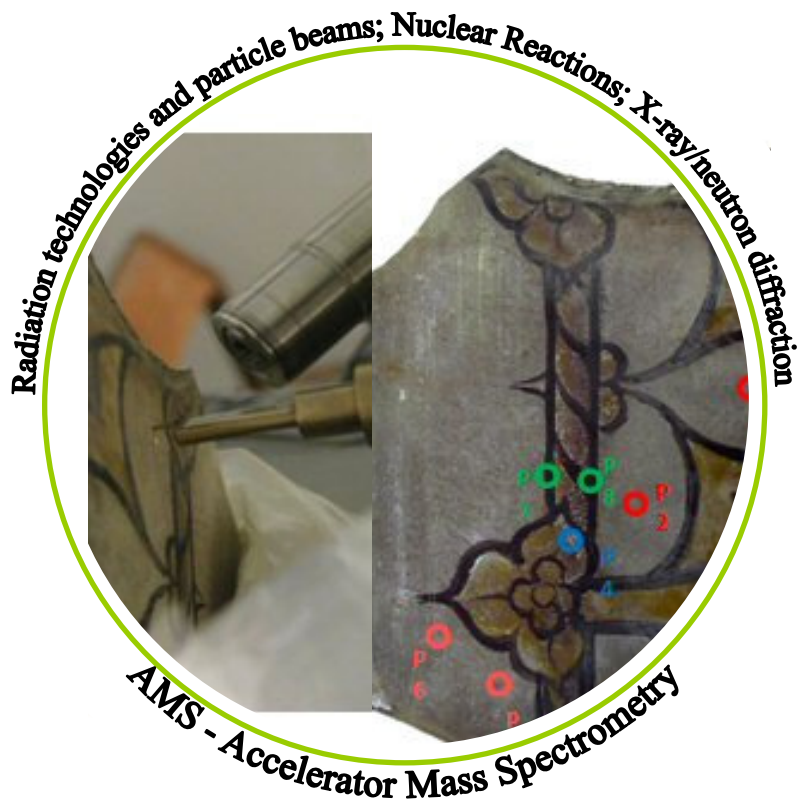


Physics and accelerators Unit



Physics and Accelerators Unit

Eduardo Alves

In 2009 the activities in the unit fostered its major goal: searching excellence biased by competence, innovation and creativity. The laboratories upgrading and new infrastructures installed under the Re-Equipment programme were completed and are fully operational.

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

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 open 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 (MA³T) equipped with a high-resolution, high-temperature diffractometer (*Hotbird*), particularly adapted to solve difficult problems in advanced materials and a D8

Discover 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 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 multidisciplinary 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 ⁶⁰Co (UTR) source 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.
L.C. ALVES, Aux.
L.M. FERREIRA, Aux., Contract
M.A. REIS, Aux.
M.L. BOTELHO, Aux.
M.T. PINHEIRO, Aux.
N.R. PINHÃO, Aux.

S. CABO VERDE, Aux., Contract (since July 2009)
V. CORREGIDOR (since July 2009)
V. DARAKCHIEVA, Aux., Contract

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) and XRD Laboratory. 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 XRD laboratory is fitted with two X-ray diffractometers, the High-temperature Hotbird diffractometer, and one Bruker AXS - D8 Discover diffractometer.

The group explores and develops ion beam techniques, X-ray diffraction and reflectometry techniques to study advanced materials e.g. wide band gap semiconductors nanostructures, oxides and other functional materials in collaboration with other groups. Among the wide band gap materials our major interests is focused on group nitrides and ZnO. These are the base of an emerging class of optoelectronic devices operating in the visible range of the electromagnetic spectrum. The potential of these materials for spintronics applications is being investigated with University of Aveiro and Faculty of Sciences of University of Lisboa. Our work aims at the optimization of the implantation conditions of magnetically and optically active dopants. In addition an intense research on the structural properties and Rare Earth doping of GaN/AlN quantum dots (QD) layers continued in collaboration with Universities of Aveiro, Grenoble and Strathclyde.

The work in insulators comprises the modification of the optical and structural properties of $\alpha\text{-Al}_2\text{O}_3$ by ion implantation.

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, was focused on the study of beryllium intermetallic and the study of surface erosion and redeposition processes as well as ^2H retention during JET operation.

Training and Education continued as a major commitment of the group firmly linked to research activities through the supervision of M.Sc. and Ph.D. thesis. Also worth to be mentioned is the new researcher joining the group under the Ciência 2008 programme.

All the referred activities have been 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).

These 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): 54

Conference and workshop contributions: 3 invited, 13 oral and 12 posters.

Running projects: 21

Research Team

Researchers^(*)

E. ALVES, Princ., Group Leader
R.C. DA SILVA, Princ.
L.C. ALVES, Aux. (75%)
U. WAHL, Princ. (70%)
K. LORENZ, Aux.
V. DARAKCHIEVA, Aux.
V. CORREGIDOR, Aux.
A. KLING, Aux. (15%)
N.P. BARRADAS, Princ. (15%)
A.C. MARQUES, Pos-doc. (FCT)
N. FRANCO, Pos-Doc, (FCT)
R. MARTINS, Pos-Doc, (FCT)

Students

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

Collaborators

C.P. MARQUES
H. CANACINH
J. VAZ PINTO
J. GABRIEL LOPES
L. REDONDO
M.R. DA SILVA
M. VILARIGUES
S. PEREIRA
SOEY H. SIE

Technical Personnel

J. ROCHA
F. BAPTISTA
P. PEREIRA

(*) Also members of CFNUL.

Erosion and re-deposition processes in JET tiles studied with ion beams

L.C. Alves, E. Alves, N.P. Barradas, P.A. Carvalho¹, R. Mateus¹, J.P.Coad², J. Likonen³

Introduction

The rising demand for energy associated with the need to reduce greenhouse gas emissions produced by fossil fuels makes nuclear fusion an important resource in the energy scenario for the future. Materials in fusion reactor are subject to high mechanical, thermal and magnetic loads. These are more prominent in plasma facing components which are exposed to extreme working conditions during the lifetime of fusion devices where erosion and re-deposition processes due to plasma interactions are dominant. This work addresses the behaviour of JET Outer Poloidal Limiters and Divertor tiles (Fig.1) under plasma irradiation.

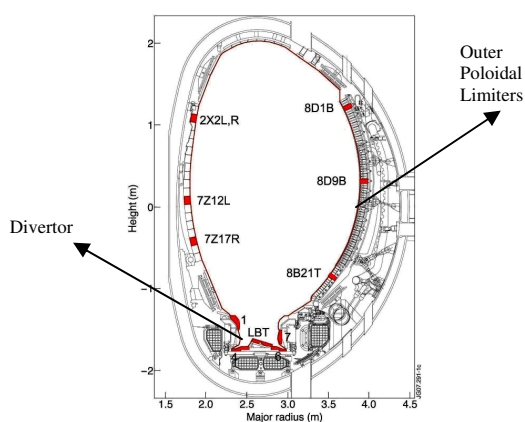


Fig.1 JET Chamber.

Results

Standard Carbon Fiber Composites and W coated tiles overlaid with a 10 micron layer of C on top were studied with RBS/PIXE to understand the erosion/redeposition processes occurring in this region of the reactor chamber. The surface morphology was studied with electron microscopy. The retention of hydrogen isotopes in the tiles was measured combining NRA and ERDA techniques (this is mostly ²H from the fuelling gas, but ³H is also present as a result of D-D fusion reactions and ¹H coming from the atmospheric exposure). Figure 2 shows a typical example of the results where the RBS, NRA and ERDA spectra obtained in the central region of tile 8D9B. Besides the presence of W, some other metal impurities and oxygen are present in the sample. Furthermore the profiles are continuous within the entire region probed by the ion beam. The ERDA and NRA results (inset of fig.2) confirm the presence of large amount of D distributed in the first microns of the samples. Since the energy of the ³He particles was 2.3 MeV the deuterium inside the samples is probed down to 6-7 μm. The thickness of the layer containing the impurities was measured by cross section analysis with a proton microbeam. The cross section maps for Ni and W show a complete overlap of the depth profile of the impurities in the first 10-15 μm of the samples. It was also observed an increase of the Ni

concentration at the ends of the tile (Fig. 3). These results are related with the plasma dynamics during operation: in the first moment the interaction happen with the tiles at the center, like tile 8D9B, causing net

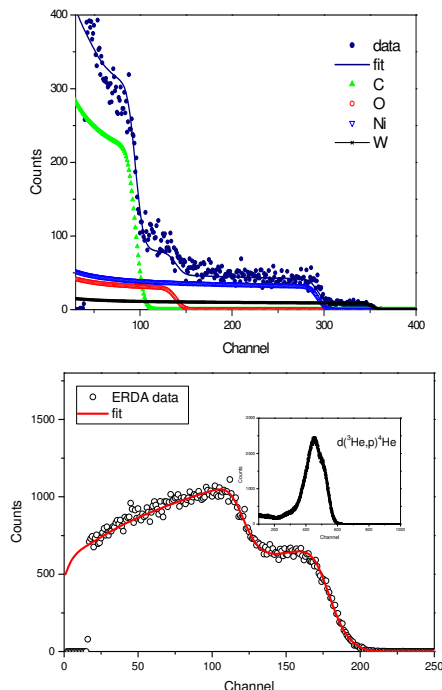


Fig.2 RBS, ERDA, NRA depth profiling for ¹H and ²H.

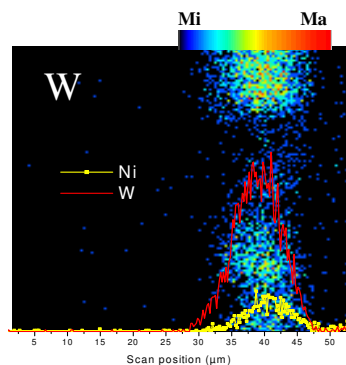


Fig.3 μPIXE cross-section analysis of a poloidal tile.

erosion, which is responsible for the removal of the 10 μm thick C coating. In this case even the W layer was removed since the composition of the first microns contains a mixture of elements from the plasma (Fe, Be, O and mostly Ni), arising from the inconel components of the chamber walls. The results also suggest that fuel retention occurs during the redeposition of the plasma impurities.

¹Associação Euratom/IST, IPFN, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.
²Culham Science e Centre Euratom/UKAEA-Fusion Association, OX14 3DB, UK.
³Association Euratom-TEKES, PO box 1000, 02044 VTT,Espoo, Finland.

Influence of temperature and plasma composition on deuterium retention in refractory metals**E. Alves, L.C. Alves, N.P. Barradas, R. Mateus¹, P.A. Carvalho¹, G.M. Wright²*

Work has been performed for the study of tungsten and molybdenum metals exposed to high flux densities ($\sim 10^{24}$ D/m².s) and low temperature ($T_e \sim 3$ eV) deuterium plasmas in Pilot-PSI irradiation facility. The hydrogenic retention in polycrystalline W and Mo targets was studied with ³He nuclear reaction analyses (NRA) and elastic recoil detection analysis (ERDA). The NRA results clearly show a two dimensional radial distribution of the deuterium with a minimum at the center and a maximum close to the edge of the targets. These distribution correlates well with the thermal profile of the sample surface, where a maximum of ~ 1600 K was measured at the center decreasing to ~ 1000 K in the edges. A maximum deuterium fluence retention of 5×10^{15} D/cm² was measured. The values of the retained fractions ranging from 10^{-5} - 10^{-6} were measured with thermal desorption spectroscopy (TDS) and compares well with IBA results. Moreover the presence of C in the plasma and its codeposition increases the retention of D in the region where a C film is formed. Both NRA and TDS results show no clear dependence of retention on incident fluence suggesting the absence of plasma related traps in W under these conditions.

¹ EURATOM/IST Association, Portugal; ² EURATOM/FOM Association, The Netherlands.

Enhancement of the photocatalytic nature of nitrogen-doped PVD-grown titanium dioxide thin films*E. Alves, N.P. Barradas, C.J. Tavares¹, S.M. Marques¹, T. Viseu¹, V. Teixeira¹, J.O. Carneiro¹, F. Munnik²*

In order to increase the photocatalytic efficiency of titania coatings it is important to enhance the catalysts absorption of light from the solar spectra. Bearing this in mind, a reduction of the titania semiconductor band-gap has been successfully attempted by using nitrogen doping from a co-reactive gas mixture of N₂:O₂ during the titanium sputtering process. The as deposited thin films were mostly amorphous, however after a thermal annealing at 500 °C in vacuum the crystalline polymorph anatase and rutile phases have been developed, yielding an enhancement of the crystallinity. Spectroscopic ellipsometry experiments enabled determining the refractive index of the films as a function of wavelength, whilst alloyed optical transmittance estimating indirect band-gap of these coatings, which decreases as the N-doping increasing. Combined RBS and HI-ERDA experiments, and subsequent spectra refining, revealed the atomic composition, thickness and level of atomic nitrogen doping of the titania layers. It was found that for a maximum of 1.19 at% of nitrogen in the titania lattice there was a clear improvement on the UV-photocatalytic efficiency towards degrading a chosen dye, acting as a pollutant.

¹ Centre of Physics - GRF, Univ. of Minho, 4800-058 Guimarães, Portugal.

² Forschungszentrum Dresden Rossendorf, D-01314 Dresden, Germany.

The role of composition, morphology and crystalline structure in the electrochemical behaviour of TiN_x thin films for dry electrode sensor materials*E. Alves, N. P. Barradas, L.T. Cunha^{1,2}, P. Pedrosa^{1,2}, C.J. Tavares², F. Vaz² and C. Fonseca¹*

A morphological, structural and electrochemical study of titanium nitride (TiN_x) thin films, obtained by DC reactive sputtering on titanium substrates, was carried out for a wide range of compositions ($0 < x < 1.34$) aiming at selections the best coatings for dry biomedical electrodes. The films displayed a columnar-type structure, with morphologies strongly dependent of the composition: a compact and smooth surface was found for the Ti-rich films, ($x < 1$), whereas the N-rich films, ($x \geq 1$) displayed a rough and porous structure. The electrochemical study of the TiN_x films was performed in synthetic sweat, aiming at simulating contact with skin. The voltammetric analysis showed anodic currents higher for TiN_x films than for titanium under low and medium polarization potentials, whereas for potentials beyond 2 V the blocking behaviour of the TiN_x films allowed them to display lower current values. The passive dissolution currents in the sub- μ A/cm² range and the charge transfer resistances of the order of the M Ω proved the excellent stability of all films in sweat conditions. Finally, the electrochemical noise analysis showed that the near-stoichiometric and N-rich films display the lowest noise, being therefore the most suitable for electrode applications, where signals in the microvolt range, such as the electroencephalographic (EEG) signals, are to be monitored.

¹ INEB – Inst. de Engenharia Biomédica, Divisão de Biomateriais; Univ. do Porto, 4150-180 Porto, Portugal.

² Physics Dept., Univ. of Minho, Campus de Gualtar, 4710-057 Braga, Portugal.

Strain dependence electrical resistance and cohesive strength of ITO thin films deposited on PVDF

L. Rubio-Peña¹, C. Oliveira², L. Rebouta², S. Lanceros-Mendez², C. Tavares², E. Alves

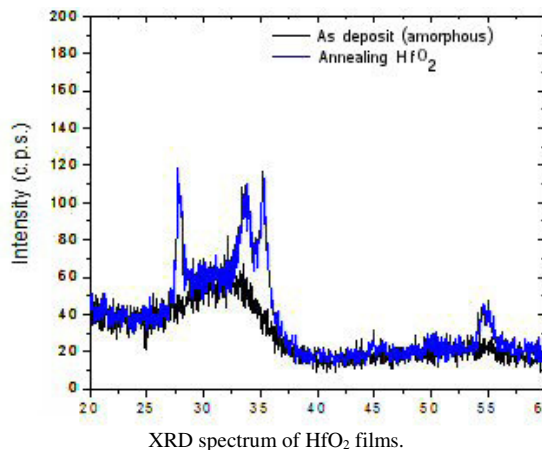
Transparent conducting Indium Tin Oxide (ITO) films have been deposited, by dc and pulsed dc magnetron sputtering, on glass and electroactive polymer - poly vinylidene fluoride – (PVDF) substrates. PVDF substrates with thicknesses of 28 μm and 110 μm were used and samples were prepared at room temperature varying the partial pressured oxygen. The deposition rate was about 20 nm/min and the thicknesses of the films were about 100 nm. Electrical resistivity around 8.4x10⁻⁴ Ω.cm have been obtained for films deposited on glass, while a resistivity of 1.7x10⁻³ Ω.cm have been attained in similar coatings on PVDF. Tensile tests were performed in order to investigate the cohesive strength of the coating and the influence of mechanical strain on the electrical properties. During the elongation test, the crack onset strain, the crack density at fragmentation saturation, as well as, the evolution of the sheet resistance has been measured. The crack onset strain is similar for the different ITO coatings and is unaffected by the substrate thickness (28 and 110 μm). The crack onset strain occurs for nominal strains around 2 %. The sudden increase in the resistance of the sample correlates with onset of cracks. The cohesive strength of the coating was evaluated from the crack onset strain and found to be between 2.8 GPa and 3.0 GPa.

¹ Univ. of Cadiz, Engineering School, C/ Chile, 1. 11002 Cádiz, Spain.
² Univ. of Minho, Physics Dept., Azurém, 4800-058 Guimarães, Portugal.

Study of multicomponent HfO₂-Al₂O₃ Gate Dielectrics

Z.L. Pei¹, L. Pereira¹, G. Gonçalves¹, P.Barquinha¹, A.M.B. Rego², R. Martins¹, E. Fortunato¹, N. Franco, E. Alves

Hafnium oxide–aluminum oxide (HfAlO) dielectric films were cosputtered using HfO₂ and Al₂O₃ targets, and their properties are studied in comparison with pure HfO₂ films. The X-ray diffraction studies confirmed that the HfO₂ films are nanocrystalline with monoclinic phase. The as-deposited HfAlO films with a chemical composition (HfO₂)_{0.86}(Al₂O₃)_{0.14} are amorphous even after annealing at 500 °C. Further, the cosputtered films show a slight reduction in leakage current. The leakage current density may be significantly reduced below 3x10⁻¹⁰ Acm⁻² at an electric field of 0.25 MVcm⁻¹ when applying the proper radio-frequency bias to the substrate.



XRD spectrum of HfO₂ films.

¹ Centro de Investigação de Materiais and Centro de Excelência de Micro e Optoelectrónica de Processos, Faculdade de Ciências e Tecnologia, Univ. Nova de Lisboa, 2829-516 Caparica, Portugal.
² Centro de Química–Física Molecular and Inst. of Nanosciences and Nanotechnology, 1049-001 Lisboa, Portugal.

Study of diffusion and oxidation processes in Zr/Hf/Zr trilayers during annealing

A.Kling, J.C. Soares¹

The Zr/Hf system is highly interesting due its various technical applications, e. g. the production of gate oxide layers with high dielectric coefficients by oxidation of Zr/Hf multilayers. For annealing under air or oxygen atmosphere the desired oxidation process may compete with unwanted metal diffusion triggered by the high chemical similarity of the two metals. Therefore the influence of these effects at low (500 °C) and high (1200 °C) annealing temperatures were studied by RBS in a Zr-Hf-Zr trilayer system (each metal layer 50 nm thick). For the measurements He⁺ ion beams with energies of 2.0, 2.3 and 2.525 MeV were used. The 2.525 MeV He⁺ beam allowed using the small resonance in the scattering MeV ¹⁶O occurring at 2.484 MeV and which facilitates the detection of oxygen in the surface region of the samples. In the case of low temperature annealing it is found that the oxidation progresses slowly starts from the surface while the interfaces between the metal layers remain stable. On the other hand, high temperature annealing leads to an asymmetric Hf-diffusion into the surface and the interior Zr-layer which is provoked by anomalous diffusion due to a phase transition in Zr. This results in two mixed Zr-Hf oxide layers sandwiching a pure HfO₂ layer.

¹ Centro de Física Nuclear da Univ. de Lisboa, Portugal.

Photosensitivity of nanocrystalline ZnO films grown by PLD

C.P. Marques, E. Alves, R. Ayouchi¹, L. Bentes¹, C. Casteleiro¹, O. Conde², A.M.C. Moutinho³, H.P. Marques³, O. Teodoro³, R. Schwarz¹

Due to their direct band gap of 3.3 eV and their high electrical conductivity, thin films of zinc oxide (ZnO) are widely used in practical applications such as transparent conducting oxides for flat panel displays, solar cells, ultraviolet (UV) lasers and thin films transistors. The properties of ZnO thin films grown by laser ablation of ZnO targets on (0 0 0 1) sapphire (Al₂O₃), under substrate temperatures around 400 °C were analysed. The films were characterized by different methods including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and atomic force microscopy (AFM). XPS analysis revealed that the films are oxygen deficient, and XRD θ - 2θ scans and rocking curves indicate that the ZnO thin films are highly *c*-axis oriented. All the films are ultraviolet (UV) sensitive. The films deposited at higher temperatures show crystallite sizes of typically 500 nm, a high dark current and minimum photoresponse. In all films we observe persistent photoconductivity decay. More densely packed crystallites and a faster decay in photocurrent is observed for films deposited at lower temperature. Sensitivity is maximum for the films deposited at lower temperature.

¹ Dept. de Física, Inst. Superior Técnico, Av. Rovisco Pais 1, P-1049-001 Lisboa, Portugal.

² Dept. de Física, Fac. de Ciências da Univ. de Lisboa, P-1749-016 Lisboa, Portugal.

³ CeFiTec, Dept. de Física, Univ. Nova de Lisboa, P-2829-516 Caparica, Portugal.

Structural and optical properties of Zn_{0.9}Mn_{0.1}O/ZnO core-shell nanowires designed by pulsed laser deposition

L.C. Alves, N. Franco, and E. Alves, V.E. Kaydashev,¹ E.M. Kaidashev,¹ M. Peres,² T. Monteiro,² M.R. Correia,² N.A. Sobolev²

Core-shell nanowires (NWs) have recently attracted considerable attention as possible candidates for building blocks of nanoscale devices in photonics, spintronics, and magneto-optics. Core-shell ZnO/ZnMnO nanowires on *a*-Al₂O₃ and GaN (buffer layer)/Si (111) substrates were fabricated by pulsed laser deposition using a Au catalyst. Two ZnO targets with a Mn content of 10% were sintered at 1150 and 550 °C in order to achieve the domination of paramagnetic MnO₂ and ferromagnetic Mn₂O₃ phases, respectively. RBS and XRD reveal that the decrease in the PLD target synthesis temperature from 1150 °C to 550 °C leads to a change in the target compound and to a change in the nanowire shell morphology from smooth to snowflake like. Cluster mechanism of laser ablation is a source of possible incorporation of secondary phases to the wire shell. Raman spectroscopy under excitation by an Ar⁺ laser revealed a broad peak related to the Mn-induced disorder and a red shift in the A₁-LO phonon. Besides the UV emission, a vibronic green emission band assisted by a ~71 meV LO phonon is also observed in the photoluminescence spectra. Core-shell structures with smooth shells show a high exciton to green band intensity ratio (~10) even at room temperature.

¹ Southern Federal Univ., 344090 Rostov-on-Don, Russia.

² Dept. de Física and I3N, Univ. de Aveiro, 3810-193 Aveiro, Portugal.

Characterization of mesoporous ZnO:SiO₂ films obtained by sol-gel method

R.M.S. Martins, N. Franco, V. Musat¹, A. Mücklich², E. Fortunato³

ZnO:SiO₂ films are intensively investigated for optical and electronic applications. Additionally, porous ZnO:SiO₂ films are very interesting as catalyst and gas sensing materials. The present study reveals the effect of the withdrawal speed on the structure, microstructure and optical properties of mesoporous ZnO:SiO₂ films obtained by sol-gel method. The morphology of the films was investigated by atomic force microscopy and the overall structure was studied by X-ray diffraction. The structure and size of the zinc oxide nanoparticles embedded in the silica matrix were investigated in more detail by transmission electron microscopy. These techniques have shown ZnO:SiO₂ films with cracks-free mesoporous morphology and high efficient embedding of ZnO nanoparticles exhibiting predominant (100) orientation. Furthermore, the studies on the optical properties revealed a variation of the optical transmittance (in visible and near infrared) and the optical band gap value with withdrawal speed. It was shown that ZnO:SiO₂ nanocomposites films possessing ZnO particles (100) oriented, with possible special applications in non-linear optics, could be prepared by low-temperature crystallization sol-gel method.

¹ Center of Nanostructures and Functional Materials (CNMF), "Dunarea de Jos" Univ. of Galati, 47 Domneasca, Galati, Romania.

² Inst. of Ion Beam Physics and Materials Research, Forschungszentrum-Dresden-Rossendorf, P.O.Box 510119, Dresden, Germany.

³ CENIMAT/I3N, Faculty of Sciences and Technology, New Univ. of Lisbon, Campus da Caparica, 2829-516 Caparica, Portugal.

Electrical, structural and optical characterization of copper oxide thin films as a function of post annealing temperature

V. Figueiredo¹, E. Elangovan¹, G. Gonçalves¹, N. Franco, E. Alves, S.H.K. Park², R. Martins¹, E. Fortunato¹

Copper oxide (CO) is a proven p-type transparent conducting oxide (TCO) semiconductor for fabricating variety of devices. The CO films in the present study were obtained through the conventional thermal oxidation of electron beam evaporated metallic copper, and the physical properties of the films were studied in order to find the possibility to use them in p–n junction-based applications. Copper oxide thin films were obtained by annealing at temperatures ranging between 100 °C and 450 °C. XRD studies confirmed that the cubic Cu phase of the as deposited films changes into single cubic Cu₂O phase and single monoclinic CuO phase, depending on the annealing conditions. The crystallite size is varied between 12 nm and 31 nm and the lattice parameters of cubic Cu and Cu₂O phases are estimated to 0.360 nm and 0.426 nm, respectively. The films with Cu₂O phase showed p-type characteristics and the conductivity decrease linearly with decreasing temperature, which has confirmed the semiconductor nature of the deposited films. The calculated activation energy varies between 0.10 eV and 0.16 eV and the direct band gap was estimated between 1.73 eV and 2.89 eV.

¹ Materials Science Dept., CENIMAT-13N and CEMOP-UNINOVA, FCT-UNL, Campus da Caparica, 2829-516 Caparica, Portugal.

² Basic Research Lab., Electronics and Telecommunications Res. Inst., Transparent Electronics Team, Yusong-gu, Daejeon, 305-350, Korea.

Magnetism in wide band gap semiconductors implanted with non-magnetic ions

R.P. Borges¹, M.M. Cruz¹, M. Godinho¹, P. Venezuela², M.D. Moreira², A.T. Costa², N. Franco, R.C. da Silva

Single crystals of ZnO, TiO₂ and LaAlO₃ have been implanted with Ar ions of 100 keV energy and fluences of 1×10¹⁷ and 2×10¹⁷ cm⁻² at room temperature. The Ar implanted crystals displayed a weak ferromagnetic-like behaviour between 10 K and 400 K. The results show that this behaviour cannot be assigned to impurities or the formation of secondary phases or aggregates and is ascribed to the lattice defects induced by the implantation. Band structure calculations (spin polarised density functional calculations) were performed in the case of ZnO considering Zn interstitials and O vacancies. No net magnetic polarisation was found for O vacancies, but in the case of Zn vacancies a magnetic moment of 1 μB was obtained. Nitrogen implanted rutile single crystals also exhibited ferromagnetic behaviour up to 380 K. By annealing at 1073 K recovery of the lattice structure lead to the decrease of the ferromagnetic moment in the case of Ar-implanted samples, while it did not change significantly in the samples implanted with nitrogen.

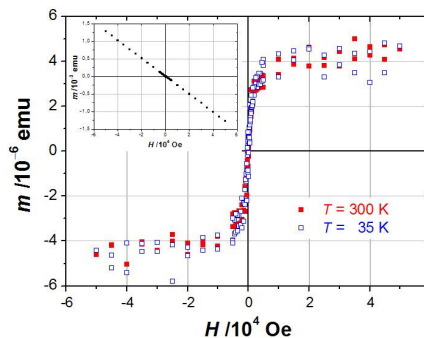
¹ CFMC-Univ. de Lisboa, and Dep. Física, Fac. Ciências, Univ. Lisboa, Campo Grande, Ed. C8, 1749-016 Lisboa, Portugal..

² Inst. de Física, Univ. Federal Fluminense, 24210-346 Niterói, RJ, Brazil.

Structural properties and magnetic behaviour of ZnO implanted with Co, Ni and Mn

R.P. Borges¹, M.M. Cruz¹, M. Godinho¹, U. Wahl, E. Alves, R.C. da Silva

Investigation of the behaviour of Co, Ni and Mn ions implanted in ZnO continued, yielding new results. ZnO single crystals were doped with Co, Ni or Mn by ion implantation with fluences of 1, 2, 5×10¹⁶ cm⁻² and 1×10¹⁷ cm⁻² and energy 150 keV. As-implanted samples display different magnetic behaviours that are related with the atomic concentration and implanted species: single domain Ni magnetic particles form while no evidence of aggregation is found for Co and Mn ions that remain diluted in the matrix. Thermal treatment induces formation and growth of metallic aggregates: it promotes aggregation of Co ions that were diluted in the matrix immediately after implantation, while for higher fluence Ni implantations it induces growth of the aggregates formed by implantation. Remarkable agreement was found between standard X-ray and magnetisation measurements: samples where no metallic phases can be observed are always paramagnetic while the observation of diffraction peaks associated with the metallic aggregates is always associated with superparamagnetism or ferromagnetism.



¹ CFMC-Univ. de Lisboa, and Dept. de Física, Fac. de Ciências, Campo Grande, Ed. C8, 1749-016 Lisboa, Portugal.

Rare earth doping of ZnO epitaxial layers by ion implantation

S.M.C. Miranda, K. Lorenz, E. Alves, H.D. Sun¹, M. Peres², T. Monteiro², T. Geruschke³, R. Vianden³

Zinc Oxide (ZnO), being a transparent wide band gap semiconductor ($E_g = 3.437$ eV at 2 K) with wurtzite structure, presents itself as a versatile oxide for transparent electronics and interesting host for optically active rare earth (RE) ions. In this work, ZnO epilayers grown by metal organic vapour phase epitaxy on (0001) sapphire substrates were doped with Pr and Eu by ion implantation, with fluences of 1×10^{13} cm⁻² and 1×10^{15} cm⁻². The as-implanted samples were either annealed in air for 20 minutes in a tube furnace or rapid thermal annealed (RTA), for 2 minutes, in a nitrogen atmosphere. The samples were characterized by RBS-C. The presented results indicate that in the as-implanted samples most of the RE are incorporated into substitutional Zn-sites. Furnace annealing at 1000 °C recovers the implantation damage but leads to an out-diffusion of the RE. RTA was then tried and results in less out-diffusion but lattice damage is not fully recovered at 1000 °C and the RE ions are now found mainly in interstitial sites. No RE emission was found after annealing upon excitation above the band gap using a HeCd laser.

¹ Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological Univ., Singapore.

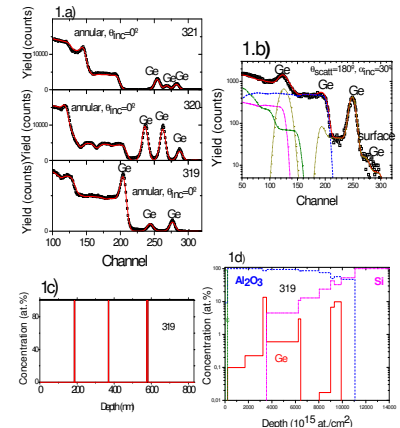
² Dept. de Física e I3N, Univ. de Aveiro, Portugal.

³ Helmholtz-Inst. für Strahlen-und Kernphysik, D-53115 Bonn, Germany.

Multilayers of Ge nanocrystals embedded in Al₂O₃ matrix: vibrational and structural studies

E. Alves, N.P. Barradas, S.R.C. Pinto¹, Pedro Sá¹, A. Khodorov¹, A.G. Rolo¹, M.J.M. Gomes¹, A. Chahboun^{1,2}, Maja Buljan³, R.J. Kashtiban⁴, U. Bangert⁴

Nonvolatile memory (NVM) devices with floating gate structure are being used widely at present for which a long retention times are very important. Nanocrystals (NCs) floating gate has been demonstrated to improve the retention time as compared with conventional continuous floating gate. Ge NCs are good candidates for this function due to their smaller bandgap which promotes better retention and faster writing/erasing times. A set of [Al₂O₃/Ge/Al₂O₃] multilayers were grown by pulsed laser ablation with different layer thicknesses and repetition. The grown samples were annealed at 900 °C to encourage the formation of Ge nanocrystals. RBS (figure) and TEM confirmed the multilayers system. GISAXS demonstrates the presence of Ge nanoclusters. Room temperature I-V measurements showed a weak carriers trapping in the system. This was explained by the leakage provoked by Ge diffusion through the multilayers.



a) RBS spectrum for (Ge/Al₂O₃)x3 multilayer as grown. Fits assuming the Ge is organised in QDs (solid lines) and in mixed Al₂O₃ layers (dashed lines) are shown b) RBS spectrum after annealing and corresponding fitted depth profile for the same sample as grown c) and after annealing d).

¹ Physics Dept., Univ. of Minho, 4710 – 057 Braga, Portugal.

² Physics Dept., Dhar Mehraz Sciences Faculty, BP 1796, Fès, Morocco.

³ Charles Univ. in Prague, Ke Karlovu 5, 121 16 Prague, Czech Republic, Rudjer Boskovic Inst., Bijenicka 54, 10000 Zagreb, Croatia.

⁴ Nanostructured Materials Res. Group, School of Materials, The Univ. of Manchester, P.O. Box 88, Manchester, M1 7HS, UK.

Probing alloy disorder in AlGa_xN ternary alloys

K. Lorenz, E. Alves, T. Geruschke¹, R. Vianden¹, K. Wang², K.P.O'Donnell², B. Hourahine², R. W. Martin², I.M. Watson³

The alloy and lattice disorder as well as the annealing behaviour of Al_xGa_{1-x}N films on sapphire substrate after implantation was studied using two different approaches. Perturbed angular correlation (PAC) measurements using the ¹⁸¹Hf(¹⁸¹Ta) probe show that the strength of the electric field gradient, which is caused by the wurtzite structure of the host lattice at the probe site, varies linearly with the concentration x of AlN in the ternary compound. The uniformity of this hyperfine interaction has its minimum at x~0.6. The photoluminescence linewidth of implanted optically active Eu ions was seen to have a maximum for x~0.6 decreasing for lower and higher AlN contents. Both techniques were proved valid to study alloy and lattice disorder in the AlGa_xN ternary and showed a maximum disorder in the same compositional region as seen for excitons in this alloy.

¹ Helmholtz-Institut für Strahlen-und Kernphysik, D-53115 Bonn, Germany.

² Dept. of Physics, SUPA, Univ. of Strathclyde, Glasgow, G4 0NG, U.K.

³ Inst. of Photonics, SUPA, Univ. of Strathclyde, Glasgow G4 0NW, U.K.

Structural and photoluminescence studies of erbium-implanted nanocrystalline silicon thin films*E. Alves, M. F. Cerqueira¹, P. Alpuim¹, S. A. Filonovich¹, A. G. Rolo¹, G. Andres¹, J. Soares², A. Kozanecki³*

A large improvement efficiency in light emission from Si-based materials is required if fully integrated silicon optoelectronics is to become reality in the near future. Rare-earth doping of silicon has consistently attracted scientific interest as a strategy to achieve this goal, together with the exploitation of quantum confinement in silicon nanocrystals. Hydrogenated amorphous and nanocrystalline silicon thin films deposited by hot wire (HW) and radio-frequency plasma-enhanced chemical vapour deposition (RF-PECVD) were erbium-implanted. Their pre-implantation structural properties and post-implantation optical properties were studied and correlated. After 1 h annealing at 150 °C in nitrogen atmosphere only amorphous films showed photoluminescence (PL) activity at 1.54 μm, measured at 5 K. After further annealing at 300 °C for 1 h, all the samples exhibited a sharp PL peak positioned at 1.54 μm, with a FWHM of ~5 nm. Amorphous films deposited by HW originated a stronger PL peak than corresponding films deposited by RF, while in nanocrystalline films PL emission was much stronger in samples deposited by RF than by HW. There was no noticeable difference in Er³⁺ PL activity between films implanted with 1×10^{14} cm⁻² and 5×10^{15} cm⁻² Er fluences. Severe PL quenching was observed in all samples when measured at RT. PL temperature dependence study indicates that the hydrogen content plays an important role on the Er³⁺ PL quenching.

¹ Dept. de Física, Univ. do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal.

² Dept. de Física, Univ. de Aveiro, Campus de Santiago, 3700 Aveiro, Portugal.

³ Polish Academy of Sciences, Inst. of Physics, 02668 Warsaw, Poland.

Europium implantation and high temperature annealing of AlN*K. Lorenz, E. Alves, T. Monteiro¹, M. Peres¹, A.J. Neves¹, F. Gloux², P. Ruterana², M. Boćkowski³*

AlN was implanted with 300 keV Eu ions within a wide fluence range from 4×10^{14} cm⁻² to 1.4×10^{17} cm⁻². The damage build-up was investigated by RBS-C. Sigmoidal shaped damage build-up curves indicate efficient dynamic annealing. A regime with low damage increase for fluences below 10^{15} cm² is followed by a strong increase for intermediate fluences. For the highest fluences the damage curve rises slowly until a buried amorphous layer is formed. High temperature annealing was performed in nitrogen atmospheres at low pressure (1300 °C, 10^5 Pa) or at ultra-high pressure (1450 °C, 10^9 Pa). Implantation damage was found to be extremely stable and annealing only resulted in slight structural recovery. For high fluences out-diffusion of Eu is observed during annealing. Nevertheless, photoluminescence (PL) measurements show intense Eu-related red light emission for all samples with higher PL intensity for the high temperature high pressure annealing.

¹ Dept. de Física and I3N, Univ. de Aveiro, Portugal.

² CIMAP, UMR 6252, CNRS-ENSICAEN-CEA-UCBN, 6 Boulevard du Marechal Juin, 14050 Caen Cedex, France.

³ Inst. of High Pressure Physics Polish Academy of Sciences 01-142 Warsaw, Poland.

Annealing and implantation studies of self-assembled GaN quantum dots*S. Magalhães, K. Lorenz, E. Alves, M. Peres¹, A.J. Neves¹, T. Monteiro¹, H. Okuno-Vila², V. Fellmann³, C. Bougerol³, B. Daudin³*

The influence of post-growth thermal annealing and ion implantation on the structural and optical properties of self-assembled GaN quantum dots (QD) in GaN QD/AlN superlattices was studied. X-ray techniques suggest smooth and high quality interfaces of the stacked multilayer structures for the as-grown, annealed and implanted samples. High-angle annular dark field images by scanning transmission electron microscopy show an intermixing between the GaN QD and AlN spacers after annealing and the QD emission shifts to lower energies (red shift) for big dots and to higher energies (blue shift) for small dots, reflecting two competitive processes taking place during the thermal annealing. Implantation leads to an increase of the *c* lattice parameter within the implanted region of the superlattice which is partly reversed during post-implant thermal annealing. Implantation induced intermixing of the layers is observed.

¹ Dept. de Física e I3N, Univ. de Aveiro, Portugal.

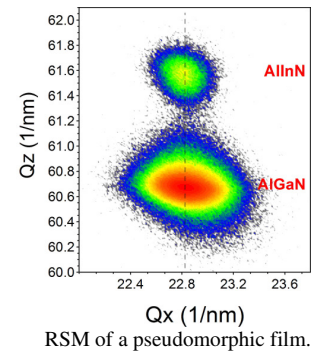
² CEA Grenoble, Département de Recherche Fondamentale sur la Matière Condensée/SP2M, Grenoble 38054, France.

³ CEA-CNRS, Inst. Nanosciences et Cryogénie, 17 rue des Martyrs, Grenoble 38054, France.

Comparison of the structural properties of $\text{Al}_{1-x}\text{In}_x\text{N}$ films grown on $\text{Al}_{1-y}\text{Ga}_y\text{N}$ templates with different AlN contents

S. Magalhães, K. Lorenz, N. Franco, E. Alves, S. Pereira¹, R.W. Martin², K.P.O'Donnell², I.M. Watson³

The group III nitride semiconductors with their wide and direct band gap are interesting for the fabrication of optoelectronic devices. The purpose of this work is to compare the structural properties of AlInN films grown on GaN and AlGaN buffer layers with different in-plane lattice constants. 100 nm thick AlInN films were grown by metal organic vapour phase epitaxy on pre-grown $\text{Al}_{1-y}\text{Ga}_y\text{N}$ templates with AlN contents varying from 0 % to 33 %. Structural, compositional and morphological analyses were performed using RBS/C, XRD and AFM. The AlInN alloy films grown on GaN have a smoother surface than those grown on AlGaN and have a lower RBS/C minimum yield in the growth direction indicating a higher crystalline quality. There are no lateral AlInN composition variations but some defect phenomena change the alloy crystal quality for different sections of the wafer. XRD reciprocal space maps reveal the absence of macroscopic tilts and show that the films are completely strained (pseudomorphic to the different buffer layers).



¹ CICECO, Dept. de Física, Univ. de Aveiro, 3810-193 Aveiro, Portugal.

² Dept. of Physics, SUPA, Univ. of Strathclyde, Glasgow, G4 0NG, U.K..

³ Inst. of Photonics, SUPA, Univ. of Strathclyde, Glasgow G4 0NW, U.K..

Electron accumulation at nonpolar and semipolar surfaces of InN

V. Darakchieva, M. Schubert,¹ T. Hofmann,¹ W. J. Schaff,² C.L. Hsiao³, L.C. Chen,³ Y. Takagi,⁴ Y. Nanishi⁴

A peculiar intrinsic electron accumulation was found to occur at polar (0001) oriented InN films. The surface electron accumulation complicates the electrical measurements masking the true bulk conductivity, which hinders the assessment of doping in the material, in particular p-type doping. Understanding the surface electron accumulation properties is a key to make further progress in this direction. In particular, surfaces other than the polar c-plane should be explored in order to probe the possibility to minimize or eliminate the surface electron accumulation density. We have studied the free electron properties of nonpolar (11-20)- and semipolar (10-11)-oriented wurtzite InN films by generalized infrared ellipsometry (GIRSE). We have demonstrated the sensitivity of GIRSE to the surface charge accumulation layer and find a distinct surface electron accumulation to occur at all surfaces. The obtained surface electron sheet densities are found to vary from $0.9 \times 10^{13} \text{ cm}^{-2}$ to $2.3 \times 10^{14} \text{ cm}^{-2}$ depending on the surface orientation and bulk electron concentration. The upper limits of the surface electron mobility parameters of $417 \text{ cm}^2/\text{Vs}$ - $644 \text{ cm}^2/\text{Vs}$ are determined and explained in the light of electron confinement at the surface.

¹ Univ. of Nebraska-Lincoln, Lincoln, USA.

² Dept. of Electrical and Computer Engineering, Cornell Univ., USA.

³ National Taiwan Univ., Taiwan.

⁴ Dept. of Photonics, Ritsumeikan Univ., Japan.

Determination of the stiffness constants of $\text{In}_x\text{Al}_{1-x}\text{N}$ ($0 \leq x \leq 1$) alloys

V. Darakchieva, F. Tasnadi¹, M-Y. Xie, I.A. Abrikosov¹, L. Hultman¹

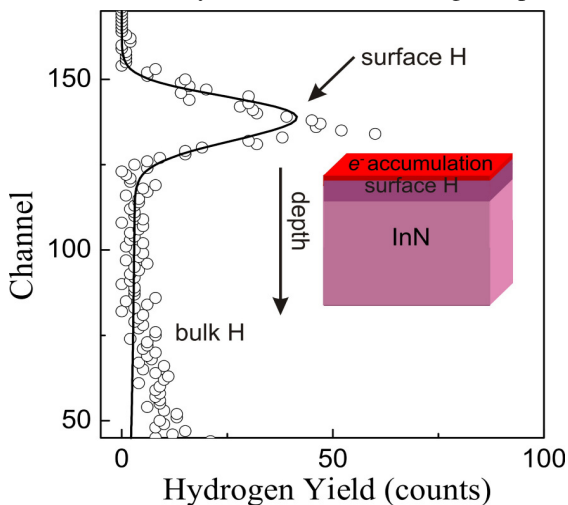
$\text{In}_x\text{Al}_{1-x}\text{N}$ alloys have potential applications in light emitting devices from the red to the deep UV range of the spectrum, and in high-power/high speed electronics. Despite the intense research in the field most of the fundamental alloy properties, such as the band gap, are still controversial and others, such as the alloy stiffness constants, remain unknown. We have obtained for the first time the stiffness constants of $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys in the whole compositional range by *ab-initio* calculations and determined their deviations from Vegard's rule to be $\delta_{C_{11}} = 98.6 \text{ GPa}$, $\delta_{C_{12}} = 22.7 \text{ GPa}$, $\delta_{C_{13}} = -4.4 \text{ GPa}$ and $\delta_{C_{33}} = 6.3 \text{ GPa}$. We have shown that the error in the alloy composition extracted from the lattice parameters of polar c-plane oriented films could be reduced by taking into account the deviations from Vegard's rule in the lattice parameters and stiffness constants. We also have determined the effect of the deviations from Vegard's rule on the accuracy of In composition for $\text{In}_x\text{Al}_{1-x}\text{N}$ films with nonpolar orientations (m- and a-plane) and on the piezoelectric polarization for polar $\text{In}_x\text{Al}_{1-x}\text{N}$ films.

¹ IFM, Linköping Univ., SE-581 83 Linköping, Sweden.

H impurity depth profiles and unintentional doping in InN films

V. Darakchieva, K. Lorenz, N.P. Barradas, S.M.C. Miranda, E. Alves, W.J. Schaff,¹ C.L. Hsiao,² L.C. Chen,² L.W. Tu,³ T. Yamaguchi,⁴ Y. Nanishi⁴

InN and its alloys with GaN hold a great potential for applications in advanced solar cells, high-speed



Elastic recoil detection profiles of hydrogen in a representative InN film with c-plane orientation and free electron concentrations in the mid 10^{18} cm^{-3} range. An enhanced concentration of H is revealed in the near surface region of the film and a bulk concentration of H of 0.5 at% is estimated from the fit (solid line) to the experimental data (circles).

electronics, THz emitters and sensors. One of the most critical issues is understanding the origin of the unintentional n-type doping in InN materials. Unintentionally introduced H is among the most plausible sources of doping. We have determined the H depth profiles in a large number of state-of-the-art InN films with different surface orientations and bulk free carrier concentrations by ERD analysis. Enhanced concentrations of H were found in the near surface regions of the films indicating post-growth surface contamination that could not be removed upon thermal annealing. Furthermore, we have found that the bulk free electron concentrations in the c-plane oriented InN films scale with the bulk H concentrations, indicating a major role of H in unintentional doping. The near surface H may have significant implications for the surface electron properties of InN and act as reservoir for co-doping the bulk.

¹Dept. of Electrical and Computer Engineering, Cornell Univ., USA; ²Center for Condensed Matter Sciences, National Taiwan Univ., Taiwan; ³Dept. of Physics, National Sun Yat-Sen Univ., Taiwan; ⁴Dept. of Photonics, Ritsumeikan Univ., Japan.

Structural properties of nonpolar InN films

V. Darakchieva M.-Y. Xie,¹ N. Franco, K. Lorenz, E. Alves, C. L. Hsiao,² L. C. Chen,² L. W. Tu,³ Y. Takagi,⁴ T. Yamaguchi,⁴ Y. Nanishi⁴

Nitride materials with nonpolar surface orientations (i.e. with the c-axis parallel to the growth plane) offer attractive opportunities to avoid the built-in electric fields in nonpolar nitride heterostructures and therefore overcome some of the current issues in the performance of light emitting diodes. However, the nonpolar growth results in typically poorer structural properties and the presence of anisotropic strain in the films, which in turn will affect the device-relevant properties of the material. We have studied the structural characteristics of nonpolar a- and m-plane InN films with respect to the growth conditions needed for minimizing the rotational disorder and enhance the lateral coherence lengths in the films. We have complemented these with results on the minimum yield determined from RBS-C experiments. Furthermore, we have measured the lattice distortions in the main crystallographic directions.

¹ IFM, Linköping Univ., Sweden.; ² Center for Condensed Matter Sciences, National Taiwan Univ., Taiwan; ³ Dept. of Physics, National Sun Yat-Sen Univ., Taiwan; ⁴ Dept. of Photonics, Ritsumeikan Univ., Japan.

Strain measurements in nitride heterostructures by ion channelling: experiment and Monte Carlo simulations

A Redondo-Cubero^{1,2}, K Lorenz, E. Alves, R. Gago^{2,3}, S. Fernández-Garrido¹, P.J.M. Smulders⁴, E. Muñoz¹, E. Calleja¹, I.M. Watson⁵

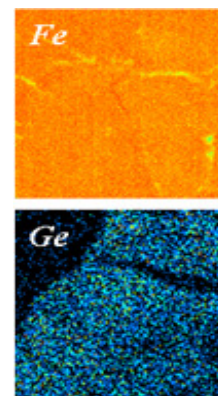
Ion steering effects in the interface of heterostructures (HS) can strongly influence the shape and position of angular channelling scans leading to considerable error in the determination of strain by ion channelling. With the help of Monte Carlo simulations, three composition/strain regions for AlInGaN/GaN HS were established for a typical beam of 2 MeV alpha particles corresponding to different intensities of the steering potential and in which strain measurements by ion channelling are (a) correct, (b) possible but require corrections and (c) not possible due to steering effects. Furthermore, the influence of the beam energy on the determination of the strain state with ion channelling was addressed: experimental results show that steering effects at the HS interface are more intense at lower ion energies. The experimental angular scans have been well reproduced by Monte Carlo simulations, correlating the steering effects with the close encounter probability at the interface. Consequently, limitations in the determination of the strain state by ion channelling can be overcome by selecting the adequate beam energy.

¹ ISOM, Univ. Politécnica de Madrid, E-28040 Madrid, Spain; ² CMAM, Univ. Autónoma de Madrid, E-28049 Madrid, Spain; ³ Inst. de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, E-28049 Madrid, Spain; ⁴ Materials Science Centre, Groningen Univ., 9747 AG Groningen, The Netherlands; ⁵ Inst. of Photonics, Univ. of Strathclyde, G40NW Glasgow, U.K.

Tin and germanium rich chalcopyrite from the Barrigão mine

F.K.M. Reiser¹, D.R.N. Rosa^{1,2}, A.M.M. Pinto², J.R.S. Carvalho², J.X. Matos³, F.M.G. Guimarães⁴, L.C. Alves, D.P.S. de Oliveira^{1,2}

Ore samples from the Barrigão mine, located in the Iberian Pyrite Belt, close to Neves Corvo, were investigated in order to determine the contents of technological important elements. Whole-rock analysis showed tin and germanium contents sometimes exceeding 200 µg/g, thus revealing their potential economical interest. Further analysis was performed through Nuclear Microprobe techniques in polished or thin section samples for obtaining elemental distribution maps and so be able not only to identify and map the several minerals present but also look for the minerals responsible for bearing the germanium and/or tin. Containing essentially tenantite and chalcopyrite, the obtained maps clearly showed that the Ge was only present in some chalcopyrite grains with contents ranging from 0.3%-0.6%. These grains also contained some amounts of tin (up to 1%) as well as arsenic (~0.15%). Electron Microprobe Analysis further explored the most interesting samples zones mapped by Nuclear Microprobe analysis. Due to its improved beam spatial resolution it may ascertain if Ge and Sn are contained in submicroscopic phases.



Composition maps of a Ore sample.

¹ INETI/LNEG, Alfragide; ² CREMINER/FCUL; ³ INETI/LNEG, Beja; ⁴ INETI/LNEG, S. Mamede de Infesta.

Ni-Ti surface modification for enhanced biocompatibility and corrosion in biomedical applications

R.M.S. Martins, N. Barradas, E. Alves, D. Henke¹, J.C.S. Fernandes²

Ni-Ti Shape Memory Alloy is characterized by a specific stress-strain diagram that is different from the deformation behaviour of conventional materials but similar to that of living tissues. In spite of its attractive mechanical properties, the use of Ni-Ti raises concerns due to its high Ni content. Ni release from Ni-Ti depends on its corrosion resistance, which relies on the presence of a passive oxide layer (TiO₂). In this study a method (using plasma-immersion ion implantation) is being implemented to modify and improve the Ni-Ti alloy surface for biomedical applications, without deteriorating the mechanical properties, aiming at forming a Ni-depleted surface, to serve as a barrier against out-diffusion of Ni. Ion implantation of oxygen into Ni-Ti has been carried out, in order to promote selective oxidation of Ti, leading to a Ni-depleted surface.

¹ Inst. of Ion Beam Physics and Materials Research, Forschungszentrum Dresden-Rossendorf, P.O. Box 510119, 01314 Dresden, Germany.

² ICEMS/DEQB, Inst. Superior Técnico, TULisbon, 1049-001 Lisboa, Portugal.

The effect of Mn, Fe and Cu ions on potash-glass corrosion

M. Vilarigues¹, R.C. da Silva

The corrosion behaviour of model potash-glasses doped with Mn, Fe or Cu ions, was studied by analysing the glass surfaces after exposure to different simulated weathering conditions. Glass samples with 56 mol.% SiO₂, 24 mol.% CaO and 20 mol.% K₂O were prepared, with 1 mol.% of the different metal oxides, a composition analogous to that of the medieval stained glasses of the XV century from the Monastery of Batalha. The experimental conditions used reproduced well the natural corrosion processes found in ancient glasses of similar composition and weathered through five centuries: silica-rich layers containing CaCO₃ were identified on the surface, with more than one such layers developing during longer weathering periods, indicating progression through a sequence of dissolution steps. The elemental profiles obtained from the attacked surfaces, showed that upon weathering glasses doped with Cu, Mn or Fe, develop a layer richer in the doping ions on the surface. Addition of ions Cu, Mn or Fe, was found to influence corrosion: the initial rates are always higher in Cu, Mn or Fe doped glasses than in undoped glasses. Copper containing glasses display the faster initial corrosion. The measurements also allowed establishing a correlation between the presence of the doping ions and the increase in the number of Si-O groups in the surface of the glasses. This is viewed as favouring the adsorption of hydronium ions and the later exchange with e.g. K and Ca.

¹ Dept. de Conservação e Restauro, Fac. de Ciências e Tecnologia, Univ. Nova de Lisboa, 2829-516 Caparica, Portugal.

Study of colouring elements in Portuguese medieval stained glasses: techniques and mechanisms*M. Vilarigues¹, P. Fernandes¹, L.C. Alves, R.C. da Silva*

Non-destructive characterisation of glasses from the 15th, 16th and 20th centuries, and belonging to Mosteiro de Santa Maria da Vitória, Batalha (Portugal), continued through use of the nuclear microprobe. Fe, Cu and Pb were the main elements identified in the grisailles of all studied periods, and Ag and Cu found in the glasses decorated with yellow silver painting. Their distributions allowed establishing a definite relation between the compositions found and the periods of production, as well as correctly reassigning the manufacturing period of some samples: the glasses analysed could be divided into two major groups: potash glasses (from the 15th and 16th centuries) and soda-lime glasses (from conservation-restoration works from the beginning of the 20th century). It was established that the grisailles were produced with a mixture of Fe, Cu and Pb, the main differences in composition laying in the contents of Pb: about 5 mol% in the original grisailles, more than 10 mol% for those produced in the 20th century. Their structure was found not to vary significantly with the production period: Fe and Cu concentrated in the form of a 15 µm thick dispersion of solid grains in the centre most region of a 30 µm thick lead silicate layer, indicating that the temperatures used were sufficient to bind the fondant to the glass substrate, but not enough to melt Fe or Cu. In what concerns yellow silver staining, the Cu-Ag association found from the elemental maps, indicates that not only a Cu-Ag mixture must have been used as the materials source, but annealing processes as well, whereby silver penetrated into the glass and precipitated, leaving Cu behind at the surface.

¹ Dept. de Conservação e Restauro, Fac. de Ciências e Tecnologia, Univ. Nova de Lisboa, 2829-516 Caparica, Portugal.

In-situ* X-ray diffraction studies during co-sputtering deposition of Ni-Ti shape memory alloy filmsR.M.S. Martins, N. Schell¹, J. von Borany², K.K. Mahesh³, R.J.C. Silva³, F.M., Braz Fernandes³*

Ni-Ti films have attracted much interest as functional and smart materials and are considered attractive candidates for micro-electro-mechanical systems (MEMS) applications. However, the deposition of Ni-Ti films with definite stoichiometry and high purity remains a challenge. In this study near equiatomic (≈ 50.0 at.% Ti-Ni) and Ti-rich (≈ 50.8 at.% Ti-Ni) Ni-Ti polycrystalline films (thickness values up to 800 nm) have been deposited by magnetron co-sputtering using a chamber installed into the six-circle diffractometer of the Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility. The *in-situ* X-ray diffraction studies enabled the identification of different steps of the structural evolution during films processing. Films exhibiting a (100) preferential orientation for the B2 phase have been successfully produced. A continuous increase of the B2(200) diffraction peak intensity has been observed for depositions on a 140 nm amorphous SiO₂ buffer layer heated at 520°C (without substrate bias voltage, V_b). A (100) texture has been observed for films as thick as 800 nm. Near equiatomic and Ti-rich Ni-Ti films deposited without and with V_b on a TiN coating with a topmost layer formed by <111> oriented grains have shown a preferential growth of <110> oriented grains of the B2 phase from the beginning of the deposition. Ni-Ti films with a thickness as low as 100 nm exhibit a (110) preferential orientation for the B2 phase.

¹ GKSS Research Center Geesthacht, Max-Planck-Str. 1, 21502 Geesthacht, Germany.

² Inst. of Ion Beam Physics and Materials Research, Forschungszentrum Dresden, Rossendorf, P.O. Box 510119, 01314 Dresden, Germany.

³ CENIMAT/I3N, Dep. de Ciência dos Materiais, Fac. de Ciências e Tecnologia, Univ. Nova de Lisboa, 2829-516 Caparica, Portugal.

AMS analysis of low dose Pt implantation in Si*H. Luís^{1,2}, N. Franco, M. Fonseca^{1,2}, L. Gasques², A.P. Jesus^{1,2}, E. Alves*

In order to study the role of isotopic effect on optical spectra, pure ²⁸Si single crystals were implanted, at an energy of 60 keV, with ¹⁹⁴Pt and ¹⁹⁸Pt, with nominal fluences around 1×10^{14} cm⁻². Since a natural Pt target was used for the implantation some isotopic contamination is expected, despite the mass selection. AMS, particularly Microbeam AMS, was employed for the verification of the implanted isotopic ratio and the determination of the amount of ¹⁹⁵Pt and ¹⁹⁶Pt contamination. For tuning up the beam transport system, a platinum powder target was used, producing current intensities at the high energy side of around 50 pA for the +4 charge state of the different isotopes. For the implanted samples, currents up to 1×10^3 particles per second were obtained. The isotopic ratios were found to be 0.76 ± 0.06 for ¹⁹⁸Pt/¹⁹⁴Pt, 0.14 ± 0.03 for ¹⁹⁵Pt/¹⁹⁴Pt and 0.24 ± 0.03 for ¹⁹⁶Pt/¹⁹⁴Pt.

¹ Fac. de Ciências e Tecnologia da Univ. Nova de Lisboa; ² Centro de Física Nuclear da Univ. de Lisboa.

Dinosaur and crocodile fossils from the Mesozoic of Portugal: neutron tomography*R.M.S. Martins, O. Mateus^{1,2}, F. Beckmann³, P.K. Pranzas³*

Portugal is ranked seventh with regard to dinosaur taxa and the area of Lourinhã is known by the Late Jurassic findings of dinosaurs and other fossils. The paleontological research in this area has been carried out by the “Museu da Lourinhã” in collaboration with the “Universidade Nova de Lisboa” and described in several scientific articles (available at <http://publicationslist.org/omateus>). In many cases, studies of the external



Tomistomidae jaw photograph and yz-slice

morphological characteristics of the fossils are not sufficient to extract all the information for a paleontological study and, thus, observations of internal morphology are required. Access to the Geesthacht Neutron Facility (GeNF) allowed a unique and non-destructive characterization of the fossils by neutron tomography. A total of 8 samples have been studied: Archosaur nest – Late Jurassic, Crocodylian egg, Temnospondyl jaw – Late Triassic, two Theropod Lourinhanosaurus Antunesi eggs, Baryonyx walkeri jaw, Tomistomidae (?) skull, Tomistomidae (?) jaw (Figure). During the experiments the samples were exposed for 16 s at equally stepped (0.25°) tilts between –180° and 180°. From the single projections, slices perpendicular to the rotation axis were reconstructed by a tomographic reconstruction algorithm using “filtered backprojection.” The slices were then collected in an image stack allowing visualization, edition and conversion into different file formats using a 3-D rendering software. The present study gives precious information about the internal morphology of the fossils, providing a direct window into the evolutionary history of development.

¹ Dep. de Ciências da Terra (CICEGe–FCT), Faculdade de Ciências e Tecnologia, Univ. Nova de Lisboa, 2829-516 Caparica, Portugal.

² Museu da Lourinhã, Rua João Luis de Moura, 2530–157 Lourinhã, Portugal; ³ GKSS Research Center Geesthacht, Max-Planck Str. 1, 21502 Geesthacht, Germany.

A new ion beam analysis data format*N.P. Barradas, M. Mayer¹, M. Thompson¹*

Computational Ion Beam Analysis (IBA) codes such as RUMP, SIMNRA, NDF, and others implement various formats to store the spectral data and to describe the experimental conditions and simulation or fit parameters. Additionally, many laboratories have developed their own internal data formats. These various data formats are isolated applications and generally incompatible. The need for a universal IBA data format (IDF) has been recognised for many years to allow easy transfer of data and simulation parameters between codes, as well as between experimentalists and data analysts. To be effective, the IDF must be transparent (easily read by an IBA practitioner), universal (catering to varying needs), and must include the most common features desired by both experimentalists who collect and archive data and by users who analyse the data. The IDF must also be readily extensible in order to include features specific to individual codes and laboratories, as well as being able to incorporate new features and options in the future. We have developed such a data format. It is currently being implemented in the most popular general purpose IBA data analysis codes.

¹ Max-Planck-Institut für Plasmaphysik, EURATOM Association, Boltzmannstrasse 2, D-85748 Garching, Germany.

² Dept. of MS&E/Bard Hall 328, Cornell Univ., Ithaca, NY 14853, USA.

Artificial neural networks for real time in-situ RBS analysis*N.P. Barradas, D. Smeets¹, J. Demeulemeester¹, A. Vantomme¹, A. Vieira², C. M. Comrie³, C. Theron⁴*

Two years ago, we revived the Artificial Neural Networks work that we had previously developed, to apply it to real time RBS characterization, i.e. performing the analysis during thin film growth. Entire systems are solved after a few days of work, as opposed to months previously. Two papers were submitted in 2009. This was done in collaboration with the Leuven University, that are the drive behind the real time RBS experiments, basically by transferring the knowledge on ANNs to Leuven, who from now on will continue to develop ANNS. We consider the role of ITN in this research to be now concluded.

¹ Instituut voor Kern-en Stralingsfysica, Dept. of Physics and Astronomy and INPAC, KU Leuven, Belgium.

² Inst. Superior de Engenharia do Porto, R. António Bernardino de Almeida 431, 4200 Porto, Portugal.

³ Dept. of physics, Univ. of Cape Town, Rondebosch 7700, South Africa.

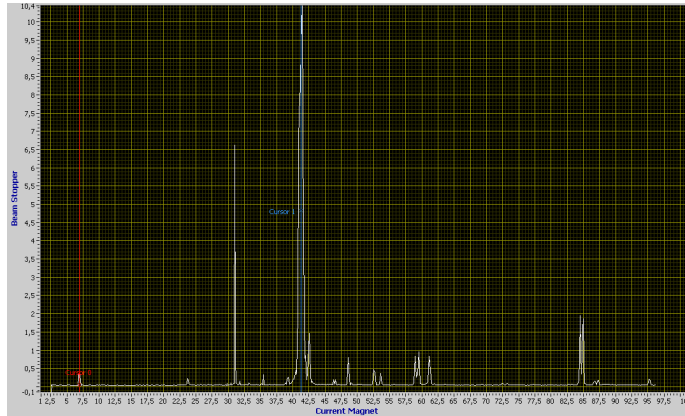
⁴ Materials research group, iThemba LABS, P.O. Box 722, Somerset West 7129, South Africa.

Ion Implantation Automation System

J. Lopes¹, J. Rocha, L. Redondo¹, F. Alegria², E. Alves

In order to obtain an accurate implantation of an isotope or to avoid the existence of more than one element on the target, mass spectrometry is fundamental. Until recently in ITN ion implanter the mass spectrum has been obtained in a plotter with the magnetic field being controlled manually through the current source. With the system developed, the mass spectrometry is made through a PC application and the mass spectrum is displayed in the PC screen in real time. The system consists of a PC, a data acquisition I/O board composed by multifunction input/output board NI USB-6251 and four electronic modules using optic fiber control. The computer control code uses a LabVIEW synoptic for interaction with the operator.

¹ ISEL, Lisboa, Portugal
² IST, Lisboa, Portugal



Mass Spectrum obtain through LabVIEW.

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) Clinical outcomes research establishing disease progression and clinical response to therapy;
- 2) environmental health research establishing new biomarkers of exposure.

New technical capabilities recently developed in ITN, such as inductive coupled plasma mass spectrometry (ICP-MS) and flow cytometry, helped consolidating achieved expertise and opened new areas of research.

Continued funding in the areas of environmental health, cardiovascular and skin diseases during the last five years had strengthened existing skills and promoted advanced training of Ph.D. and M.Sc. students.

The main achievements are summarised in the following pages.

Research Team

Researchers

T. PINHEIRO, Aux., Group Leader
L.C. ALVES, Aux.

RITA P. E. M. GODINHO VELOSO, Post-Doc.

Students

P NAPOLEÃO, Ph.D., BI grant
P. FELIX, M.Sc. BI, ITN grant
C. FRANCO, M.Sc., student, FC-UL
B. BATISTA, M.Sc., student, FC-UL
L. G. BORGES, M.Sc., student, FC-UL
A. BORGES, M.Sc., student, FC-UL
S. ANDRADE, M.Sc., student, FC-UL
S. VELOSO, M.Sc., student, FC-UL

Technical Personnel

R. PINHEIRO, Lab. Assistant

Collaborators

R.C. FERREIRA, M.D., CHLC/EPE, Hospital Sta. Marta
M. MOTA CARMO, Ass. Prof., FCM-UNL
A. TOSTE, M.D., Hospital Sta. Marta
M. SELAS, Nurse, Hospital Sta. Marta
M.C. MONTEIRO, Ass. Prof., CESPU, Porto
A.M. VIEGAS-CRESPO, Princ. Researcher, FC-UL
A. TURKMAN, Full Prof., CEAFC, FC-UL
V. ANDREOZZI, PosDoc. CEAFC, FC-UL
A. BARREIROS, Aux. Resarcher, INETI
A.B.ALMEIDA, Full Prof., FM-UL/Hospital Sta. Maria
P. FILIPE, Aux. Prof., FM-UL/Hospital Sta. Maria
R. SILVA, M.D., Hospital Sta. Maria
R.FLEMING., M.D., Hospital Sta. Maria
M.D. YNSA, Researcher, CMAM, Univ. Autónoma Madrid, Spain
I. GOMEZ-MORILLA, Researcher, Technische Univ. Dresden, Germany

Biomarkers of Disease, Therapy and Exposure

T. Pinheiro, L.C. Alves, M.A. Barreiros¹, R. Fleming², P. Filipe³ and R. Silva³

Clinical outcomes research - Skin iron as a diagnostic tool in hemochromatosis

Background: Hemochromatosis is a hereditary disease that causes an inappropriate intestinal absorption of Fe resulting in its accumulation in multiple organs, such as liver, heart and skin. Fe metabolism indicators in the circulation do not provide reliable indication of organ overload as they can be influenced by other clinical conditions. Assessing metabolism organs such as liver often requires invasive procedures which is not adequate to patient's serial observations.

The project finished in June 2009, when final data for the last patients enrolled in the study was collected. Results have been partially published in peer review journals and one comprehensive paper including all results is being prepared to be submitted to a specialty journal.

Objectives: Our aim was establishing cross sectional and longitudinal information on the amount of Fe that deposited in skin and liver during a life period, how iron is cleared out by therapy intervention and study the relationship of these changes between the two organs using non-invasive methods.

Methods: The study used conventional and innovative laboratory tests to differentiate distortions of iron metabolism. Patients were genetically characterized and studied before initiating therapy (Phase 1) and continued to be surveyed along therapy, at the end of the phlebotomy programme (Phase 2) and 6 months after (Phase 3). Nuclear microprobe (NMP) and nuclear resonance techniques provided iron quantitative imaging and physiological information on skin and liver. Biochemical methods provided hepcidin contents in serum and markers of iron metabolism and organ function.

Results: Skin features can be easily observed with NMP techniques, enabling the accurate localization of Fe deposits. At hemochromatosis diagnosis time point patients (25 phlebotomy naïve patients) showed remarkable Fe deposits in skin epidermis (Fig. 1).

At Phase 1, hemochromatosis patients also showed high transferrin saturation values, and remarkably elevated concentrations of ferritin, serum and plasma iron when compared to controls. Hepatic Fe was also high. At this time point before starting the phlebotomy therapy, skin and liver Fe concentrations could be associated to serum indicators of Fe overload, such as ferritin content and transferrin saturation.

As therapy progresses Fe blood indicators, skin and hepatic Fe concentrations sharply decrease. Hepatic Fe content shows a similar trend to skin Fe concentration (Fig. 2).

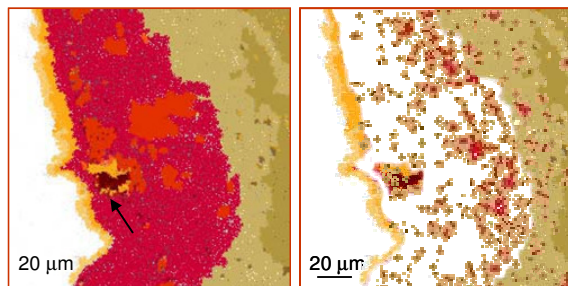


Fig.1 NMP Images of skin morphology and Fe distribution in hemochromatosis. Left image: epidermis in red, dermis in green, stratum corneum and hair shaft in yellow, hair in dark red (arrow). In the right image, iron (red) map overlapped on density image (left), shows that Fe is mainly deposited in epidermis.

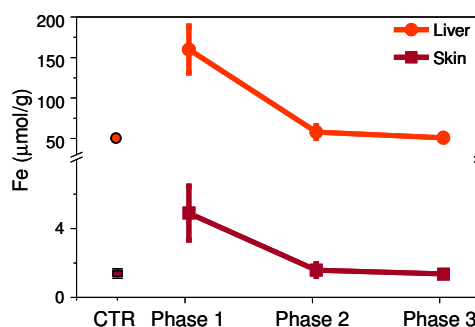


Fig.2 Skin and liver Fe content in patients and controls.

However, the decrease of ferritin and transferrin values did not correlate with the decline of skin and liver Fe content. Opposite, the Fe decrease observed along therapy (from Phase 1 to Phase 3) in skin and liver was correlated at all phases and the Fe decreasing rate from Phase 1 to Phases 2 and 3 was similar in both organs.

Conclusions: 1) skin Fe deposits is a non-invasive procedure enabling serial patient's assessment and therapy efficacy evaluation; 2) skin iron concentration alone or in combination with the hepatic Fe content may constitute alternative and reliable biomarkers for iron overload diseases.

Acknowledgements: The study was supported during 2004-2009 by Sociedade Portuguesa de Dermatologia e Venereologia.

¹ LNEG, Lisboa

² Hospital de Sta Maria, Serv. Imuno-hemoterapia

³ Hospital de Sta Maria, Serv. Dermatologia/FM-UL

Clinical outcomes research – New biomarkers for Coronary Artery Disease

T. Pinheiro, P. Napoleão, R. Cruz Ferreira¹, M. Mota Carmo^{1,2}, M. Selas¹, A. Toste¹, M.C. Monteiro³, A.M. Viegas-Crespo⁴, F. Caeiro⁴, A. Turkman⁵, V. Andreozzi⁵, A. Borges⁴, L.G. Borges⁴, S. Andrade⁴, S. Veloso⁴

Continuous efforts are being developed in the translation of basic biomedical research carried out into novel diagnostics and therapies for the benefit of patients with coronary artery disease. Current projects join teams with know-how in intervention cardiology, biochemists, biologists, geneticists and statisticians. Cohort studies were undertaken to study new biomarkers in coronary syndromes. Indicators of inflammation, thrombosis and oxidative stress such as the molecules TNF- α , C-reactive protein, CD40 ligand, P-selectin, oxidized LDL, microparticles released by the endothelial cells and platelets and inflammatory cells surface markers, have been studied in acute, instable and stable clinical conditions. Under the scope of a FCT project, specific proteins and molecules that may be indicators of plaque activity (cathepsins) and endothelial dysfunction (nitric oxide and VEGF) will be related to virtual histology intravascular ultrasound (VH IVUS)-derived measurements of the atherosclerotic plaque. The major aim is to find biomarkers that can be associated to plaque composition. Major achievements were 1) the association of the serial changes of inflammatory markers with adverse clinical outcomes in patients with acute myocardial infarction; 2) the differentiation of patients with ST-elevation myocardial infarction based on soluble CD40 ligand variations. During 2009 a Ph.D. thesis in Biology was completed and two M.Sc. theses were carried out under the current projects.

Project funding: LAHSM/2005-2009 - Liga de Amigos do Hospital de Sta. Marta, FCT/PIC/IC/82734/2007, FCT grant SFRHI/BD/ 18822/2004.

Environmental health research - new biomarkers of exposure.

T. Pinheiro, M. Almeida, A. Bugalho de Almeida⁸, S. Garcia⁹, A. Barreiros⁷, P. Félix, M. F. Araújo, M. Santos, M.C. Freitas, L.C. Alves, C. Franco⁴, B. Batista⁴

The project is a joint initiative of ITN units UFA and UR, together with the Instituto de Soldadura e Qualidade and the Hospital de Santa Maria. The primary objective is to develop a new non-invasive human bioindicator - Exhaled Breath Condensate (EBC) - that could be employed for a better risk assessment among workers exposed to lead. Major achievements during 2009, were: 1) the validation of methods of collection and analysis of EBC; 2) decision on reliable biomarkers that can be determined in EBC – metals and cytokines have been examined. Methodologies to sample, store and analyse the EBC were tested and established. EBC elemental concentrations were determined by ICP-MS in ITN at the ICP-MS laboratory of UCQR, in collaboration with the Environmental and Analytical Chemistry Group. The whole analytical methodology is being controlled by comparing results with TXRF which is accredited at LNEG by the Portuguese Quality System following the regulations of ISO/IEC 17025. Also, cytokine concentrations in EBC were inspected by ELISA. The Pb, Cr, Mn and Cu concentrations in EBC can be used as indicators of occupational exposure. On the other hand cytokine measurements in EBC revealed to be inadequate due to the instability of the analyte or to the low concentration levels.

Detailed information about this project in URSN/ANANE.

Project funding: FCT/PTDC/AMB/65828/2006

¹ Hospital Sta. Marta EPE, Serv. Cardiologia; ² Faculdade de Ciências Médicas, FCM-UNL; ³ CESPU, Porto; ⁴ Centro de Biologia Ambiental, FC-UL; ⁵ Centro de Estatística Aplicada, FC-UL; ⁷ LNEG, Lisboa; ⁸ Hospital de Sta Maria, Serv. Pneumologia/FM-UL
⁹ Instituto de Soldadura e Qualidade

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, imbedded 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, which has been kept operational. The overall international scientific context of the field, as well as funding sources have, nevertheless promoted of the work on analytical instrumentation, PIXE fundamentals and software developments, previously maintained at a reduced emphasis level.

In more concrete terms, the installation in 2008 of the High Resolution High Energy PIXE (HRHE-PIXE) set-up at ITN, the world first PIXE system using a cryogenic microcalorimeter high resolution EDS X-ray detector (a POLARIS detector produced by Vericold Tech. GmbH, presently an Oxford Instruments Group company), the recent international recognition of the importance of the work carried out in the decade 1990 on x-ray production cross-sections,

the recent achievements of the team on relative intensities of x-ray lines induced by proton beams and on the development of new software tools for PIXE, were at the basis for this revision of the main objectives of the CEEFI work line, towards an enhanced emphasis on fundamentals and technical developments.

Nanoparticles and other particulate matter (airborne or not), as well as thin film samples, nevertheless, do still come into the main scope of the line application work.

Recent results on the health impact of airborne PM2.5 chlorine, published in 2009 after five years of quest and after the compilation of a twelve years database on airborne particles composition, also contributed to emphasise the need for new techniques able to handle speciation issues in minimal sized samples, the core subject of the work line.

Strategically, it is nevertheless assumed that it is important not to depend exclusively on collaborations neither for sampling nor for data handling processes. This and historical reasons imply the maintenance of some effort on the preservation of the operational condition of the airborne particle sampling and data handling capabilities, even if at a low priority level.

PIXE services are also provided to the community in general, and to the scientific community in particular, upon request.

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

Research Team

Researchers

M.A. REIS, Aux., Group Leader

Students

P.C. CHAVES, Ph.D. student, FCT grant

A. TABORDA, Ph.D. Student, FCT grant

Technical Personnel

R. PINHEIRO

Collaborators

N. BARRADAS, ITN

A. CARVALHO, CFMC-UL, ESTeSL

L. CARVALHO, Ass. Prof., CFA-UL, FC-UL

A. FERRAZ, Aux. Prof., CFMC-UL, IST

V. PRIOR, IM

P.O. RODRIGUES, (MD) Ass. Prof., FCM-UNL

S. CORREIA, IM

R. TEIXEIRA, Graduation student

Fundamentals and Experimental Developments and Applications of PIXE

M.A. Reis, N. Barradas, A. Carvalho¹, L. Carvalho², A. Ferraz³, P.O. Rodrigues⁴ (MD)

Objectives

Elemental and speciation characterization methodologies for small mass samples, like airborne particles are nowadays a more and more important issue, needed for a better monitoring of airborne particulate matter and its impacts, including nano particulate matter hazards, but also for new technical and industrial developments niches associated to particulate matter engineering. During 2009 all the work line activities therefore converged towards a single subject of "Fundamentals and Experimental Developments and Applications of PIXE", which even though it is multi-branched, it is in fact a single problem because of the established and explored inbreeding between its three different aspects, namely fundamentals, experimental development and applications.

Results

Regarding applications, 2009 has seen the publishing of one of the most important results achieved during the last five years, the evidence for a highly probable existence of a cause effect relation between events of high concentrations of chlorine in PM_{2.5} and the raise in the incidence of diabetes in the exposed population.

In the bottom left picture of Fig. 1 the time series relation between one and the other is shown. Understanding its mechanisms requires chlorine speciation in PM_{2.5} using high through put techniques, presently non-existing.

A step towards those has been given by the team during 2009, by showing that a microcalorimeter detector used in PIXE work is an invaluable tool that allows the detection of highly resolved and low background X-ray spectra from complex targets. The bottom right picture in Fig. 1 bellow illustrate this, by showing a Sr-L signal from a less than 4 nm thick film of SrTiO₃, present in an 1 μm thick bilayer target deposited on a silicon wafer.

Finally, these very new experimental developments demand more from PIXE software and computational implementations of supporting theoretical developments, than are presently available. The work done on this aspect therefore provides support to the other two. The top picture of Fig. 1 shows the universal curves established in 1993 for ionization of the L-shells by proton impact and its extension to cross-section by alpha particles impact made during 2009.

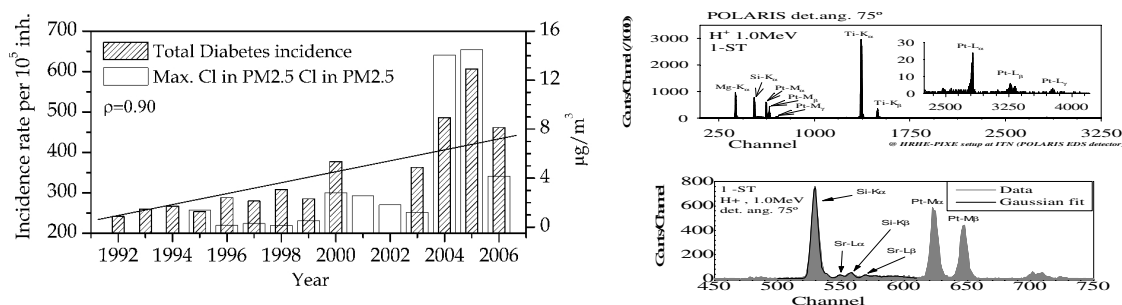


Fig.1 Long run monitoring of airborne particles composition showed a relation between high concentration levels of chlorine in (PM_{2.5}) and the incidence of diabetes in the exposed population(left), while experimental developments allow the profiling of medium Z (Sr) thin films in a complex bilayer target deposited on a silicon wafer. New developments on fundamental results relative to the calculation of ionization cross-sections (top) are essential to support the development of PIXE software necessary to properly exploit new application and experimental developments.

¹ Escola Superior de Tecnologias da Saúde 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.

⁴ Fac. de Ciências Médicas da Univ. Nova de Lisboa.

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 Advanced Materials Research Group of ITN and CFNUL. ISOLDE is a European Large Scale Facility where more than 750 isotopes and 80 elements are produced and delivered as ion beams of high isotopic purity, which is unique 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. The ITN-CFNUL infrastructure and related projects are refereed and reevaluated each year within the scope of FCT-supported CERN projects. The scientific work in 2009 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 (e.g., Si, Ge, ZnO, GaN and GaAs) are studied by means of the EC technique. Important elements, which have only suitable short-lived isotopes can now be studied, as in the particular case of the ^{27}Mg (9.5 min) isotope, which was for the first time successfully tested in 2009.

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 chromites ACrO_2 (A = Ag, Cu) as a function of the elements R, A, and of temperature. By combining PAC data with first principle simulations of charge density distributions on these materials, local phenomena that correlate the coexistence of ferroelectricity, ferromagnetism and ferroelasticity are studied. 2009 was a year of innovation on the materials being studied, together

with the development of new analyzing tools. A new program was developed from scratch that will allow fitting PAC spectra as shaped by dynamic hyperfine interactions, which reveal the existence of transient fields on the materials to study.

c) On a different subject, first experiments regarding proposal IS481 (K. Lorenz) "The role of In in III-nitride ternary semiconductors", have combined γ - γ with e^- - γ PAC using the $^{111\text{m}}\text{Cd}/^{111}\text{Cd}$ and the $^{117}\text{Cd}/^{117}\text{In}$ isotopes. The aim is to study the intrinsic nature of In defects in GaN and AlN, with isotopes, which are unambiguously free of "after effects".

In what R&D projects are concerned, first electron detection tests were successfully done with a highly pixelated $512 \times 512 \times 28 \times 28 \text{ mm}^2$ Si detector (TimePix) using both low and high-energy conversion electron and beta sources. In parallel, a new high-resolution goniometer from Panmure, dedicated to on-line experiments with short-lived isotopes, was delivered in 2009. This allowed the planning and design of the special standing and support system as well as of the annealing station to be commissioned at the on-line emission chamber in 2010.

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, ISEL as well as from Leuven in Belgium. During 2009 two Ph.D. and two M.Sc. students defended their thesis; four other Ph.D. and three M.Sc. students performed their work using this infrastructure within the scientific proposals and R&D projects.

Research Team

Researchers

J. G. M. CORREIA, Princ.
U. WAHL, Princ.
K. LORENZ, Aux.

Students

A.C. MARQUES, PhD student, FCT grant (till Oct 2009)
T. MENDONÇA, PhD student, FCT grant
J. N. GONÇALVES, PhD student, FCT grant
L. PEREIRA, PhD student, FCT grant
C. SOUSA, PhD student, FCT grant
S. DECOSTER, PhD student IKS-Leuven grant (till June 2009)
L. AMORIM, MSci Student FCT projects
M. BARBOSA, MSci Student FCT projects
G. OLIVEIRA, MSci Student FCT projects

Collaborators

V. AMARAL, Ass. Prof., U. Aveiro
J. P. E. ARAUJO, Aux. Prof., U. Porto
M. R. SILVA, Ass. Prof., IST, Lisboa
J. C. SOARES, Cat. Prof. Emeritus, U. Lisboa
L. REDONDO, Ass. Prof., ISEL, Lisboa
H. HAAS, Emeritus Researcher, ITN
A. VANTOMME, Prof., IKS Leuven
S. DECOSTER, Post-Doc, IKS Leuven (from June 2009)
A. L. LOPES, Post-Doc, FCT grant

IS453 experiment: Emission channelling lattice location studies

U. Wahl, J.G. Correia, L. Amorim, A.C. Marques, E. Alves,
S. Decoster¹, A. Vantomme¹, M.R. da Silva^{2,3}, J.P. Araújo⁴, L. Pereira⁴,
and the ISOLDE collaboration⁵

Objectives

The aim of this work is to study the lattice location of dopants and impurities in technologically relevant semiconductors and oxides by means of electron emission channelling (EC) from radioactive isotopes. With this technique information is available for very low dopant concentrations and independent from the host lattice elemental composition. The experiments are carried out using the ITN/CFNUL infrastructure installed at CERN's ISOLDE facility.

Results

1. Lattice location of transition metals in Ge

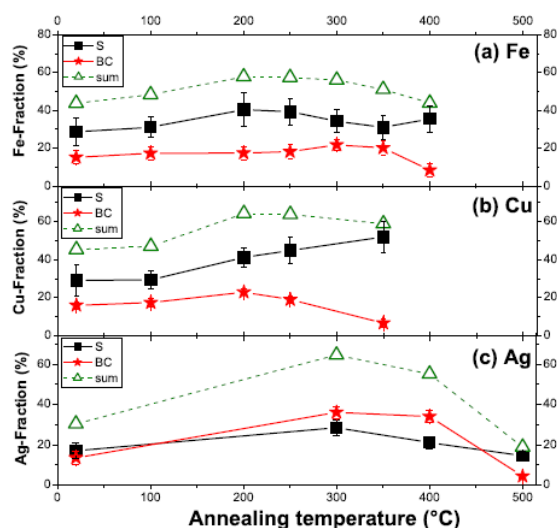


Fig.1 Fractions of implanted ⁵⁹Fe (45 d), ⁶⁷Cu (62 h) and ¹¹¹Ag (7.5 d) probes on S and BC sites in Ge, together with the total fraction (sum = S + BC), as a function of annealing temperature.

We have determined the lattice location of transition metals (TMs) following room temperature implantation into undoped Ge with an energy of 60 keV to fluences around $5 \times 10^{12} - 1 \times 10^{13} \text{ cm}^{-2}$. It was found that Fe, Cu, and Ag do not exclusively occupy substitutional sites but bond-centered (BC) sites as well. In order to understand these experimental results, the heat of formation and most stable

structural configuration of the following three Cu, Fe and Ag-related complexes in Ge was calculated using ab initio density functional theory: TM on the substitutional S site, TM on the tetrahedral interstitial (T) site, and TM paired with a Ge vacancy (S+V). Corroborated by theory, the BC fraction is attributed to impurity-vacancy complexes in the so-called "split-vacancy" configuration. It was concluded that mobile vacancies, created in our case during the ion implantation process, will be trapped by substitutional impurities, resulting in the spontaneous occupation of the BC site. This result contributes significantly to the understanding of the properties of transition metals in germanium, in particular their interaction with vacancies, which are known to be introduced in some processing steps of Ge technology.

2. Emission channelling with short-lived isotopes

Using our emission channelling on-line setup, which is now mounted permanently at the ISOLDE GHM beamline, we performed a number of lattice location experiments with short-lived radioactive isotopes. During the 2009 Mn beam time we determined the lattice location of ⁵⁶Mn (1.5 h) implanted into Si as a function of annealing up to 800 °C. It was found that substitutional Mn is dominant, while interstitial Mn cannot be quenched in large amounts. Surprisingly the behaviour of Mn in Si is more similar to Cu than it is to Fe (which we have studied previously). We have recently performed also the first direct lattice location experiments of the magnesium acceptor in nitride semiconductors. For that purpose short-lived ²⁷Mg (9.5 min) probes, which were extracted from a proton-irradiated SiC target by thermal outdiffusion and ionized in a laser ionization source, were implanted with 50 keV into single-crystalline GaN and AlN thin films. The β^- emission channelling patterns showed that the large majority of implanted Mg is incorporated in to Ga or Al sites. Preliminary analysis of the GaN data by means of fitting the experimental patterns to the results of simulations for ²⁷Mg in different lattice sites gave no indication for large fractions of Mg in interstitial sites.

¹ Inst. voor Kern- en Stralingsfysica (IKS), Katholieke Univ. Leuven, 3001 Leuven, Belgium.

² Centro de Física Nuclear da Univ. de Lisboa (CFNUL), Av. Prof. Gama Pinto 2, 1649-003 Lisboa.

³ Inst. Superior Técnico, 1049-001 Lisboa.

⁴ Dept. de Física, Univ. do Porto, 4169-007 Porto.

⁵ CERN, 1211 Geneva 23, Switzerland.

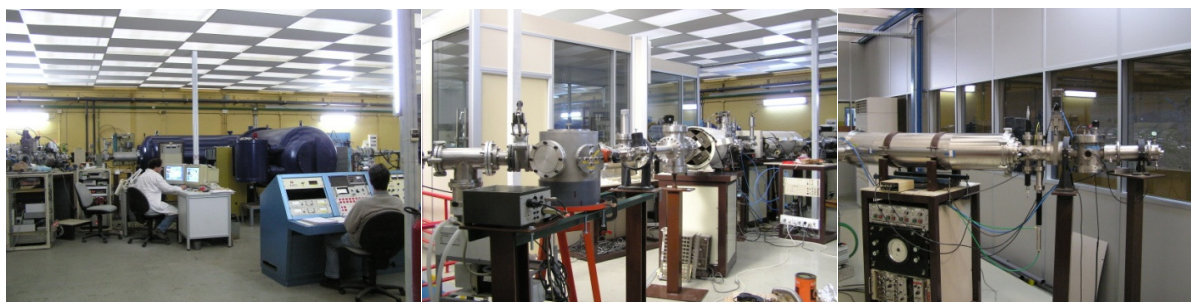
Nuclear Reactions

Adelaide Pedro de Jesus

The 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.

A new line has been installed in the Tandem 3MV accelerator, for nuclear reaction studies for fundamental nuclear physics and nuclear astrophysics, both 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) (*)
L. GASQUES, Pos-Doc (CFNUL)
D. GALAVIZ, Pos-Doc (CFNUL)

Students

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

(*) Also members of CFNUL.

Experimental Study of Nuclear Reactions by AMS

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

Objectives

Following its experimental work in nuclear reactions relevant for primordial and stellar nucleosynthesis (hydrogen burning) [1,2], the group is focusing now in later stages of stellar nucleosynthesis, namely alpha, carbon and oxygen burning and p-process.

While some of the studies proceed within international collaborations, making use of facilities such as ERNA, FAIR, ISOLDE, others are being 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.

In the short term, studies will be made of the reactions that lead to the production of ^{10}Be and ^{26}Al , also in order to open new perspectives of applied work.

Results

In the AMS line tests of the PIP and E/ Δ E detectors were performed, using Pt as a target.

Fig. 1 shows a high-energy mass spectrum and fig. 2 presents the isotopic ratios. These results have been obtained with the PIP detector. Optimization for Be detection is going on.

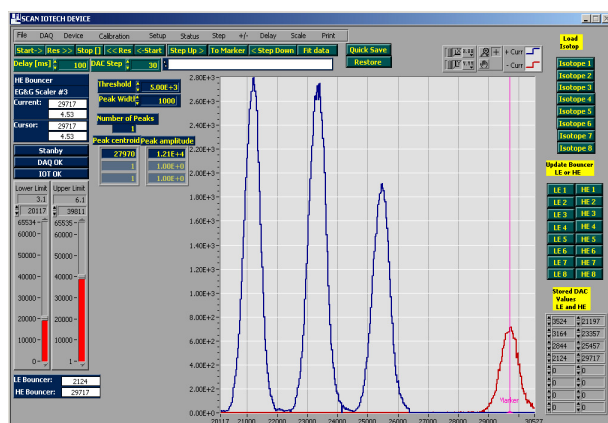


Fig.1 High energy mass spectrum of natural Pt from 194 to 198.

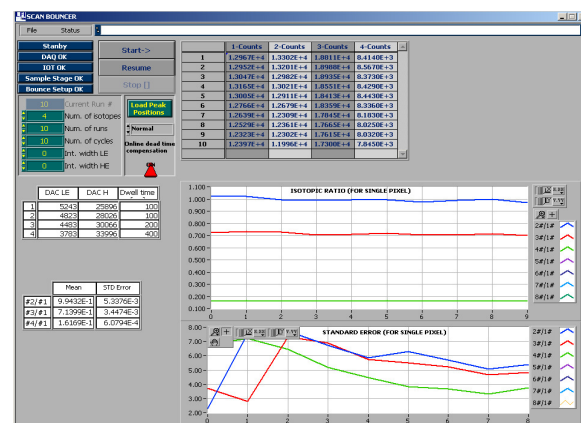


Fig.2 Labview control of the bouncing system, showing ratios relative to mass 194 isotope of the 195, 196 and 198 isotopes.

References

LUNA Collaboration; D. Bemmerer, F. Confortola, A. Lemut, R. Bonetti, C. Brogginì, P. Corvisiero, H. Costantini, J. Cruz, A. Formicola, Zs. Fülöp, G. Gervino, A. Guglielmetti, C. Gustavino, Gy. Gyürky, G. Imbriani, A. P. Jesus, M. Junker, B. Limata, R. Menegazzo, P. Prati, V. Roca, C. Rolfs, D. Rogalla, M. Romano, C. Rossi-Alvarez, F. Schümann, E. Somorjai, O. Straniero, F. Strieder,

F. Terrasi, H. P. Trautvetter, Nuclear Physics A779, 297-317 (2006).

J. Cruz, H. Luis, M.Fonseca, Z. Fülöp, G. Gyürky, F. Raiola, M. Aliotta, K. U. Kettner, A. P. Jesus, J. P. Ribeiro, F. C. Barker, C. Rolfs, Journal of Physics G 35, 014004 (2008).

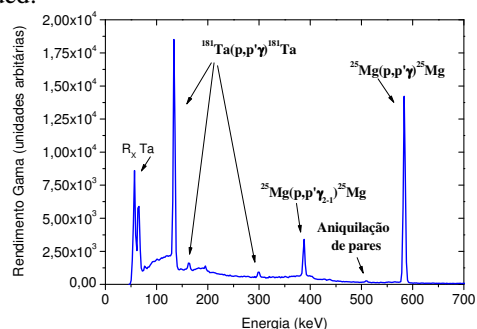
Development of a PIGE Set-up

M. Fonseca, R. Mateus, L. Gasques, A.P. Jesus, H. Luis, D. Galaviz, J.P. Ribeiro

The aim 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. A precise method based on a code [4] that integrates the nuclear reaction excitation function along with the depth of the sample was implemented for thick and intermediate thickness samples. For that purpose some reaction excitation functions were measured in the same analytical conditions. The energy steps needed to accurately define the excitation function were used as energy intervals for the integration procedure. The excitation functions for $^{27}\text{Al}(p,p'\gamma)^{27}\text{Al}$ and $^{25}\text{Mg}(p,p'\gamma)^{25}\text{Mg}$, were obtained. Thick target gamma yields for several samples containing Al and Mg were measured to be compared with calculated yields. Results for Al have already been published and the analysis of Mg (gamma spectrum in figure) was concluded.

Beam Energy (keV)	Sample	Y _{exp} /Y _{cal}
2400	Mg(OH) ₂	1.020
	MgH ₂	1.030
	MgSO ₄	1.032
2200	Mg(OH) ₂	1.043
	MgH ₂	1.046
	MgSO ₄	1.052
2000	Mg(OH) ₂	1.007
	MgH ₂	1.099
	MgSO ₄	1.054

Table: Ratios between experimental and calculated yields for several samples containing Mg



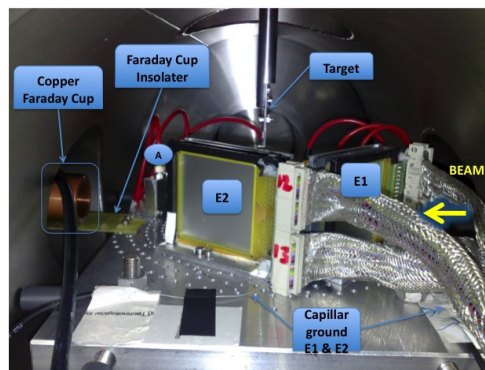
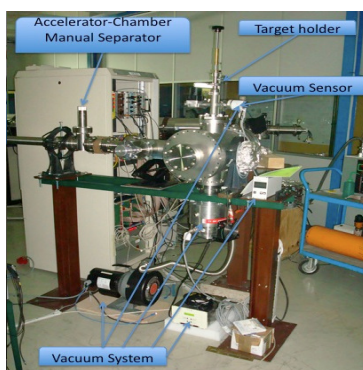
Gamma-ray spectrum of a sample of MgSO₄ obtained for 2.4 MeV protons.

A nuclear reaction line was assembled at the 3 MV Tandem accelerator to extend the work to higher energies. Excitation functions for proton inelastic scattering in from F and Li have been obtained.

Elastic Scattering of Protons by ^{58}Ni

L. Gasques, D. Galaviz, J. Cruz, M. Fonseca, H. Luis, A.P. Jesus, J.P. Ribeiro and international collaboration

Several groups coming from CNA-Seville, CSIC- Madrid, IPN-Orsay and IFN-USP-Brasil, joined with the NR group at ITN to assemble an elastic scattering experiment. Using the new reaction line installed at the 3 MV Tandem facility, a chamber equipped with a position sensitive fragmented silicon detector, a E/ΔE detector and several PIPs, brought from CNA-Seville together with its acquisition system, was installed. A 24 h schedule was arranged to measure the elastic scattering of protons by ^{58}Ni in the energy range from 2.5 MeV to 5.0 MeV. Following the previous work (of IFN-USP-Brasil) at higher energies, this experiment at energies near the Coulomb barrier had the goal to test the validity of the “S. Paulo” potential in this energy range. Results were obtained simultaneously for several scattering angles and for three different targets, ^{58}Ni , Au and ^{58}Ni and pure Au, in order to monitor and normalize the experiment. The stoichiometry of the Au and ^{58}Ni target was measured by alpha-particles RBS. Result analysis is going on.



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 Universities of Aveiro and Coimbra, Laboratoire Léon Brillouin (CEA-CNRS-Saclay), KFKI, Budapest, and the Budapest Neutron Centre. The main effort has been made to characterise the hybrid materials and copolymers prepared by gamma irradiation using the ^{60}Co source of UTR.

The systems studied involved hybrids prepared from mixtures of a polymer (PDMS) and different metallic alkoxides. Characterization of selected samples prepared by gamma irradiation continued, making use of a wide range of techniques, most of them available at ITN.

In 2009 sol-gel hybrid materials prepared in Aveiro University were also studied.

Some selected samples of hybrids prepared by irradiation have been measured by small angle neutron scattering in the Budapest Neutron Centre in Hungary.

During 2009 a PhD thesis has been concluded on the development of new copolymers (HEMA grafted on LPDE thin films) suitable for bioapplications. The elaboration of the necessary report for registration of a National Patent for the new polymeric material and its respective method of preparation is being resumed.

In collaboration with the RPI staff, a thorough evaluation of the present status of the neutron beam equipment was made, the perspectives of research and training activities at RPI were also evaluated and a strategy for future development agreed upon. To try to overcome the chronic lack of funds allocated to the neutron beam activities at ITN, a project entitled *Neutron diffraction for the scientific community* was submitted for funding to the Foundation for Science and Technology, led by a researcher recently hired in the framework of the program *Ciência 2008*. The pace at which changes can occur is somewhat dependent on the assessment of the project submitted to FCT.

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%)

M.H. GIL, Dep. of Chemical Engineering, Faculty of Sciences and Technology, Coimbra University

Collaborators

I.M.M. SALVADO, Dep. of Glass and Ceramics Engineering
UIMC, University of Aveiro

The role of Zirconium as thermal stabilizer of PDMS-TEOS hybrids

F.M.A. Margaça, I.M.M. Salvado¹, M. M. Portela Marques¹, L.M. Ferreira and A.N. Falcão

Objectives

To study the influence of the addition of small percentages of zirconium in the thermal stability of TEOS-PDMS hybrid materials.

Results

Hybrid materials were prepared using Tetraethylortosilicate and Polydimethylsiloxane silanol terminated with the addition of small contents of Zirconium Propoxide ≤ 5 wt%. The thermal stability of the sol-gel prepared samples was studied by Infra-red spectroscopy, ²⁹Si Nuclear Magnetic Resonance, Thermal Analysis and Scanning Electron Microscopy. All samples were monolithic after drying at 120 °C. After heat treatment at 400°C the samples prepared with 0 wt% in Zirconium Propoxide present high porosity. It was found that the content in Zirconium Propoxide is directly related with the thermal stability of the hybrid materials [1,2].

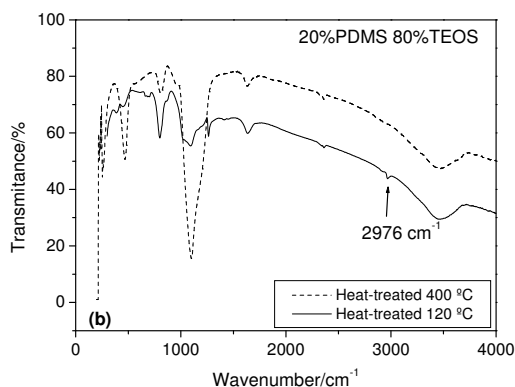


Fig.1 and Fig. 2 show Infra-red spectra of samples dried at 120°C and heat treated at 400 °C, with (a) and without (b) zirconium propoxide addition.

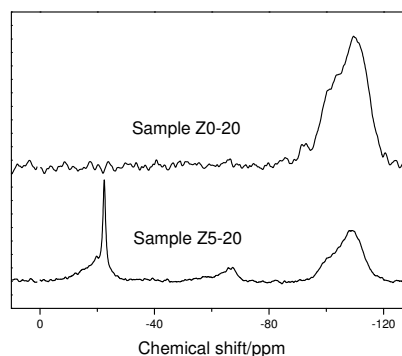
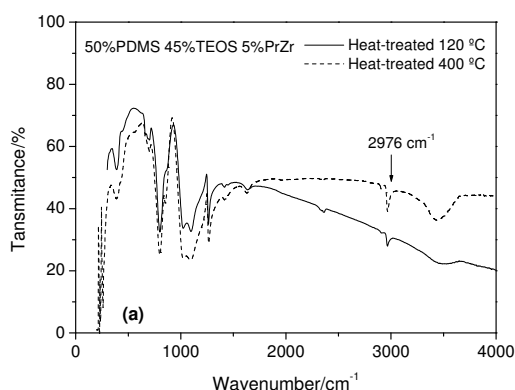


Fig.3 ²⁹Si MAS NMR results for two samples, heat treated at 400°C, one with zirconium addition (Z5-20) and another without zirconium addition (Z0-20).

Monolithic samples of PDMS-TEOS hybrids were obtained after drying at 120°C. Upon heat treatment at 400°C the samples prepared without zirconium propoxide addition were highly porous whereas the addition of zirconium propoxide allows retaining the dense monolithic character of the hybrid materials.

The characteristic IR bands associated to PDMS decrease in intensity or disappear with the heat treatment at 400°C for samples prepared without zirconium propoxide while these bands are still observed in samples prepared with zirconium propoxide heat-treated at the same temperature. The fact that no IR resonances due to units related with PDMS are observed for samples prepared without zirconium propoxide is indicative that the polymer degradation occurred during the heat treatment until 400 °C. These IR results were further confirmed by ²⁹Si NMR and thermal analysis.

It was found that the thermal stability of TEOS-PDMS hybrid materials can be increased by small additions of zirconium.

Published Work

S.R. Gomes, L.M. Ferreira, F.M.A. Margaça, I.M. Miranda Salvado and A.N. Falcão, Thermal analysis of hybrid materials prepared by gamma irradiation, *J. Thermal Analysis and Calorimetry*, 95(1) (2009) 99-103.

Portela Marques M.M., Miranda Salvado I.M., Margaça F.M.A., and Ferreira L.M., The role of Zirconium as thermal stabilizer of PDMS-TEOS hybrids, *Jour. Thermal Analysis and Calorimetry*, Online first: June 2009, Doi 10.1007/s10973-009-0180-7.

¹Dept. Of Ceramic and Glass Eng., CICECO, Univ. Aveiro

Modification of Polyethylene by Grafting Copolymerization Induced by Gamma Radiation – Its Application in Biomaterials Field

L.M.Ferreira

Polyethylene, due to its excellent chemical resistance, high impact resistance and gas permeability, has been extensively used as a backbone for radiation grafting of different monomers. However its hydrophobicity restricts its use as biomaterial. Several studies showed that the graft of 2-hydroxyethyl methacrylate (HEMA) onto a range of polymeric substrates results in an increase of materials hydrophylicity and biocompatibility.

In this context, HEMA was used as graft monomer and gamma radiation, from ITN ^{60}Co facility, as energetic source for the initiation of grafting process. Copolymers of polyethylene-g-2-hydroxyethyl methacrylate (PE-g-HEMA) were prepared in two final forms: granules and films. The optimization studies revealed that the radiation grafting process is sensitive to monomer concentration, irradiation environment and dose-rate. The best experimental conditions were determined (highest grafting yield and efficiency) and were used to produce PE-g-HEMA films.

The characterization of copolymeric materials showed that, even the high grafted samples, maintain good structural cohesion resulting mainly from the radiation protective effect of poly(HEMA) branches grafted onto polyethylene backbone. In particular, copolymeric films exhibit a rough surface, suitable for bio-interaction for cell adhesion and/or proliferation. The films surface roughness can be tailored by means of the radiation dose during the preparation stage.

It was observed in PE-g-HEMA films, improved hydrophylicity (up to 95%), non-hemolytic effect (*in vitro* biocompatibility) and low contamination. These findings point out for very interesting biological properties, suggesting multiple bioapplications possibilities for this grafted material, mainly in the biomedical area.

The elaboration of the necessary report for registration of a National Patent for the new polymeric material and its respective method of preparation is being resumed.

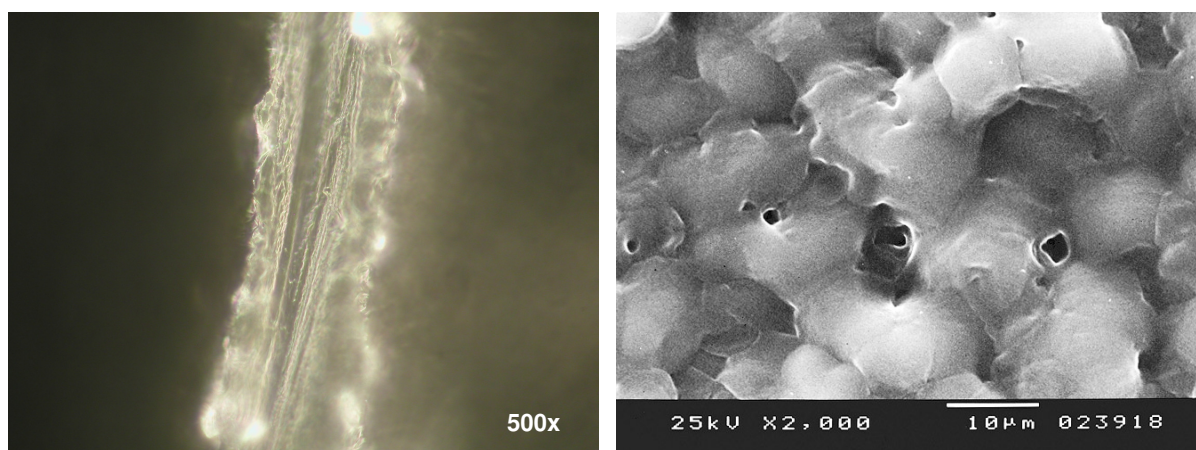


Fig.1 Micrographs of the cross section and surface of a copolymeric PE-g-HEMA film grafted at 403% (D= 9,0 kGy) obtained by optical microscopy (left) and SEM (right).

Collaboration in the Development of Instruments for Neutron Scattering at RPI

A.N. Falcão, F.M.A. Margaça

In 2009 and in collaboration with the RPI staff, a thorough evaluation of the present status of the neutron beam equipment was made, the perspectives of research and training activities at RPI were also evaluated and a strategy for future development agreed upon. To try to overcome the chronic lack of funds allocated to the neutron beam activities at ITN, a project entitled *Neutron diffraction for the scientific community* was submitted for funding to the Foundation for Science and Technology, led by a researcher recently hired in the framework of the program *Ciência 2008*. The pace at which changes can occur is somewhat dependent on the assessment of the project submitted to FCT

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.

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.

Following this concept in 2009 a collaboration was started with a multidisciplinary group named “Investigação em Aplicações Avançadas de Potência Pulsada” (GIAAPP- <http://sites.isel.ipl.pt/giaapp/>) that intends to apply high-intensity pulsed electric fields (PEF) as a decontamination/sterilization process for liquid products, in food and pharmaceutical line production. The group activities focus on the delineation, development, validation and application of technologies and processes in various fields, such as Environment, Food and Pharmaceuticals. 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 solicited 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).

Being aware of society’s current needs and the demand of Quality, Innovation and Development, the upgrading and renewal of facilities are being carried

out in the scope of project REEQ/996/BIO/2005. In the course of this project, modelling tools (Monte Carlo simulations) have been applied to the pre-upgrading phase of ionizing radiation equipments (*e.g.* gamma experimental facility). Other domain of this project has been the design of a renewed layout of an existing building transforming it in an interdisciplinary laboratory with controlled environment in order to assist new applications for radiation technology, among others. These facilities together with the inclusion of automation/robotic systems, in a further stage, have as main purpose to allow researchers of National and International Institutions and Industries to develop radiation technologies and/or to suppress the need of environmental control areas (clean areas) for their work.

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 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 bio-diversity profile of environmental samples.

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

Researchers

M.L. BOTELHO, Aux., Group Leader
S. CABO VERDE, Aux.

Students

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

Technical Personnel

H. MARCOS, system operator, ITN

Collaborators

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
L. REDONDO, ISEL, Professor
H.CANACSINH, ISEL, Professor

LETAL up to date

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

Objectives

The Laboratory of Technological Assays in Clean rooms (LETAL) is a multidisciplinary laboratory renewed under the scope of project REEQ/996/BIO/2005. Benefiting of the new infrastructures capabilities microbiologic studies are being developed, either as research experiments, or as a requested service. The outputs and milestones of these studies will be further detailed.

Results

Monitoring of Bonelike® product bioburden – The sterilization process of Bonelike product was previously established by the Group in 2008. As recommended by ISO 11137-2:2006, once the sterilization dose has been established, periodic audits shall be carried out to confirm appropriateness of the sterilization dose. This work is being carried out (requested service for Lusomedicamenta and Medmatinnovation) based on the validated methodology to assess Bonelike bioburden. These assays permit a review of environmental and manufacturing controls and if this follow up indicates lack of control, appropriate action should be taken. Until now the product bioburden has ranged between < 1 and 3 cfu/sample and the determined dose of 26 kGy remain in conformity to sterilize the Bonelike product.

D_{min} establishment of biomaterial based products – In the scope of ionizing radiation processes application it was requested by Ceramed® to establish the sterilization dose (D_{min}) of six pharmaceutical biomaterial products. The followed methodology was based on the validation of specific procedures to characterize products microbiota. The bioburden knowledge was used to correct the production lines and further on to estimate gamma radiation doses that guarantee products safety and quality. As outputs it was identified the critical control points for each product production line and corrective actions were implemented (e.g. use of nonpyrogenic water; raw material autoclavation) in order to lower and homogenize the products bioburden. For all the products it was able to validate a Sterilization Dose that guarantees the probability of a non sterile product item in one million processed items (SAL = 10⁻⁶). The estimated D_{min} ranged between 17 and 25 kGy. The applied dose establishment methodology allowed a product specific sterilization dose, reducing potential gamma radiation effects on functional and mechanical proprieties of the analyzed products. A strict collaboration with Ceramed continues to improve the stability to ionizing radiation of one of the studied products. This work is being developed by a common fellow.

MycoArchive project – A collaboration project with Coimbra University is being developed since 2007. This project aims to establish a disinfection process for a book archive using gamma radiation. Presently, book contamination sources are being followed up. Archive air and insects were collected and analysed to establish a contamination link with books microbiota. The most

frequent microorganism type found were the fungi (63%) and the isolates are being morphologically and genotypically characterized to analyse their relatedness. The archive air point out to be a significant cross source in book contamination.

LPM/MDN PIDDAC project – This collaboration project intended to study the microbiological environment of operating rooms of the Portuguese Military Hospital (HMP) for the prevention of nosocomial infections. During past years a microbial collection of surgical room environment has been collected and typified by bacteriological and molecular methods. The hospital microbial isolates showed to be very genetically diverse (Fig. 1) although it was noticed the persistence of some airborne microorganisms. As project milestone a database of nosocomial microorganisms was construct to be used in the HMP as infection control tool.

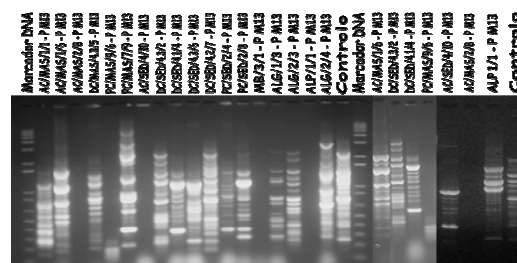


Fig.1 M13 fingerprinting of some airborne nosocomial microorganisms (n = 25) of HMP surgical rooms.

TradeLabor partnership – The air bioburden in national health care services is being evaluated for Air Quality maintenance. All surgical rooms tested presented airborne contamination bellow 10² ufc/m³. Comparing with corresponding previous results the surgical rooms air bioburden is decreasing, suggesting the effectiveness of the proposed corrective actions.

HomeEnergy service - The European Directive no. 2002/91/CE relative to energetic certification of buildings was transposed to the Portuguese law with the inclusion of Indoor Air Quality requirements, such as the evaluation of microbial parameters. As a requested service by HomeEnergy it is being evaluated the bacterial, fungal and *Legionella* spp. bioburden in several building air samples.

Published work

Internal Reports to LusoMedicamenta; February to December 2009: Sterilization dose certificates of Bonelike product batches (n=4).

Internal Report to Ceramed; August 2009: “Validation of sterilization process of biomaterial based products”, pp. 1 - 32.

Internal Report to “Clínica do Poetas”; October 2009: “Monitorization of Microbial Indoor Air Quality”, pp. 1 - 10.

Internal Reports to HomeEnergy (n=80); since October 2009. Microbial parameters of Indoor Air Quality.

R&D in Chemical Field*R. Melo, J.P. Leal¹, S. Cabo Verde and M. L. Botelho*

The applicability of ionizing radiation in the environmental remediation of wastewater is being researched. The presence of biorecalcitrant compounds in wastewater blocks the biological processes. Therefore, radiation degradation of complex compounds is a promising technology to achieve the aforementioned goal. Gallic acid (GA) is a biorecalcitrant phenolic compound and could be considered as a model pollutant of the wastewater generated in the cork boiling process. The chemical oxidation of GA is being studied but there is a lack of information on its radical reactions pathways and degradation products. The evaluation of rate constants as well as the establishment of the partial contributions of the direct and radical reactions pathways to the global process and the identification of potential stable by-products was studied using pulse radiolysis technique and Electrospray ionization (ESI), respectively. The OH[•] radical and H[•] atom intermediates of water radiolysis react with the GA molecules yielding cyclohexadienyl type radicals which could react by two ways: (1) loss water molecule forming phenoxy type radical or (2) reacts with superoxide leading to benzenic ring opening and formation of stable structures. These structures could rearrange and reacts with phenoxy radical generating stable by-products. The main stable by-products were identified by ESI. Biodegradation studies are being developed using four different carbon sources in a minimal growth medium (Colby&Zatman): (a) without carbon source; (b) with 0,1% methanol; (c) with 0,1 mM gallic acid solution and (d) with irradiated 0,1 mM gallic acid solution. The different substrata were inoculated with *Methylobacterium extorquens* and kinetic growth curves are under study. The present results suggest that there is no effect of carbon source on *M. extorquens* growth. Other Chemical field of study is the validation of dose rate by reference Fricke dosimeter in the upgraded experimental Co-60 source. In the highest dose rate local, the value is approximately 1.1 kGy/h. Several studies are being made to establish isodose curves to a better definition of the irradiator and chamber geometry.

¹ Chemical and Radiopharmaceutical Sciences (UCQR) Unit, ITN**Advanced applications of high-intensity pulsed electric fields – A2P2***V. Dorés, B. Batista, H. Canacsinh¹, L. Redondo¹ and M. L. Botelho*

Recent advances in the field of high-intensity pulse power technology allowed the development of new nonthermal sterilization methods. This technology has as main advantages an energy saving, environmental friendly, increase of added-value products, process optimization and cost reduction. The aim of present research in this field is the application of high-field electric pulse technology to inactivate microorganisms in order to develop an industrial scale non thermal sterilization method. Presently the performed studies focus the perception of critical parameters and potential microorganism's inactivation mechanisms for an effective method optimization. This R&D work is under a Protocol in development between several entities and could be seen the participants at <http://sites.isel.ipl.pt/giaapp/>.

¹ Electrotenic and Automation Engineer Department, ISEL**Implementation of techniques to assess virus infectivity***S. Cabo Verde, S. J. Nascimento¹ and M. L. Botelho*

Environmental virology is an emergent field due to the importance of food- and water-transmitted viruses. This area of research is being implemented at LETAL with the purpose of study the inactivation of enteric viruses (e.g. norovirus and adenovirus) by ionizing radiation for disinfection purposes. Murine norovirus (MNV) and human adenovirus 2 (HAd2) stocks were propagated using RAW 264.7 and A549 cell lines, respectively. The viral stocks yields were estimated by plaque assay that is the gold-standard method to measure virus infectivity. This method relies upon (1) the use of confluent monolayers of cells which are susceptible to the virus, (2) the induction of a visible cytopathic effect by the virus and (3) the use of a semisolid overlay which prevents virus diffusion from one infected cell to other nearby cells. As a result, small round plaques (clear areas) form in the cell monolayer as the virus replicates. The estimated MNV titre was 10⁶ PFU/ml and sub-lethal gamma irradiations will be carried out further on. For HAd2 the plaque assay technique is being optimized, namely in the type of cell vital staining, for an enhanced visualization of plaques forming units.

¹ Pharmacy Faculty, UP

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-phase 2 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 conversion of methane by a non-thermal plasma is been studied, using He/CH₄/O₂ or He/CH₄/CO₂ mixtures on DBD (dielectric barrier discharge) system. The dependency of the conversion efficiencies (for methane and the oxidant) and the selectivities for H₂, CO, CO₂ and C₃ compounds on helium concentration and the specific input energy

was characterized. Different methods for the measurement of the plasma power consumption were compared. The development of a kinetic model for the discharge was started with the study of the electron kinetics.

2. The development of the PLASMAKIN modelling package has continued with the build up of a database of species properties.

Development of software for control and data analysis

A gamma spectrometry system based on the EPICS system for instrument communication and control was optimized and extended with the support of simultaneous multichannel acquisition boards. The system uses a client-server architecture allowing remote operation and integration of diverse instrumentation.

Instrumentation and Technical Assistance

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.

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, Department of Automation and Electrotechnical Engineering.
3. 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)
A. JANECO, Project Grantee (NP)
M. VRÁNIC, Grantee (NP, 25%)
R.P.F. MENDES, Grantee, FC/UL (NP, 20%)

Technical Personnel

T. JESUS, Electronic Technician
N. INÁCIO, Electronic Technician
M. CABAÇA, Mechanical Technician

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) An “Experimental Laboratory” for training in nuclear sciences and science promotion activities has been installed
- (iii) Development and maintenance of electronic equipment to UFA, UPSR, URSN, UCQR and UTR.



Summary of the more relevant Services/Equipments rendered in 2009

Activity	Qty	Client
Electronic Equipment Laboratory equipment for the determination of radioactive element traces by electrodeposition	1	DR. WESTREIR GMBH (Alemanha)
	1	SOUTH CAROLINA STATE UNIVERSITY (USA)
	1	CITY CORPORATION (Jordânia)
	1	AIEA (Kuwait)
	Disks	AIEA (Bangladesch)
Electronic Equipment Personal Radiation Dosimeter Equipment	13	J. ROMA, LDA
Electronic Equipment 6 Channel Micro Current Equipment	4	UNIVERSITÉ DE RENNES (França)
	3	ITN/UCQR (Portugal)
	2	UNIVERSITÉ DE ANGERS (França)
Electronic Equipment High Voltage Power Supply	1	ITN/UPSR
Electronic Equipment Technical Assistance to Nuclear Equipment	32	EMA21 – Portucel/Soporcel (Figueira da Foz)
	12	EMA21 – Portucel/Soporcel (Figueira da Foz)
	3	ITN/URSN
	4	MINISTÉRIO DA MARINHA
	1	FACULDADE ENGENHARIA PORTO
	1	ORTOGNÁTICA
Prices including TAX (VAT)		Total Amount: 28 963,94 €

Participation of ITN in the n_TOF ph.2 experiment at CERN

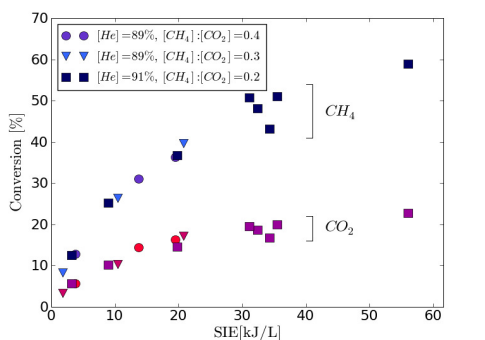
I.F. Gonçalves, P. Vaz, C. Cruz, J. Neves, C. Carrapiço, R. Sarmiento, L. Tavora

The n_TOF ph.2 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 2009.

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 BaF2 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 BaF2 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 BaF2 calorimeter.

Conversion of methane by a non-thermal plasma using CH₄/O₂/He and CH₄/CO₂/He mixtures on a dielectric barrier discharge system.

J. Branco, N. R. Pinhão, A. Janeco, A. G. Ferreira, L. Redondo, A. P. Gonçalves



Experimental results for the conversion of CH₄ and CO₂ obtained with a He/CH₄/CO₂ mixture.

The conversion of methane by a non-thermal plasma produced by a DBD (dielectric barrier discharge) is being studied, using He/CH₄/O₂ or He/CH₄/CO₂ mixtures. The dependency of the conversion efficiencies and the selectivities for H₂, CO, CO₂ and C3 compounds on helium concentration and on the specific input energy was characterized. Although with O₂ we were able to reach a CH₄ conversion of 70%, the use of CO₂ has the advantage of the conversion of CO₂ (up to 30%), a greenhouse gas, and selectivities for H₂ and CO between 70-80%. The development of a kinetic model was started with the study of the electron kinetics. The electron transport parameters and rate coefficients were obtained and the results show the presence of a maximum for the dissociation of methane as a function of the reduced electric field and helium concentration.

Development of a database for the PLASMAKIN modelling package

N. R. Pinhão

The development of the PLASMAKIN modelling package has continued with the support of data input from a database and the build up of a database of species properties and reactions. The database is based on the public domain and widely deployed serverless SQLite library.

The database can be accessed using standard SQL commands or through a wide range of available programs. The library supplied with the package includes properties for a large number of gases, level information for the rare gases and a collection of sample reactions.

Development of a distributed system for data acquisition and treatment in gamma spectrometry

R. P. F. Mendes, N. R. Pinhão

A gamma spectrometry system based on the EPICS system for instrument communication and control was optimized for asynchronous operation and extended with the support of simultaneous multichannel acquisition boards.

The system uses a client-server architecture allowing remote operation and integration of diverse instrumentation. Data acquisition is done on a PC running a real-time Linux kernel and equipped with multichannel acquisition boards while data treatment can be done in any PC running a client application and communicating by TCP/IP. The project has included the development of a Linux device driver for the EG&G 916A multichannel board.