.

Published work

A. L. António, I. C. F. R. Ferreira, A. Bento, P. Teubig, M. Luísa Botelho *"Influence of gamma radiation on the antioxidant properties of edible chestnuts*" Isotope Technologies and Applications – New Horizons. NAARRI International Conference – NIC 2010; Vol. II: pp. 170-175.

[1] School of Agriculture, IPB.

Cork wastewater chemical evaluation

R. Melo, J.P. Leal[1], T. Silva, S. Cabo Verde and M. L. Botelho

The effects of ionizing radiation in the degradation of cork wastewater pollutants are being studied. Among the several complex present in cork wastewater, phenolic compounds play an important role on the wastewater toxicity. Radiolytic degradation of acetovanillone, as model compound, has been studied. Acetovanillone is known for its anti-inflammatory capabilities which are attributed to its ability to selectively prevent the formation of free radicals, oxygen ions and peroxides in the body. Acetovanillone is a NADPH oxidase inhibitor and it is effective in preventing the superoxide in human white blood cells. However, its presence in cork wastewater increases its toxicity. Irradiations were performed in the Co-60 experimental source (IRIS) at 2.1 kGy/h for the absorbed doses of 2 and 41 kGy. The obtained results show that almost all acetovanillone was degraded (~93%) at 41 kGy. The radiolytic products were identified by GC-MS with previous derivatization of samples. The main detected products were malonic acid, benzoic acid, oxalic acid and succinic acid.
In other point of view, phenolic content, antioxidant activity and the presence of gallic acid, ferulic acid and hydroquinone were determined in cork wastewater samples due to the potentiality reuse of phenolic compounds as antioxidants. Samples were collected in the cork boiling process and in the end of cork process. The obtained results show that phenolic content is higher in the cork boiling wastewater; however there is no difference between the samples concerning the antioxidant activity. Gallic acid was the only phenolic compound detected. Further studies will be done to better understand the cork wastewater samples as well as the potentiality of antioxidants extraction to reuse.

Xanthines scavenging capacity towards superoxide radical anion

P.M.P. Santos, A.J.S.C. Vieira[2] and M.L. Botelho

Oxidative stress in living tissues has been well characterised as the result of chemical changes in biological molecules (e.g. proteins, lipids and DNA) induced by endogenous or exogenous oxidising species. The agents of oxidative stress are UV or ionising radiations (γ- and X-rays) or chemical agents such as metabolites, xenobiotics and, mainly, free radicals, in particular the so-called reactive oxygen species (ROS) and reactive nitrogen species (RNS). Among the several classes of antioxidants studied to protect biological molecules against oxidative stress, xanthines play an important role. These compounds are found in human tissues and fluids (xanthine, xanthosine) or present in several beverages and foods like coffee, tea, chocolate and cola (e.g., caffeine, theobromine and theophylline) and their significant antioxidant effect can protect biological targets against damage by ROS, namely HO• hydroxyl radical. Other N-alkyl xanthines are used as cardiovascular and anti-inflammatory drugs, and their pharmacological activity is supposed to be related, at least partially, to their ability to scavenge ROS. Under oxidative stress conditions, dismutation of O2•− superoxide anion radical (a mild reactive species) leads to the formation of H2O2 which is known to produce HO• via Fenton reaction. Therefore, studies were conducted in order to evaluate the scavenging capacity of several N-methylated xanthines towards O2•−. This radical was produced by irradiating O2 saturated aqueous solutions of the studied xanthine and NaHCOO in the experimental 60Co chamber irradiation Precisa22 (10 kGy). Under these conditions, all primary radiolytic species are converted into O2•−. In each case, a predominant oxidation product different from the well-known corresponding uric acids was detected by HPLC-DAD. Further studies are in progress to characterize these products and to evaluate the influence of the methyl groups number and position of these compounds in the O2•− scavenging capacity.

---

[1] Chemical and Radiopharmaceutical Sciences (UCQR) Unit, ITN
[2] Requimte, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, Portugal

---

Microbial growth and inactivation patterns in art objects

S. Cabo Verde, I. Nunes, T. Silva, M. Oliveira, V. Dores, and M. L. Botelho

The assessment of bioburden is a major factor for a reliable evaluation of microbial inactivation. Facing different materials (e.g. ancient tiles, books and parchments), and the need to study the inactivation profile of its microbiota without damaging the sample, several methodologies were developed. The bioburden determination methodologies were outlined based on swab sampling technique and validated using artificial contamination with known microbial inoculums. For tiles, the bioburden ranged between 1 – 100 cfu/cm^2 and the microbial population dynamics were closely dependent of the exposition environment. The parchments bioburden were mainly composed by fungi with an average concentration of 10^4 cfu/m^2. The ancient book presented a bioburden ranging 100 – 1000 cfu/page depending of sampling site (cover, interior and back cover). Preliminary inactivation studies were performed at the Co-60 experimental source (IRIS) only after the complete knowledge of samples bioburden. Sub-lethal doses (1 – 5 kGy) were applied to verify microbial population inactivation profiles. Considering the applied low radiation doses it was achieved approximately 20% of population inactivation for the tested ancient art objects. Being aware of the historical value of the referred art objects, the study milestones were the microbial decontamination (not sterilization) for preservation proposes and the conservation of its characteristics. Higher radiation doses are being tested to guarantee a stable decontamination preservation and conservation of the ancient art objects. These studies are under the scope of the projects RADIART (1 BIC) and MYCHOARCHIVE (1 PhD; 1 McS).

Nuclear Instruments and Methods

João B. Manteigas

The strategy of the group involves activities in the following lines:

1. Modelling of radiation fields, calculation of neutron physic parameters, measurement of neutron cross-sections;
2. Modelling and applications of gas discharges;
3. Development of software for control and data analysis;
4. Design of electronic instrumentation for nuclear applications;
5. Instrumentation and technical assistance;
6. Co-operation with other institutions.

Modelling of radiation fields, calculation of neutron physic parameters

Monte Carlo calculations have been carried in the framework of the n_TOF Collaboration (ITN participation on the n_TOF-Ph2 experiment at CERN).

Measurement of neutron cross-sections

The analysis of the data for cross-section measurement, taken in the TOF spectrometer installed at the CERN, was carried out.

Modelling and application of gas discharges

1. The study of methane conversion by a non-thermal plasma produced by a dielectric barrier discharge system (DBD) to obtain Syngas and other hydrocarbons has continued with (a) the study of conversion, selectivities (for H_2, CO, CO_2, C_2H_6 and C_3H_8) and abilities in mixtures of CH_4/O_2 or CH_4/CO_2 with a rare gas (helium or argon), (b) coupling the plasma with a catalyst, either using commercial catalysis or catalysts developed on ITN, (c) study of the influence on voltage pulse shape, and (d) development of theoretical models to explain the variation of i) breakdown voltage with rare gas concentration and, ii) conversion with the specific input energy.
2. The development of a corona discharge system for processing of polymers by a non-thermal plasma was started.

Development of software for control and data analysis in nuclear spectrometry

The gamma spectrometry system developed in the group was adapted to measure the half-life of radionuclide with interest to nuclear astrophysics. The OpenSource *PyMCA* for X-ray analysis software was extended to support equipments based on EPICS.

Technical assistance in nuclear spectrometry

The group has started to provide a service of maintenance and repairing of HPGe detectors as well as technical advice in the installation of gamma spectrometry equipment.

Instrumentation and technical assistance

1. The main objectives are the development of equipment for ITN groups, fabrication of equipment for specific applications and assistance to industrial companies and scientific institutions as well as technical consulting.
2. The technical assistance takes mainly the forms of specialised consultant engineering advice, installation of nuclear gauges, including calibration maintenance and repair and recharging of gauges with imported radioactive sources.

Co-operation with other institutions

1. Plasma Physics Centre / Gas Electronics Group, IST;
2. ISEL, Dept. of Automation and Electrotechnical Engineering;
3. Comenius Univ., Dept. of Experimental Physics, Bratislava, Slovakia;
4. Nuclear Physics Centre of the University of Lisbon.
5. n_TOF collaboration, a consortium of several laboratories in Europe, USA and Japan.

Research Team

Researchers

J. MANTEIGAS, Aux., Group Leader
C. CRUZ, Aux.
I. F. GONÇALVES, Aux.
J. NEVES, Aux.
N. PINHÃO, Aux.

Students

C.M.CARRAPIÇO, PhD Student, IST (IG)
R. SARMENTO, PhD Student, IST (IG)
R.P.F. MENDES, Collaborator (NP, 20%)
A. JANECO, Project Grantee (NP)
S. BARROS, Project Grantee (IG)

Technical Personnel

T. JESUS, Electronic Technician
N. INÁCIO, Electronic Technician
M. Cabaça, Mechanical Technician
Gabriel Silva, Collaborator (20%)

Technical Assistance in the Field of Engineering Applications of Radiation and Radioisotopes

J.B. Manteigas, J. Neves, C. Cruz

Objectives

The main objectives are the development of equipment for internal groups, fabrication of equipment for specific applications and assistance to industrial companies and scientific institutions as well as technical consulting.

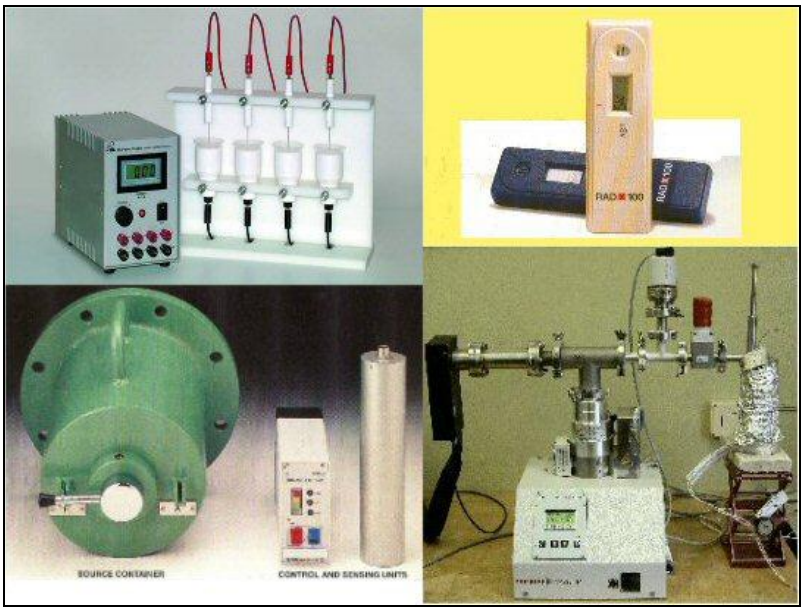
Results

A summary of the more relevant work carried out is:

(i) Collaboration in corrective and preventive maintenance of the "Ion Beam Laboratory" – TANDEM 3 MV" at the Physics Unit.

(ii) Optimization of the electronic device "Photo-multiplier Divider" for the BaF_2 calorimeter under the project n_TOF-Ph2 experiment at CERN.

DEVELOPMENT AND MAINTENANCE OF ELECTRONIC EQUIPMENT TO UFA, UPSR, URSN, UCQR AND UTR.



Summary of the more relevant Services/Equipments rendered in 2010

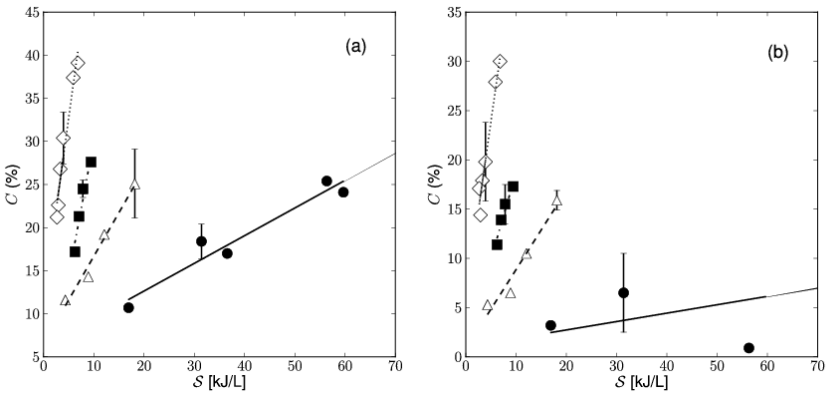
Activity	Qty	Client
Electronic Equipment Laboratory equipment for the determination of radioactive element traces by electrodeposition	1	NATS (Arabic Emirates)
	1	IAEA (Qatar)
	1	RPII (Ireland)
Electronic Equipment Personal Radiation Dosemeter Equipment	2	PORTUCEL/SOPORCEL (Portugal)
	2	TECNILAB (Portugal)
Electronic Equipment Gamma Level Indicator	4	CIMPOR (Souselas/Portugal)
Electronic Equipment Technical Assistance to Nuclear Equipment	21	EMA21 – Portucel/Soporcel (Portugal)
	20	EMA21 – Portucel/Soporcel (Portugal)
	1	EMA21 – Portucel/Soporcel (Portugal)
	6	SIDERURGIA NACIONAL (Portugal)
	6	SIDERURGIA NACIONAL (Portugal)
	32	EMA21 – Portucel/Soporcel (Portugal)
	4	MINISTÉRIO DA MARINHA (Portugal)
	4	ITN/URSN, ITN/UCQR, ITN/UPSR (Portugal)
Prices including TAX (VAT)		**Total Amount: 26 581,77 €**

Participation of ITN in the n_TOF-Ph2 experiment at CERN
I.F. Gonçalves, P. Vaz, C. Cruz, J. Neves, C. Carrapiço, R. Sarmento, S. Barros

The n_TOF-Ph2 project is the continuation of the involvement of ITN in the activities of the n_TOF Collaboration. The intention of the n_TOF Collaboration is to build a second beam-line and a new experimental area. ITN was involved in the commissioning of the new target, the construction of the new micro Megas detector and the data taken of 2010.

ITN was strongly involved in collaboration with INFN-Bari and CEA-Saclay in the following areas: Monte Carlo full and detailed simulation of the geometry of the new experimental area and the new spallation target, data analysis of the data on neutron capture on U-233, taken during 2004 using the BaF_2 calorimeter, data on neutron-induced fission on U-236, Am-241, Am-243 e Cm-245, taken during 2004 using the FIC ("Fast Ionization Chambers") detectors, analysis of the data sets relative to the neutron capture cross-sections, that were taken during 2009 using the BaF_2 calorimeter and the C6D6 detectors for the Fe and Ni isotopes (of relevance for innovative technological systems and for Nuclear Astrophysics), and electronics developments for the DAQ and the BaF_2 calorimeter.

Conversion of methane by a non-thermal plasma using rare-gas/CH_4/O_2 and rare-gas/CH_4/CO_2 mixtures on a dielectric barrier discharge system
J. Branco, N. R. Pinhão, A. Janeco, A. Ferreira, L. Redondo



Dependency of conversion for (a) CH_4 and (b) CO_2 with the specific energy for different values of helium concentration: •, ——: 55%, Δ, - - - -: 75%, ■, — · —: 85%, ◊, · · · · · ·: 95%. Symbols: experimental values, lines: regression curves. For each set of data only a representative error bar is indicated.

The conversion of methane by a non-thermal plasma produced by DBD (dielectric barrier discharge) was studied using mixtures of CH_4/O_2 or CH_4/CO_2 with a rare gas (helium or argon). The dependency of conversion, selectivities (for H_2, CO, CO_2, C_2H_6 and C_3H_8) and abilities on rare gas concentration and the specific input energy (SIE) were characterized. The variation of breakdown voltage with rare gas concentration and conversion with SIE were explained by theoretical models. The study of synergies between catalysts and the plasma was started using both commercial catalysts and catalysts developed by the Inorganic and Organometallic Chemistry Group. The influence of the electric excitation of the plasma on the results is under way using sinusoidal and pulsed power supplies.

Development of software for control and data analysis in nuclear spectrometry
R. P. F. Mendes, N. R. Pinhão

The development of Open Source software for gamma and X-ray spectrometry has continued with the (a) an extension of the software to the measurement of the half-life of radionuclide with interest to nuclear astrophysics, and (b) the extension of the Open Source software for analysis of X-ray spectra, *PyMCA*, to support online acquisition from equipments based on EPICS.