Physics Sector

Physics

Eduardo Alves

During 2006 the activities in the Physics Department kept focused on Applied and Fundamental Research of Materials, Environment and Health Sciences. The groups maintained their commitment to engage post graduated students (M.Sc., Ph.D.) in the running projects. This collaboration has been instrumental for the high output and scientific level of the research work in the department. The Physics department was enriched by new equipments and instruments bought under the framework of a reequipment programme. These have been integrated in the existing facilities.

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

2 – High Temperature Materials Laboratory (MA^3T) is equipped with a high-resolution, high-temperature diffractometer (*Hotbird*) with a new high resolution line for low dimensional structures studies. The *Hotbird* with its high specificity and enhanced capabilities is used to solve difficult problems in advanced materials, *e.g.* materials used in the electronics industry, high temperature alloys for fusion applications, superconductors, *etc*. The research activity in the laboratory is merged with the Advanced Materials Research Group.

3 – Neutron Spectrometers Laboratory at the RPI, the nuclear research reactor facility, comprises one 2-axis diffractometer (*DIDE*), one SANS instrument (*EPA*), and a TOF diffractometer for educational purposes. A new detector assembly for the *DIDE* instrument is projected and awaits a funding decision. To improve the signal-to-noise ratio at the *EPA* facility a cryostat is being designed for the installation of a 20 cm long Be filter in the neutron beam line. R&D on new copolymers (HEMA grafted on LPDE thin films) suitable for bioapplications and hybrid materials prepared by γ-irradiation are in progress in collaboration with groups in Coimbra, Aveiro, Saclay, and Budapest. Activities are presented under the heading ***Condensed Matter Physics.***

4 – Ionising Radiation Laboratory has been running to develop applied research for industrial purposes. The research makes use of a Co-60 irradiation unit, UTR, with a semi-industrial dimension. In order to develop new radiation technology applications, the upgrading and renewal of the equipment have been carried out by the "*Radiation Technologies: Processes and Products Group*". This project implies ionizing radiation equipment, *e.g.* electron accelerator and gamma experimental facilities, a multidisciplinary laboratory with controlled environment and application of robotic--automation systems in the facilities. The main R&D activities for the application of ionising radiation are described under the heading ***Radiation Technologies: Processes and Products Group.***

5 – Nuclear Instruments and Methods Laboratory activities are focused 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, which are presented under the title ***Nuclear Instruments and Methods.***

Physics Staff

Researchers

- E. ALVES (Principal Researcher)
- F. MARGAÇA (Principal Researcher)
- J.G. CORREIA (Principal Researcher)
- R.C. DA SILVA (Principal Researcher)
- U. WAHL (Principal Researcher)
- C. CRUZ (Auxiliary Researcher)
- I. GONÇALVES (Auxiliary Researcher)
- J. MANTEIGAS (Auxiliary Researcher)
- J. NEVES (Auxiliary Researcher)
- L.C. ALVES (Auxiliary Researcher)
- M.L. BOTELHO (Auxiliary Researcher)
- M.T. PINHEIRO (Auxiliary Researcher)
- M.A. REIS (Auxiliary Researcher)
- L.M. FERREIRA (Assistant Researcher)

Techniciens

- 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) is responsible for running the Ion Beams Laboratory (IBL). The laboratory is equipped with a 2.5 MV Van de Graaff accelerator, an ion microprobe presently being fitted with an external beam facility, a recently installed 3 MV tandem accelerator with an Accelerator Mass Spectrometry (AMS) line, and a 210 kV high fluence Ion Implanter.

The work carried out during the last two decades allowed the group to achieve a large expertise in the field of applications of ion beams to Materials Science. The group activities are focused on the processing and characterisation of advanced materials using ion beam based techniques. Several national and international collaborations allow a continuous exchange of expertise and mobility of researchers, an important condition to keep the scientific activity in the group at the forefront of research in its field.

The current research activities of the group were focused in two kinds of materials: wide band gap semiconductors, and nanostructures and insulators. Wide bandgap semiconductors are under intense research all over the world due to the possibility of developing optoelectronic devices working in the visible wavelength range of the electromagnetic spectrum. Our work aims at the optimization of the implantation conditions of optically active dopants. Other relevant research work is being carried out in quantum well structures and quantum dots. An intense study of the structural properties of GaN/InGaN structures is under way in collaboration with the Universities of Aveiro and Strathclyde. Structural and optical studies of Ge and GaN quantum dots are a new field of research in collaboration with the Universities of Aveiro and Grenoble.

The work in insulators is a continuation of ongoing projects or bilateral collaborations. Of these particular interest resides in the modification of the optical and electrical properties of α-Al_2O_3 and laser materials (KTP and RTP), and also of the magnetic and electrical properties of MgO and rutile doped with ions of magnetic transition metals by high fluence implantation. Besides this and due to the potential of ion beam techniques to study thin films and multilayers, important collaboration work continued in the characterisation of magnetic thin films and layers for magnetic spin valves, diluted semiconductors and tunnel junctions, as well as in the field of protective oxynitride coatings.

The activity in the technology programme of the European Fusion Development Agreement (EFDA), in association with the Centro de Fusão Nuclear of the Instituto Superior Técnico continued with studies on the oxidation behaviour of beryllides, and on the characterization of the new Eurofer (ODS) steel.

Integrated in these research activities the group has also been strongly involved in training graduate and undergraduate students, through the supervision of M.Sc. and Ph.D. thesis.

All these activities were financially supported by a large number of projects, both European and National (FCT), either in collaboration with other Institutions or lead by members of the group.

The scientific activity of the group in 2006 was materialized in:

Publications (peer review journals): 91
Conference and workshop contributions: 9 invited talks, 13 oral and 34 posters.
Running projects: 12

Researchers(*)

E. ALVES, Principal researcher (Coordinator)
R.C. DA SILVA, Principal researcher
L.C. ALVES, Auxiliary researcher (75%)
U. WAHL, Principal researcher
N. BARRADAS, Principal researcher (10%)
A.R. RAMOS, Auxiliary researcher (10%)
A. KLING, Auxiliary Researcher (10%)
K. LORENTZ, fellow FCT

Students

A. FONSECA, Ph.D. student, Project grant**
C.P. MARQUES, Ph.D. student, FCT grant
E. RITA, Ph.D. student, FCT grant
J. VAZ Pinto, Ph.D. student, FCT grant
M. VILARIGUES, Ph. D. student***
N. FRANCO, Ph.D. student, FCT grant**
S. MAGALHÃES, Project grant**

Technical Personnel

J. ROCHA
M.F. BAPTISTA
P. PEREIRA

Collaborators

L. REDONDO
M.R DA SILVA
P.A. RODRIGUES
S. PEREIRA

(*) Also members of CFNUL.
(**) High Temperature Materials Lab.
(***) Technician, Dep. Cons. & Rest., UNL

Structural analysis of nitride quantum structures

K. Lorenz, N. Franco, S. Magalhães, N. Barradas, E. Alves, I.M. Watson[1], R.W. Martin[1], K.P. O'Donnell[1], B. Amstatt[2], B. Daudin[2]

An issue of fundamental importance in semiconductor physics continues to be the measurement of strains and crystal quality within quantum structures. These include strained-layer structures incorporating wide-gap group III nitride semiconductors which have an impressive variety of realized and proposed applications in (opto-) electronic devices, such as lasers, LEDs, transistors, sensors etc.

Rutherford backscattering/channelling spectrometry (RBS/C) and X-ray diffraction (XRD) were used to study the composition and structural properties of AlInN/GaN bilayers and AlN/GaN superlattice structures.

The ternary AlInN is attracting much research interest due to the possibility of growing AlInN lattice-matched on GaN for InN concentrations around 17-18 %, promising low misfit dislocation densities. Furthermore, AlInN alloys are candidates for opto-electronic devices covering an extremely wide spectral region from deep UV to IR since the band gap can range from 6.2 eV (AlN) to 0.7 eV (InN).

Near-lattice-matched $Al_{1-x}In_xN$ layers were grown by metal organic chemical vapour deposition (MOCVD) on micrometer thick GaN buffer layers on sapphire at different growth temperatures between 760 and 840 ºC. As expected, with increasing growth temperature the amount of InN introduced into the layer decreases and the crystalline quality is improved.

Discrepancies between composition determination by XRD and RBS indicate a deviation of this alloy from Vegard's law as it was also predicted by density functional theory calculations. A tentative correction to Vegard's law reconciles the XRD and RBS/C measurements.

Steering effects in the interface influence the angular yield from the GaN-layer in RBS/C and cause failure of the conventional means of assessing strain by RBS/C. We have shown for the first time that Monte Carlo simulations are viable as a routine tool to correct channeling results for such steering effects, leading to an excellent agreement of RBS/C and XRD strain measurements. The in plane strain in high crystalline quality AlInN-on-GaN films was found to change from tensile to compressive as the InN fraction increases from 13 to 19 %. Lattice matching is predicted to occur at 17.1(9) %.

Self-assembled GaN quantum dots in AlN multilayers consisting of 150 periods were investigated. Using RBS in grazing incidence geometry the first eight bilayers can be clearly separated, and it is possible to draw information on layer thickness, composition and quantum dot properties.

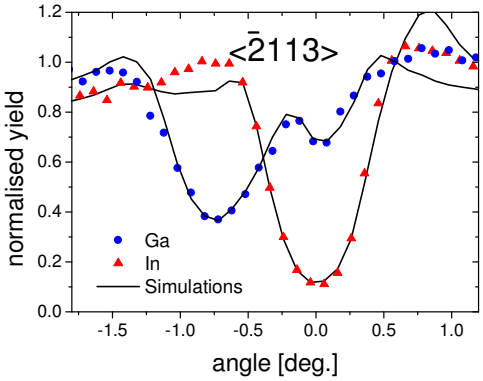


Fig. 1: Ga and In RBS/C angular scans across the $<\bar{2}113>$ axis of a AlInN/GaN bilayer with 13 % InN content. The second dip in the Ga-scan with a minimum at the same position as the In-scan is due to steering effects in the interface. The effect is well reproduced by Monte Carlo simulations, which allow the correct determination of strain in the layer.

Angular scans across the <0001> axis show a low minimum yield of 8 % indicating a perfect stacking of the layers along the growth direction. Further investigation will focus on the determination of strain in the multi-layers and aim to explain the influence of strain in the process of vertical self assembly of the GaN quantum dots.

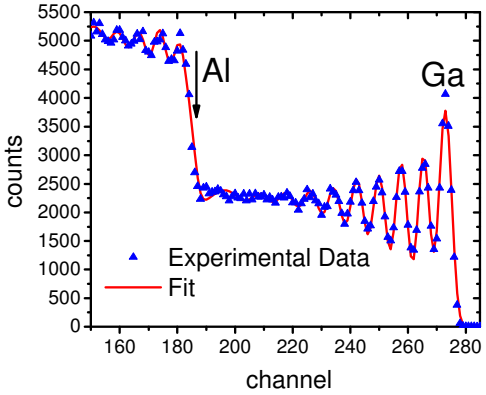


Fig. 2: RBS spectra and fit of a GaN-QD/AlN superlattice taken with the sample tilted by 86º in order to improve the depth resolution. The NDF simulation program was modified in order to describe cylindrical quantum dots.

[1] University of Strathclyde, Glasgow, U.K.
[2]CEA/CNRS, Grenoble, France

Rare earth doping of III-nitride alloys by ion implantation

K. Lorenz, E. Alves, T. Monteiro[1], A. Cruz[1], M. Peres[1], A.J. Neves[1], M.J. Soares[1], I.S. Roqan[2], K. Wang[2], R.W. Martin[2], C. Trager-Cowan[2], K.P. O'Donnell[2]

Rare earth (RE) doped nitrides are widely studied with respect to potential applications in electroluminescent devices. While GaN is the most studied nitride host for RE implantation, AlN and the ternary alloys $Al_xGa_{1-x}N$ are also promising host candidates. Their wider band gap allows exploitation of higher lying RE levels and a lower thermal quenching of the luminescence is expected. Furthermore, those Al containing alloys are more resistant to implantation damage than GaN.

$Al_xGa_{1-x}N$ ($0 \le x \le 1$) epilayers grown by HVPE or MOCVD were implanted with Eu and Tm. Rutherford backscattering/channelling (RBS/C) was used to study structural properties and the lattice site location of the implanted ions. Optical studies were performed using photoluminescence (PL) and cathodoluminescence (CL) spectroscopy. $Al_xGa_{1-x}N$ with $x \ge 0.08$ was shown to be more resistant to implantation damage than GaN and no surface amorphisation occurs. Furthermore, the samples are stable at annealing temperatures well above 1000 ºC while GaN at these temperatures requires a special protection of the surface, for example by a thin AlN cap layer. The RE are found slightly displaced from the substitutional cation sites with stronger displacements for higher Al concentrations. The near substitutional fraction and PL characteristics of Eu implanted AlN are influenced by the annealing ambient and temperature.

The PL intensity at room temperature of Eu implanted $Al_xGa_{1-x}N$ increases strongly when the Al content is increased from 0 to 30% and drops steeply when the Al content is further increased.

The possibility to exploit higher lying RE levels in AlGaN as compared to GaN was shown for the blue lines of Tm.

[1] Dep. de Física, Universidade de Aveiro, Aveiro, Portugal
[2] Department of Physics, SUPA, University of Strathclyde, Glasgow, G4 0NG, U.K

Optical and structural study of Ge/Si quantum dots on Si(100) surface covered with a silicon oxide layer

A. Fonseca, E. Alves, J.P. Leitão[1], N.A. Sobolev[1], M.C. Carmo[1], A.I. Nikiforov[2]

Si/Ge low-dimensional structures attract the attention of the scientific community due to their potential to develop new electronic and optoelectronic devices. Among the different ways to produce Ge islands on Si substrates, a technique was recently developed that is based on the Wollmer-Weber growth mode, which relies on the growth of the Ge islands on top of a SiO_2 interlayer. Through this mode, we may obtain smaller Ge islands with extremely high density.

The formation of Ge quantum dots (QDs) grown on an ultrathin interlayer of SiO_2 on top of a Si(001) substrate was investigated, as a function of the thicknesses of the SiO_2 interlayer (0.5, 0.75 or 1 monolayer) and of the Ge layer (0.3, 0.6 or 0.9 nm). The structural characterization was performed by Rutherford backscattering spectroscopy (RBS). Photoluminescence (PL) was used to characterize the optical behaviour of all samples. Hydrogen treatment was performed in order to passivate non-radiative recombination channels, thus enhancing the PL intensity. The results suggest the formation of Ge nanoislands for the sample with 1 ML of SiO_2 and 0.9 nm of Ge, and exclude their formation for samples with lower SiO_2 and Ge layer thicknesses. We also observe an influence of the SiO_2 interlayer thickness in the QDs formation.

[1] Dep. de Física, Universidade de Aveiro, Aveiro, Portugal
[2] Institute of Semiconductor Physics, 630090 Novosibirski, Russia

Implantation of nanoporous GaN with Eu ions

S. Magalhães, K. Lorenz, E. Alves, M. Peres[1], T.Monteiro[1], S. Tripathy[2]

Nanoporous GaN samples were implanted with 150 keV Eu^+ ions with a fluence of 5×10^{15} cm^{-2}. Channeling and x-ray diffraction (XRD) measurements indicate a high crystalline quality. After implantation the optical activity of the GaN is quenched by the implantation damage. The <0001> aligned spectrum reveal broad damage distribution over the entire porous layer responsible for an expansion along the c-axis with a parameter increase of 0.3% as indicated by XRD. Photoluminescence due to above band gap excitation at low temperature indicates the presence of two regions with different optical properties after annealing. We observe a transparent zone with UV and yellow-green broad emissions and a pale brown region where the UV emission is absent. In both regions the intraionic 4f ^{6} Eu^{3+} emissions are present. XRD and channeling confirm the good crystalline quality of the samples after the annealing and the incorporation of Eu into near substitutional Ga sites.

[1] Dep. de Física, Universidade de Aveiro, Aveiro, Portugal
[2] Institute of Materials Research and Engineering, 117602, Singapore

Effect of annealing and ion implantation on AlN/GaN quantum dot heterostructures

S. Magalhães, K. Lorenz, E. Alves, B. Amstatt[1], B. Daudin[1]

The incorporation of quantum dots in III-nitride heterostructures aims at exploiting novel optical and electronic properties due to quantum confinement effects. The development of devices may include processing steps like high temperature annealing or ion implantation which can alter the structural and optical properties of the heterostructures. Ion implantation presents an alternative to incorporate dopants into heterostructures but the implantation damage can deteriorate the structural and optical properties of the samples.
In this work multilayers consisting of up to six GaN quantum dot layers separated by AlN buffer layers grown by molecular beam epitaxy were studied. Eu ions were implanted into the heterostructures with 120 keV to a fluence of 1×10^{15} cm^{-2} (see figure). Structural properties and the effects of thermal and ion beam processing were analysed using X-ray diffraction (XRD), X-ray reflection (XRR) and Rutherford backscattering and channelling spectrometry (RBS/C). High resolution RBS with grazing beam incidence, of as grown samples enabled the individual GaN-dot layers to be resolved and XRD reveals the existence of a second peak corresponding to a region in AlN which is deformed by the strain caused by the GaN quantum dots. Annealing performed in nitrogen atmosphere for 20 min at temperatures between 1000 ºC and 1200 ºC produced slight changes of the multilayer period with high temperature annealing as shown by XRR. For 1200 ºC annealing the broadening of the XRD profile indicates the deterioration of the crystal mainly due to surface degradation. The implantation damage in the AlN/GaN quantum dot heterostructure will be compared and discussed with respect to the results found in thick GaN and AlN layers.

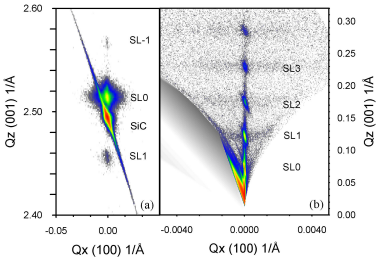


Fig.: (a) (002) Reciprocal Space Map (RSM) of the as grown sample. The SiC and superlattice peaks are indicated as SiC, SL0, SL-1 and SL1, respectively. (b) corresponding XRR RSM.

[1] CEA/CNRS GROUP, "nanophysique et semiconducteurs", Dépt. de recherche fondamentale sur la matière condensée

Study of InGaN/GaN single quantum wells grown by metal-organic chemical vapour deposition

E. Alves, N.P. Barradas, S. Pereira[1], A. Kholkin[1], I.M. Watson[2]

Strong interest has recently developed in the transfer of excitations from InGaN quantum wells into other luminescent media. Previous work specifically relevant to the current investigation involves non-radiative energy transfer from near-surface InGaN quantum wells to either colloidal semiconductor quantum dots or light emitting polymers. In this context, the accurate measurement of the fundamental structural parameters in SQW and MQWs such as the well compositions and thickness, and in particular cap layer thicknesses are fundamental from a technological and scientific point of view. However, accurately measuring these parameters in ultra-thin (~2 nm), buried epitaxial layers is extremely difficult, particularly for SQWs with low (<0.05%) InN mole fraction.
Here we report detailed structural characterization results of InGaN/GaN MQWs and SQWs obtained from grazing incidence Rutherford backscattering (RBS) analysis. Careful simulation of the RBS spectra could provide precise estimations of individual well/barrier compositions, thickness and the extent of In/Ga intermixing. Moreover, in the case of low InN content SQWs grown with different GaN cap thickessess (nominal values of 5, 7.5 and 15 nm) the cap layer thickness could be determined with a good precision.

[1] CICECO
[2] University of Strathclyde, Glasgow, U.K

Ni induced growth of crystalline silicon nanowires

A.R. Ramos, E. Alves, I. Ferreira[1], L. Pereira[1], P. Vilarinho[2], E. Fortunato[1], R. Martins[1]

The transition from crystalline silicon aggregates to silicon nanowires (SNWs) films produced by Low Pressure Chemical Vapour Deposition (LPCVD) of pure SiH4 gas on Ni covered corning glass substrates was studied. Scanning electron microscopy (SEM) images and X-ray diffraction patterns confirm that transition when the substrate temperature varies from 823K to 923K. Rutherford Backscattering Spectrometry (RBS) analyses quantify the film composition in depth and the progression of Ni buffer layer from substrate to top film surface. We have demonstrated the production of silicon crystalline films and nanowires by LPCVD technique at relative low temperature (923K) compatible with corning glass substrates workable temperature. We expect that by controlling the Ni buffer layer thickness we may obtain nanowires where Ni is either present at the top surface, or along the entire film to form NiSi silicides. The anisotropic SNWs growth achieved can be a disadvantage for certain applications, those that need straightforward and well aligned nanowires, but can also be an advantage for other applications such as the ones were light must be trapped.

[1] CENIMAT, Dep. de Ciência dos Materiais, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, and CEMOP-UNINOVA, Campus da Caparica, 2829-516, Caparica, Portugal
[2] CICECO, Departamento de Engenharia Cerâmica e do Vidro da Universidade de Aveiro, 3810 193 Aveiro, Portugal

Structural evolution in ZrN_xO_y thin films as a function of temperature

E. Alves, A.R. Ramos, N.P. Barradas, F. Vaz[1], L. Rebouta[1], U. Kreissig[2]

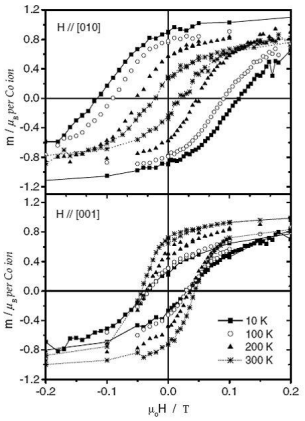
Single-layered zirconium oxynitride (ZrN_xO_y) thin films have been deposited on steel substrates at a constant temperature of 300 °C, by radiofrequency (rf) reactive magnetron sputtering of a pure Zr target in an argon-oxygen-nitrogen atmosphere. The variation of the flow rate of the reactive gases enabled changes in the composition and structure of the films. X-ray diffraction (XRD) and glancing incidence X-ray diffraction (GIXRD) were used to study the as-deposited films and their structural changes during or after heat treatment, from 400 °C to 900 °C, in controlled atmosphere and in vacuum. The as-deposited films revealed the occurrence of a face-centred cubic (fcc) phase (Zr-N type), but a Zr-N oxygen-doped phase (Zr-N-O) may be also present depending on the oxygen content in the films. Heat treatment above 600 °C reveals the appearance of a tetragonal phase of zirconium oxide. The results are discussed as a function of the chemical composition of the films, annealing temperature, and type of the annealing process.

[1] Universidade do Minho, Dept. de Física, Campus de Azurém, 4800-058 Guimarães, Portugal
[2] Forschungszentrum Rossendorf e.V., Postfach 510119, 01314 Dresden, Germany

Stuctural and magnetic properties of oxides implanted with transition metals

J.V. Pinto, M.M. Cruz[1], M. Godinho[1], E. Alves, R.C. da Silva

We extended previous studies on the behaviour of the transition ions Co, Ni and Fe in MgO to the case of TiO_2, a potential candidate for spintronics applications. The goal is to fully characterize the behaviour of the implanted ions. Magnetic, electrical and structural (RBS and XRD) characterization were used to study these systems.



For 10^{17} cm^{-2}, 150 keV Co-implanted single crystalline α-TiO_2 rutile, the as implanted state exhibits superpara-magnetic behaviour attributed to the formation of ~5 nm sized hcp cobalt clusters. Vacuum annealing at 1073 K induces anisotropic ferromagnetic behaviour, the easy axis direction lying in the (001) plane of rutile, due to the $(002)_{Co}$ and $(100)_{Co}$ // $(100)_{rutile}$ orientations of the cobalt clusters (see figure). Enhanced electrical conductivity exhibits also anisotropy at low temperatures, following the same general trend as in reduced rutile. No magnetoresistive effects were detected, indicating that there are no polarization effects of the charge carriers induced by the cobalt ions. Annealing in air promotes the segregation of cobalt to the surface of rutile, pointing to the role of oxygen vacancies in stabilizing the aggregates in reduced rutile. It is suggested that vacancies accommodate at the interface between the aggregates and the TiO_2 host. Results for Ni implanted α-TiO_2 rutile are similar. Studies with Fe have been initiated.

Fig.: Hysteresis loops taken at different temperatures in the hard and easy magnetization in-planar directions for vacuum annealed sample (reproduced from The European Physical Journal-B., 55 (2007) 253-260)

[1] Dep. de Física, Faculdade de Ciências da Universidade de Lisboa.

Friction and wear mechanisms in orthopaedic prostheses: influence of the composition of the periprosthetic fluid[1]

E. Alves, R.C. da Silva, B. Saramago[2]

Osteoarthritis and rheumatoid arthritis often require substitution of natural joints by prostheses, especially of hip and knee. The most common cause of failure and lack of durability of total hip prostheses is related with the generation of wear debris of UHMWPE from the acetabular part, when sliding against the ceramic or the metallic ball which substitutes the femoral head.

Studies of Cl-implanted TiN deposits intended as protective coatings of the metallic components of prostheses continued. The work at ITN concerned the implantation with high fluences of Cl-ions and characterisation of the coatings and of the chlorine distribution profiles in the as-implanted state and after tribological experiments. The Cl-implantations led to significant polymeric wear reduction when HBSS is the lubricant. With BSA added to HBSS, a strong decrease of both friction and polymeric wear is observed both for implanted and non-implanted TiN coatings, but still the Cl-implanted TiN coating led yields the best tribological results. Wear reduction is attributed to the substitution of the hard TiN counterface by a less hard titanium oxide layer which is a less wear-aggressive for the polymer surface, while the behaviour of the friction coefficient is explained by the slow precipitation of calcium phosphate.

[1] Project POCI/SAU-BMA/55493/2004
[2] Departamento de Química, Instituto Superior Técnico

Synthesis of ZnO nanoprecipitates on sapphire through ion implantation
C. Marques, N. Franco, R.C. da Silva, E. Alves

Following previous results obtained on sapphire implanted with Zn, the role of crystalline orientation of the substrate was studied, aiming at the production of a surface layer with ZnO precipitates. Samples of c- and m-cut sapphire were implanted with several fluences of Zn and O and annealed up to 1300 ^{o}C in air or vacuum. RBS, TEM and XRD results show that only m-cut samples implanted with Zn and annealed at 900 ^{o}C in vacuum produced polycrystalline ZnO nanoprecipitates embedded in the host matrix. At higher temperatures most Zn is lost through evaporation while annealing in air favours the production of mixed oxides. Annealing at 900 ^{o}C followed by annealing at higher temperatures is underway in order to increase the crystalline quality of the ZnO precipitates (bulk ZnO is stable up to 1800 ^{o}C).

AFM studies of transition metal implanted sapphire
C. Marques, R. Colaço[1], R.C. da Silva, E. Alves

Changes in surface topography of single crystalline sapphire (α-Al_2O_3) upon heavy ion irradiation were studied with atomic force microscopy (AFM). Prior to implantation the samples were annealed at 1000 ^{o}C in ambient atmosphere to recover from polishing damage. The implantation were carried out with nominal fluences up to 5×10^{17} cm^{-2}. Rutherford backscattering spectrometry was used to measure the implanted fluence and evaluate the extent of the implantation defects. The build-up of surface damage and the changes introduced in the topography of the samples were analyzed with AFM and correlated with the implanted fluence, energy and current density during implantation. The role played by the particular crystallographic orientation of the implanted sample and the nature of the transition metal ion used are also investigated. The development of nanostructures at the surface is observed for the highest implantation fluences, the signature of which is also recognized by the development of plasmon resonance effects seen through optical absorption measurements.

[1]Dep. Engenharia de Materiais, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.

Miscellaneous
C. Marques, E. Alves

Several studies were carried within collaboration work with other groups, namely:

- IFPAN (Poland): Fe doped GaN samples were analysed through PIXE and RBS under channelling conditions, to measure the iron content as well as the crystalline quality and to locate the Fe atoms on the GaN lattice.
- Wayne State University (USA): *i*) study of the composition of new lead-free solder, extremely important for device industry, was carried by RBS analyses; *ii*) research on vanadium oxides deposited by inorganic and organic sol-gel processes, onto sapphire, aiming at optimizing the deposition conditions to achieve epitaxial growth. Characterization performed by RBS and RBS-C; *iii*) doping of steel by ion implantation and subsequent compositional and structural studies by RBS and RBS-C measurements; *iv*) RBS studies of pure titanium oxide films and of transition metal doped (5% or 7%) titanium oxide films deposited onto crystalline Si or Al_2O_3 samples, aiming at determining its composition.
- FCT-UNL: RBS analyses of Al and Cu thin films deposited on Si or glass substrates, in order to measure the effective gradients for comparison with nominal values from the deposition method; RBS analysis of Al and Ti thin films deposited onto Si substrates in vacuum or in N_2 atmosphere in order to study the influence of the deposition atmosphere and to compare effective and nominal composition gradients.
- IST-UTL: Si-based detectors were irradiated with helium ions or protons and its photoelectric response measured *in situ*. The composition of the targets was also measured. ZnO films deposited with Au onto crystalline Si and Al_2O_3 were analysed with RBS and RBS-C to measure the composition, crystal quality and epitaxy of the films.

Installation of a 3 MV tandem accelerator with IBA and AMS at the LFI-ITN
GIMA *staff and collaborators*

After acquisition and delivery of the 3 MV tandem accelerator in mid 2006, assembly and installation of the equipment and beam lines followed. The accelerator, its HV power supply, vacuum and electrical subsystems were tested and brought to operational status. Operational tests of the H and He (alphatross) ion sources, conventional IBA beam lines and beam transport and steering systems were also tested and brought to operational status. An experimental chamber for PIXE analyses is already operational. The AMS beam line was assembled and the control software migrated to PC-based OS, debugged and upgraded to LabView v7. Work proceeds with the installation of specialised end-station equipment and components.

Characterization of potash-glass corrosion in aqueous solution

M. Vilarigues[1], R.C. da Silva

We continued to study the corrosion processes of potash-glass surfaces in contact with aqueous solutions, using Ion Beam Analysis techniques, Optical Microscopy and Fourier Transform Infra-Red (FTIR) spectroscopy.
Glass samples with base compositions of 56 mol.% SiO_2, 24 mol.% CaO and 20 mol.% K_2O, and added with CuO and MnO as colorants, were prepared.
Testing with and without stirring of the aqueous solutions was used as they lead to different surface morphologies. Silica rich-layers and Ca-carbonates are always found in the surfaces exposed to longer immersion tests. For the tests without stirring the surface reaction is slower and the carbonates structures have time to grow, while stirring accelerates the reaction leading to smaller average size and more uniform distribution of the surface structures. Evidence was found that glass dissolution progresses through a sequence of steps. When Cu, Mn and Fe are introduced in the glass matrix a layer richer in the transition metal ion added is formed in the glass surface. Cu-containing glass displays a faster initial dissolution that may be due to its particular oxidation state (2+). Since the findings indicate that both Cu and Mn are present in the glass matrix in octahedral coordination, while Fe is tetrahedrally coordinated, we suggest that the octahedral configuration eases the exchange between these ions and hydronium ions.

[1] Departamento de Conservação e Restauro, Universidade Nova de Lisboa.

Quality control and oxidation behaviour of Nuclear Fusion Reactor materials*

E. Alves, L.C. Alves, A. Paúl [1], N. Franco, M.R. da Silva [2], J. A. Odriozola [1]

Nuclear microprobe analytical techniques were used for the elemental characterisation of ODS steel samples. The main goal was to ascertain if the inhomogeneity of yttria distribution, that was found in previous analysis of other batches of ODS steels, could again be established. The obtained elemental maps show that, within the beam spatial resolution (~3×4 μm^2), all the elements are homogeneously distributed.
Aiming to a more detailed study of the oxidation behaviour of titanium beryllides, the previously analysed Be-5 at%Ti and Be-7 at%Ti samples supplied by JAERI were analysed before and after two oxidation stages obtained by annealing at 800 ºC in air atmosphere. Both oxidation steps were done during two hours each. The behaviour is similar for both samples, with the RBS spectra showing Be diffusion to the surface and subsequent Be oxidation, and no marked difference for the 2 h or 4 h annealing procedure. The surface formation of BeO was confirmed for the Be-5 at%Ti sample by XRD analysis.

* Euratom/IST association
[1] Instituto de Ciencia de Materiales de Sevilla, Spain; [2] Centro de Física Nuclear da Universidade.de Lisboa, Portugal.

Formation of Nanoclusters by Thermal Oxidation of SiGe and Deposition of Discontinuous SiGe Layers

A.Kling, A. Rodríguez[1], T. Rodríguez[1], J. Sangrador[1], M.I. Ortiz[1], C. Prieto[2], M. Avella[2], J. Jimenez[2], C. Ballesteros[3], J.C. Soares[4]

Nanoparticles of Ge, Si or SiGe embedded in a SiO_2 matrix are highly interesting for the formation of luminescent devices compatible with established Si-technology. It has been demonstrated previously that their fabrication by direct deposition of discontinuous SiGe layers sandwiched by SiO_2 using conventional low pressure chemical vapour deposition (LPCVD) is a very promising approach. In order to increase the luminescence yield the formation of multilayer structures containing the nanoparticles has been investigated. The dependence of the luminescence emission on structural parameters like the diameter of the nanoparticles and the oxide interlayer thickness, as well as the annealing conditions have been studied using grazing incidence RBS, TEM and cathodoluminescence. Structures with small nanoparticles (3-4.5 nm) separated by thick oxide barriers (≈ 35 nm) annealed at 900 ºC for 60 s yield the maximum intensity as a result of a compromise between the appropriate crystallization of the small nanoparticles and a reduced degradation of their composition by Ge diffusion due to the thick barriers.

[1] Departamento de Tecnología Electrónica, ETSI de Telecomunicación, Universidad Politécnica de Madrid, [2] Departamento de Física de la Materia Condensada, ETSI Industriales, Universidad de Valladolid, Spain, [3] Departamento de Física, E.P.S., Universidad Carlos III de Madrid, [4] Centro de Física Nuclear da Universidade de Lisboa

Measurement of proton elastic scattering cross sections for light elements – validation of a "bulk sample" method

A.R. Ramos, N.P. Barradas, E. Alves

The present research project proposes to measure (p,p) elastic cross sections for nitrogen and lithium in the 500-2500 keV energy range and for scattering angles between 160º and 130º. The measurements will be used, together with existing evaluated cross sections for other light elements, to validate a new automated method of proton elastic cross section measurement. The method will be applied to the determination of cross sections using bulk samples. The research carried out will result in improved data analysis algorithms in existing simulation programs for IBA. The improved algorithm, which accurately calculates proton backscattering spectra in the presence of cross section resonances, constitutes a desirable benchmarking tool for evaluated/measured cross-sections using standard bulk samples.

Appropriate samples for cross section measurements were prepared or acquired and their composition determined by He-RBS. The proton elastic cross sections for nitrogen were determined using a thin aluminium nitride (AlN) film deposited over vitreous graphite. Measurements were performed in the 700-2400 keV energy range and for scattering angles of 160º, 150º and 130º. In addition, the 110º scattering angle was also measured. Cross section values were obtained from the areas of the Au and N peaks, using appropriate formulae. The values thus obtained were compared with the values produced by an automated algorithm. The algorithm application to bulk samples was tested using the same spectra, but concentrating on the C signal. The C cross sections obtained were compared with the evaluated cross-sections found in the literature.

Advanced data analysis for IBA

N.P. Barradas, M.A. Reis, C. Jeynes[1], C. Pascual-Izarra[2]

Ion Beam Analysis (IBA) is a cluster of techniques dedicated to the analysis of materials. Our goal is, on the one hand, to improve the accuracy of the data analysis by developing advanced physical models and introducing them in computer codes available to the community, and on the othe hand to automate the data analysis. In 2006 the main development was the application of the joint RBS and PIXE analysis capabilities to real cases, revealing the power of such a combined approach. Also, a new model was developed to improve the calculation of RBS and ERDA spectra in the low energy region. Non-Gaussian energy resolution shape was introduced, which is important in the near-surface region in high resolution experiments. An accurate algorithm to calculate pile-up effects was developed. The model to calculate the influence of voids and inclusions was further developed, and the influence of local variations of density is now also included. The work on artificial networks was concluded. Eight papers were published in 2006 in international journals, including a review on IBA software.

[1] University of Surrey Ion Beam Centre, Guildford GU2 7XH, England, [2] Universidad Autónoma de Madrid, Madrid, Spain, [3] Instituto Superior de Engenharia do Porto, R António Bernardino de Almeida 431, 4200 Porto.

Development of external analytical microbeam at the ITN nuclear microprobe[1]

P.A. Rodrigues, L.C. Alves, R.C. da Silva

Started in the last quarter of 2005 the project aims at developing and installing an external microbeam analytical end-station at the nuclear microprobe facility and fit it with the ion beam techniques, PIXE and RBS, with the intent of applying it mainly to the field of patrimonial studies, particularly artwork and archaeology.

After design, assembly and vacuum testing different solutions a beam transfer end-section became ready to be used in the external beam analytical end-station. Fitted with 100 nm thick Si_3N_4 on Si-frame beam transfer window, beam alignment and focusing were tested. A 70×75 μm^2 fwhm beam was obtained in air 3 mm away from the beam transfer window. Reproducibility tests showed it is currently possible to obtain 80×80 μm^2 beams by using standard alignment and focusing procedures typical of vacuum microprobe, without special care. Tests proceeded with the collection of PIXE and RBS spectra of a Cu-grid and alumina control samples in air and in He atmosphere, 3 mm away from the beam exit window. Helium sprayed at 4-5 l/min improved the beam spread to 60×65 μm^2 fwhm, while allowing resolving a 50 mesh Cu-grid in a 530×530 μm^2 scan. A novel dedicated He injection cap is being designed that fits the RBS detector allowing more efficient spraying of the target irradiation spot. A laser positioning device is also being developed for precise positioning of the target area in relation to the microbeam.

[1] Project POCTI/CTM/60685/2004

Biomedical Studies

Teresa Pinheiro

The research activities during 2006 within the Biomedical Studies group made use of focused ion beam techniques to image tissue and cell morphology, as well as other microscopy techniques and methodological procedures to assess molecular indicators of cell/tissue response, e.g. using flux citometry technique, molecular biology and biochemistry assays.

The outcome of past and ongoing research projects in the context of atherosclerosis paved the way to the present main activities. Since 1991, several projects gathering different teams of the Faculty of Sciences and ITN among others, allowed to carry out a number of human health studies involving Portuguese populations in health and disease conditions. Examples of these applications are the study of skin permeability to nano--particles dispersed in cosmetics, skin as a surrogate marker in metabolic diseases (e.g. haemochromatosis), oxidative stress and inflammation markers for chronic pulmonary diseases, and for atherosclerosis. Beyond their strict scientific interest, they also revealed to be important in terms of Public Health for the studied populations and allowed comparative analyses of data from different regions.

The studies on dermatology and haematology, combining indicators of the inflammatory response and metabolism, are naturally continuing as confirmed by renewed financial support of private and international entities.

The recent and significant funding of several projects in association with the Serviço de Cardiologia, Hospital de Santa Marta, Lisboa, stimulated the research activities to develop a clinical registry of inflammation in acute coronary syndromes and to monitor the alterations of that process during the recovery period. The expected results will have important impact on the understanding of the inflammatory process and cell signalling, and consequently may be useful in prevention and treatment of acute myocardial infarction. These issues are being recognized by the scientific community, as attested by the increasing number of publications in high impact journals.

The work performed is carried out exclusively under research contracts that associate several national and international research centres. The multidisciplinary characteristic of the joint teams also permit to attract young scientists.

Apart from research activities, technical services are provided to private institutions, mainly characterisation of raw materials for the pharmaceutical industry.

The main achievements of the research developed during 2006 are summarised in the following pages.

Researchers(*)
T. PINHEIRO, Aux. Researcher
L.C. ALVES, Aux. Researcher

Students
P. NAPOLEÃO, Ph.D. student, FCT grant

Technical Personnel
R. PINHEIRO, laboratory assistant

(*) Also member of CFNUL

Inflammation in the evolution of acute myocardial infarction and cardiac failure

P. Napoleão, R. Cruz Ferreira[1], M. Selas[1], M.C. Monteiro [2], A.M. Viegas-Crespo[3], M.C. Santos[4], L. Veiga[5], A. Melão[4,5] and T. Pinheiro

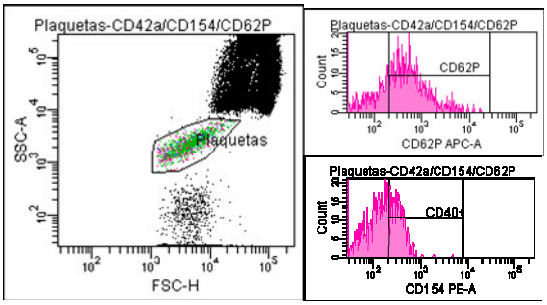
Inflammation and endothelial injury are now considered key components of atherosclerosis from fatty streak formation to plaque rupture, subsequent thrombosis, and progressive mechanical and dynamic obstruction. Rupture of the fibrous cap of arterial plaque, exposes tissue factors present in the necrotic core, triggering inflammatory signalling, cell adhesion, and coagulation cascade that eventually leads to thrombus.

Cell activation plays a predominant role in the progression of atherosclerosis as microparticles are produced by blebbing of the activated cell and their release in circulation may irreversibly amplify inflammation. In this process pro-inflammatory cytokines play a significant role, since they elicit the expression of adhesion molecules and other cytokines, which induces expression of acute-phase reactants, and thus contribute to a state of chronic inflammation.

Based on this outcome the major objective of the current projects is to investigate the microparticle production by the endothelium, platelets and lymphocytes and to identify the expression of inflammatory molecules in the cells that originate them in cardiovascular diseases. Also, soluble forms of indicators of the inflammatory response are assessed in circulation. Blood measurements of nitric oxide, iron, and oxidised LDL, of the cytokine TNF-a, soluble CD40L and soluble adhesion molecules such as intercellular adhesion molecule-1 (ICAM-1) and P-selectin, are some of the parameters being assessed. Data is being linked to risk factors, co-morbidity indicators and therapy. Measurements are carried out using multiple approaches from immuno-assays supported by spectrophotometry to flux citometry. The groups of study consist of patients with acute coronary syndrome (MI), cardiac failure (IC), which are compared with a reference group of healthy volunteers and/or a group control for coronaries. A longitudinal follow-up of MI group is being carried out at three different occasions: in the first 24 hours of evolution of the acute myocardial infarction (considered as day 0); two days after (day 2); and approximately two months after (day 40). In cardiac failure, patients are assessed before intervention and after intervention at the first and sixth month of recovery.

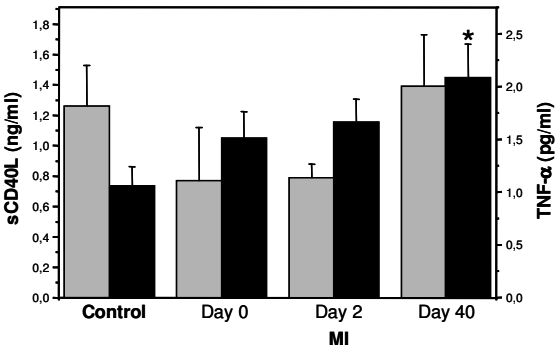
Variations in the number of microparticles were observed as well as in inflammatory markers measured, emphasizing the importance of systemic inflammation in the disease evaluation. The increased concentration and expression of sP-selectin at the infarct onset evidenced the functional state of thrombocytes and the endothelial cells that play an important role in the rupture or erosion of atherosclerotic plaque (Fig. 1).

Fig. 1: Expression of P-selectin (CD62P) and CD40L (CD154) in platelets assessed by flux citometry.



Later on during recovering period when haemodynamic variables lean to stability in part due to synergistic action of physiological and pharmacological effects, the increase in circulating sCD40L levels and cytokine levels as TNF-α (Fig. 2) may express the role of these molecules in the endothelial and myocardial tissues recuperation.

Fig. 2: Concentrations of soluble CD40L (gray) and TNF-α (black) in blood of control and MI groups (*significantly different from control group, $p<0.05$).



[1] Serviço de Cardiologia, Hospital de Santa Marta, Lisboa
[2] CESPU-CRL, Porto
[3] Centro de Biologia Ambiental, FC-UL
[4] Centro de Química e Bioquímica, FC-UL
[5] IPL-ESTESL, Lisboa

Using skin as a diagnosis tool in hemochromatosis and psoriasis

L.C. Alves, R. Fleming [1], R. Silva[2], P. Filipe[2], J.N. Silva[2], A. Barreiros[3], C. Ralheta [3] and T. Pinheiro

1 - The causes of hemochromatosis include defects in genes encoding HFE, ferroportin, hepcidin, among others. The liver dysfunction in hepcidin synthesis has been associated to most known forms of hemochromatosis. The present study aim at diagnosing hemochromatosis before irreversible damage develops. The study used conventional and innovative laboratory tests to differentiate distortions of iron metabolism. So far, 24 patients were genetically characterized and studied before starting and along the phlebotomy therapy. Nuclear microscopy and nuclear resonance techniques provided iron quantitative imaging and physiological information or skin and liver. Biochemical methods provided hepcidin contents in serum and markers of iron metabolism and organ function e.g., ferritin, transferrin saturation, transferase activity, glucose, etc. Before starting and at initial phases of therapy high concentration levels of Fe in skin, liver and plasma were observed, followed by a sharp decrease in all tissues as therapy advances. These variations are all correlated. When therapy is interrupted there is a trend of Fe increase in plasma/serum. Hepcidin concentration in serum does not discriminate between controls and patients but associates inversely with skin Fe. This suggests that iron loading in hemochromatosis is not due to inappropriate hepcidin concentration in serum. The associations between iron concentrations in skin and liver and circulating contents of hepcidin in patients before starting and along treatment will help to a better understanding of iron pools mobilisation. The study is supported by the projects SPDV 2004-2007 and IAEA CRP 2005-2007.

2 - Psoriasis is a skin disorder characterised by an increased proliferation and disturbed differentiation of keratinocytes. Current therapies, photo(chemo)therapy and systemic biological agents for moderate to severe psoriasis can control the disease but are not curative. The main objective of the study is to characterise the immune pattern and the markers of the inflammatory cascade, hyperproliferation and keratinisation in the psoriatic lesions of patients with moderate to severe plaque psoriasis. The individual response to conventional PUVA and narrow band UVB therapies and systemic immuno-target drugs, such as, etanercept and efaluzimab will be assessed through Psoriasis Area and Severity Index (PASI) and histological indexes based on keratinisation and epidermis hyperplasia reduction. T-lymphocyte profile in responders and non-responders, their activation profile and how it correlates with TNF-a and keratinocyte hyperproliferation and keratinisation, the skin barrier function and the involvement of calcium and other divalent ions distribution in skin strata, are some of the aspects that are being covered in the project. This Project is supported by SERONO, Fundación Salud 2000 (Research Prize "Investigação Clínica em Psoríase" - 2006-2008).

[1] Dept. Immunohemotherapy, Hospital Sta. Maria, Lisboa; [2] Dep. Dermatology, Hospital Sta. Maria, Lisboa; [3] LAACQ/INETI, Lisboa

Skin permeability to nanoparticles

T. Pinheiro, L.C. Alves, A. Veríssimo, R. Silva[2], J.N. Silva[2], P. Filipe[2], P. Moretto[3], J. Pallon[4], T. Butz[5]*

Nanoparticles of TiO_2 and ZnO are widely used in commercial sunscreens by their capacity to scatter UV wavelengths of sunlight. Skin exposure to commercial products containing nanoparticles of Ti, Zn, and Si oxides, among others and their trans-epidermal diffusion has been studied using nuclear microscopy techniques. One of the major achievements of the work was establishing the percutaneous penetration depth of Ti oxides and ZnO. Therefore, methodologies were adjusted to enable the validation of elemental distribution maps or profiles with high-resolution images originated in transmission mode (STIM, Scanning Transmission Ion Microscopy). The work has been carried out under a consortium EC/QLK4-CT-2002-02678.

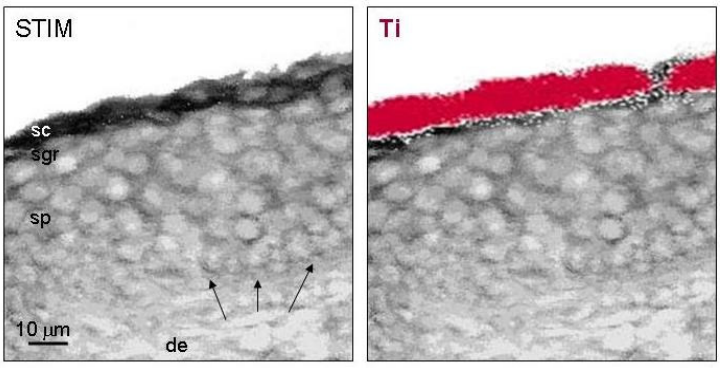


Fig.1: High-resolution images of skin (STIM). Each cell layer can be identified enabling the accurate determination of the penetration depth of nanoparticles. sc- str. corneum; sgr - str. granulosum; sp - str. spinosum; de - dermis; arrows - str. germinativum.

[2] Dermatology Dep. Hospital. Sta. Maria, Lisboa, Portugal; [3] CNBG/CNRS, Bordeaux, France; [4] Lund Institute Technology, Lund, Sweden; [5] University of Leipzig, Leipzig, Germany; *on leave Virginia Institute of Marine Science, Gloucester Point, VA 2306, USA.

Elemental Characterization and Speciation
CEEFI

Miguel A. Reis

The Elemental Characterization and Speciation Group of the LFI (CEEFI), was born as such in 2003 in the sequence of a small reorganization of activities using the 2.5 MV Van de Graaff accelerator of ITN. It carries out work of research, development and application of ion beam based nuclear analytical techniques for the characterization of elemental composition of samples, aiming also at speciation methodologies. So far, the main focus has been on particle induced X-ray emission (PIXE) and airborne material. Atmospheric environment related samples like airborne particulate matter and/or biomonitoring samples being different faces of this focus. A tuning of this working line is presently being undertaken in order to cover a broader but more concise focus on small mass samples such as particulate matter (airborne or not), nanoparticles, macromolecules or thin film samples.

Strategically, the group assumes that it is important not to depend exclusively on collaborations neither for sampling nor for data handling processes. Therefore, a strong R&D effort is put on airborne particle sampling and data handling methods. Data handling R&D includes both spectral analysis, as well as environmental data analysis (e.g. inverse methods for source apportionment).

Taking into account that PIXE is already a matured analytical technique, services are provided to the community in general, and to the scientific community in particular. In this cases, analysis of samples other than small mass ones is carried out, and it is not rare that important spin-offs associated to details or specific developments of the PIXE technique, do emerge in this framework.

Within the organics of the Ion Beam Laboratory (LFI), CEEFI is responsible for the maintenance and improvement of PIXE facilities, and assures that, at least, no losses on the installed capacity occur.

In 2006, the groups' activity was focused on launching a large re-equipment project the: Laboratory for Characterization and Speciation of Aerosols (LCEA). Equipment selection, acquisition and installation was therefore one of the main tasks. This project contributed to the acquisition of a refurbished tandem accelerator where the new setup for High Energy-High Resolution PIXE is under installation. The first high energy spectra are scheduled to be obtained during the first two weeks of 2007.

Apart from this the following results were attained: (1) high resolution PIXE (spectra made in IJS, Lubljana) confirmed uncertain results from past low statistics experiments, these results being studied now in the framework of a Ph.D. thesis in ion beam analysis speciation; (2) improvements on the existing data handling software were made and a few papers were published on the subject; (3) the problem of chemical mass balance equations with unknown source signatures was addressed and has been solved for the case of two sources, the general case solution being underway; and (4) the database on airborne element content measurements in Portugal dating back to January 1995 was completed and is now being formatted for publication in the beginning of 2007.

Researchers

M. A. REIS, Aux. researcher (Coordinator)

Students

P. C. CHAVES, Ph.D. student
A. QUARESMA, M.Sc. student
G. DIAS, graduation student

Technical Personnel

R. PINHEIRO, laboratory assistant

Characterization and Speciation of Aerosols

M.A. Reis, P.C. Chaves, A. Quaresma, R. Pinheiro

Objectives

The characterization and speciation of aerosols, is the basis and central issue of the CEEFI group work, since it is based on this data that uptake and/or impact models are tentatively established. Each of the specific activities of the group therefore converges towards this aim, or emerges from it. During 2006, the main activity undertaken was the operation of an airborne particle sampling unit at ITN campus, and the launching of the Laboratory for the Characterization and Speciation of Aerosols (LCEA). So far most of the equipment was acquired and the installation procedures are underway. LCEA will be a major demonstration unit infrastructure intended to characterize as best as possible the aerosol present at the ITN Campus, as well as airborne particulate matter sampled in a few locations that will configure a small network spread across the country.

Results

During 2006 the monitoring protocol used was identical to that used during 2005, namely an intermittent (6 minutes on, 18 minutes off) all day sampling with filters being replaced every week. In this way an almost continuous monitoring is achieved while preserving the number of samples within reasonable limits. In parallel to this, a database structure, which includes a historic record of samples, was created. During 2006 this database was under thorough debugging of both structure and data. In the sequence of this work, it was decided to recover data from old work and a large set of samples was analysed. In this way the whole database could be made to contain data starting in January 1995, therefore holding 12 years of airborne elemental contents in airborne particles sampled in Portugal. Data from late November and December 2006 is being analysed in January 2007 prior to publication of the database.

In Fig.1 the time series of annual averages and maxima of chlorine in airborne fine particles (PM2.5) determined in the Lisbon area since 1995 (near Setubal up to 1998 and at ITN since then) is presented. This shows that events of very high Cl concentrations in fine particles identified in 2004 and 2005 were already observed in smaller scale in 1995 in Faralhão and every year since 2000, becoming worse in the last three years. Further data gathered from 2004 and 2005 samples leads to a hypothesis of a problematic situation originated from a combination of anthropogenic emissions (pollution) clear sky and strong marine influence. Still no information is available yet on the chemical species holding this chlorine although the NaCl possibility can be practically excluded based on results from XRD. Further investigation will be necessary to trace this PM2.5 chlorine origin. Studies on possible consequences of these events may now be searched for since there is already a meaningful annual time series to start with.

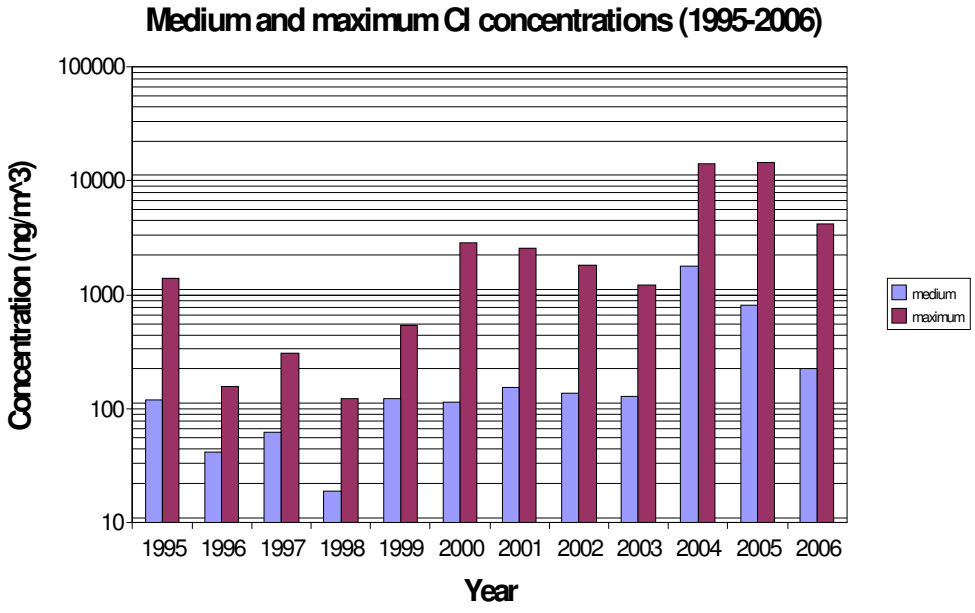


Fig. 1: Variation of airborne chlorine average and maximum concentration in PM2.5 determine at Faralhão (1995 to 1998) and ITN during (1999 to 2006). The growth of the maximum value to unreasonable numbers is clear.

Materials Characterization with Radioactive Nuclear Techniques

João Guilherme Martins Correia

A laboratory infrastructure on materials characterization is maintained and developed at ISOLDE-CERN by the Nuclear Solid State Physics group of ITN and CFNUL. ISOLDE is a European, and unique facility in the world, where more than 750 radioactive isotopes of 80 elements are produced and delivered as ion beams of high elemental and isotopic purity. In this context nuclear techniques such as Emission Channeling (EC) and Perturbed Angular Correlations (PAC) provide (atomic scale) information complementary to the material analysis capabilities available at ITN. 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 2006 was currently centered in three research subjects, which have been approved with beam time at ISOLDE by the ISOLDE Scientific Committee:

a) IS368 "Lattice Location of Transition Metals and Rare Earths in Semiconductors". Within this subject, the lattice sites of impurities in technologically relevant semiconductors (e.g. Si, Ge ZnO, GaN) and oxides (e.g. $SrTiO_3$, $BaTiO_3$) are studied by means of the emission channelling technique.

b) IS360 "Studies of High-Tc Superconductors doped with radioactive isotopes". The PAC technique is used to study the atomic ordering of fluorine and oxygen dopants at the Hg planes of the first three members of the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ high-Tc family of superconductors. The aim is to understand if dopants ordering and consequent lattice deformations are related or unrelated with charge ordering stripe formation at the superconducting planes.

c) IS390 "Studies of colossal magnetoresistive oxides with radioactive isotopes". PAC is used to probe local lattice deformations and relaxation of the $Mn^{3+}O_6$ octahedra on manganites as a function of doping and temperature. In this way phase coexistence and polaron dynamics are studied, which are local phenomena that are correlated with charge transport mechanisms in giant magnetoresistive materials.

The group has also accomplished technical development of position-sensitive Si pad detectors to implement fast readout of self-triggered detectors. On-line EC experiments with short lived isotopes shall run in 2007.
Since the obtained information, i.e., the precise lattice location and rms displacements of impurities, or the incoherent relaxation of elements in crystalline solids, are not accessible by more traditional techniques, the radioactive methods have also the potential for being applied to different subjects or new materials.
Together with the development of the new detector, a sophisticated new experimental chamber has been developed that will allow new EC experiments at low measurement temperatures, to provide high precision insight of phenomena such as element relaxation in semiconductors and superconductors.

Of interdisciplinary nature, these activities integrate and initiate young students, from different backgrounds and universities, in applied nuclear physics. With shared work between the different environments of ITN, CFNUL and ISOLDE-CERN, there participate students and senior researchers from the universities of Lisbon, Aveiro, Porto, Braga, as well as from Leuven, and Bonn. Presently, six Ph.D., one M.Sc. and three diploma students accomplish their work using this infrastructure, within the scientific proposals. Two students have finished Ph.D. in 2006, one of such still working as post-Doc in the group.

Researchers(*)
J.G.M. CORREIA, Principal Researcher
U. WAHL, Principal Researcher
E. ALVES, Principal Researcher

Students
A.C. MARQUES, Ph.D. student, FCT grant
E.C. RITA, Ph.D. student, FCT grant
A.L. LOPES, Ph.D. student, FCT grant
S. DECOSTER, Ph.D. student, IKS-Leuven grant
B. DE VRIES, Ph.D. student, IKS-Leuven grant
T. MENDONCA, B.I. fellowship, POCTI
S. COSTA, B.I.I. fellowship, POCTI

(*) Also member of CFNUL

Emission channelling lattice location studies

U. Wahl, J.G. Correia, A.C. Marques, E. Rita, E. Alves, B. De Vries[1], S. Decoster[1], A. Vantomme[1], M.R. da Silva[2,3], J.P. Araújo[2], L. Pereira[4], J.C. Soares[2], and the ISOLDE collaboration[1]

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 dopants 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 implanted Ca and Sr in GaN

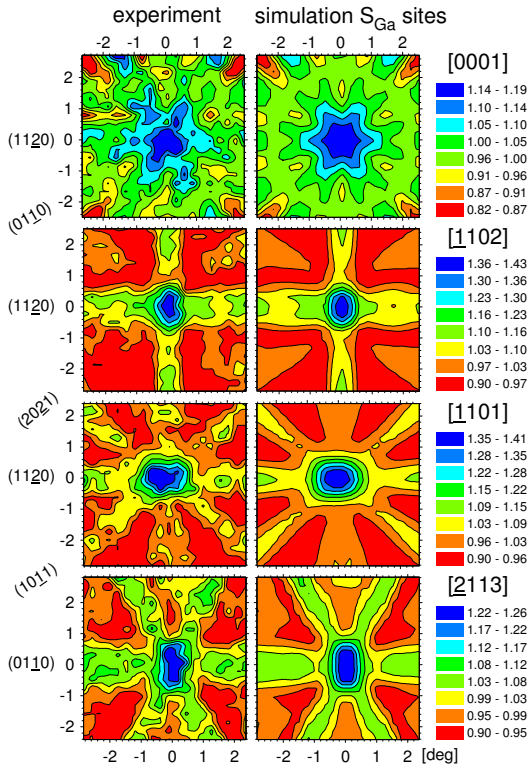


Fig. 1: Experimental EC patterns from ^{45}Ca in GaN (left) and simulations for Ca on Ga sites (right).

Using the emission channelling technique, the angular distributions of β^--particles emitted by the radioactive isotopes ^{45}Ca and ^{89}Sr implanted into thin films of single-crystalline wurtzite GaN were monitored with a position-sensitive detector. The experiments give direct evidence that ~90% of Ca and ~60% of Sr atoms occupied substitutional Ga sites with root mean square displacements of the order of 0.15-0.30 Å, i.e., larger than the expected thermal vibration amplitude of 0.074 Å. Annealing the Ca implanted samples at 1100-1350 °C in high-pressure N_2 atmosphere resulted in a better incorporation into the substitutional Ga site. The Sr implanted sample showed a small decrease in rms displacements for vacuum annealing up to 900 °C, while the substitutional fraction remained nearly constant. The annealing behaviour of rms displacements can explain why annealing temperatures above 1100 °C are needed to achieve electrical and optical activations, despite the fact that the majority of the acceptors are already located on Ga sites immediately after ion implantation.

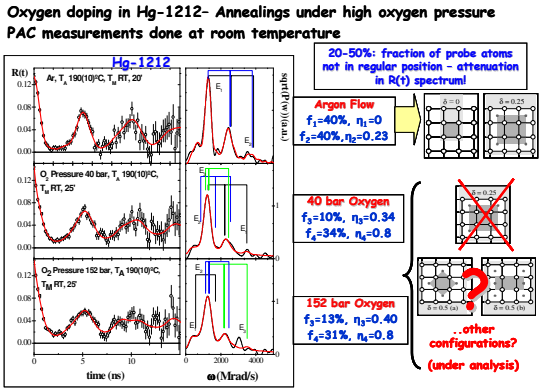
2. Emission channelling with short-lived isotopes

Due to count rate and noise-related limitations of the detection systems, electron emission channelling experiments using position-sensitive detection were restricted to isotopes with half lives above 6 h and electron energies above 40 keV. Recently, major technical developments have been realized and new equipment has been implemented which has allowed these limitations to be overcome. The main new development supported by the ITN Sacavém/CFNUL Lisbon group in collaboration with CERN, was the implementation of self-triggering readout chips for position-sensitive Si pad detectors. These new readout systems allow count rates of several kHz, sufficient to measure samples in the MBq range, and with energies below 40 keV. A scientific proposal for lattice location studies using short-lived isotopes produced at CERN's ISOLDE facility has been approved by the CERN research board on 29.11.06 with 20 shifts of beam time. The physics case of the presented proposal will be to extend the successful work in the fundamentally and technologically relevant field of the lattice location of transition metals and dopants in semiconductors using as new probes the isotopes ^{65}Ni (2.5 h), ^{61}Co (1.6 h), and ^{27}Mg (9.46 min).

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

IS360 experiment – Atomic ordering of high concentrations of oxygen in $HgBa_2Cu_nCa_{n-1}O_{2n+2+\delta}$ for n = 2,3 high-Tc superconductors

T. Mendonça, J.G. Correia, H. Haas, M.R. Silva, P. Odier[1], J.P. Araújo[2], A. Pereira[2], M. Pereira[2], J.C. Amaral[3], R. Ferreira[4] and ISC[4]



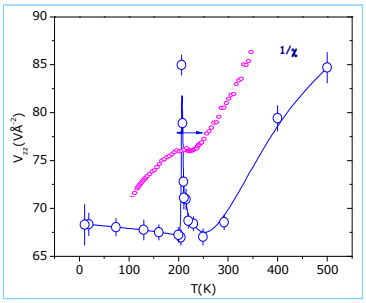
Collective ordering of highly oxygen doped samples of $HgBa_2Cu_nCa_{n-1}O_{2n+2+\delta}$ (n = 2,3 Hg1212, Hg1223) were investigated with the perturbed angular correlation (PAC) technique by measuring the electric field gradients induced at ^{199m}Hg nuclei. The experiments were performed at different annealing conditions, under Ar flow or O_2 pressure up to 152 bars. In comparison with the data and calculations already published for equivalent fluorine doping in Hg1201 (n = 1), the preliminary analysis hints that at high concentrations the oxygen atoms order in different way, other than the atomic-like stripes found for fluorine. In addition, these experiments have been performed at different temperatures, above and below the superconducting transition, which have revealed further differences in the charge distribution of the Hg surroundings. A full set of PAC, SQUID (Tc) and X-ray data has been obtained that is now being analyzed to be further compared to first principle calculations of charge density in these materials obtained for different oxygen configurations.

[1] Lab.Crystalographie, CNRS, Av. des Martyrs 25, F-38042 Grenoble CEDEX 9, France, [2] Department of Physics and CICECO, Aveiro University, 3810-193 Aveiro, Portugal, [3] Department of Physics IFIMUP and CFP, Porto University, 4169-007 Porto, Portugal ,[4] ISOLDE Collaboration, CERN, 1211 Geneva 23, Switzerland.

IS390 experiment – Studies of Free percolative phase transition on ferromagnetic insulator manganites

A.M.L. Lopes[1], J.C. Amara1[1], V.S. Amaral[1], J.P. Araújo[2], A. Pereira[2], J.J. Ramasco[2], J.G. Correia, and ISC[3]

We report atomic scale studies of the Pr-$CaMnO_3$ system using PAC spectroscopy. No macroscopic measurements were up to date able to detect electric polarization in the Pr-$CaMnO_3$ (PCMO) systems. The present set of data provides first experimental evidence for local electric dipoles in charge ordered PCMO. We hint that the electric dipole is localized to a small region (nm?) and that the ferroelectric behaviour occurs below the CO/orbital ordering phase transition.

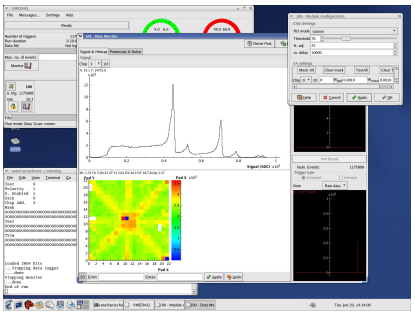


[1] Department of Physics and CICECO, Aveiro University, 3810-193 Aveiro, Portugal.
[2] Department of Physics IFIMUP and CFP, Porto University, 4169-007 Porto, Portugal.
[3] ISOLDE Collaboration, CERN, 1211 Geneva 23, Switzerland.

R&D development – new self-triggered Si pad detectors for position sensitive electron detection

A.C. Marques[1], U. Wahl, J.G. Correia, M.R. Silva, P. Weilhammer[2], E. Chesi[2], A. Rudge[2]

This work is made in collaboration with CERN's Compton camera project on new positron emission tomography (PET) devices http://xray.web.cern.ch/xray/publications/Lyon2000PaperCERNPreprint.pdf, whose technology and detectors also fulfill the requirements for electron emission channeling experiments. In 2006 the readout program was developed to the 1 mm thick 22×22 Si pad detector, mounted on a newly designed printed circuit board equipped with fast VATAGP3 preamplifier chips. The figure shows the acquisition program visual interface during first tests with ^{111}In implanted SrTiO3, of the new detector to be installed online in 2007.



[1] CFNUL, Lisbon University, Portugal. [2] CERN, 1211 Geneva 23, Switzerland.

Nuclear Reactions

Adelaide Pedro de Jesus

This group has been involved in the study of proton-induced nuclear reactions with the objectives to obtain cross sections of nuclear reactions relevant to nuclear astrophysics and to extend analytical capabilities to light elements.

So far, at the national level, the experimental work has relied upon ITN – Ion Beam Laboratory, based on a 2.5MV Van de Graaff accelerator. Internationally, the group has joined LUNA (Laboratory for Underground Nuclear Astrophysics) collaboration and also established collaboration with Prof. Claus Rolfs group of Bochum University. The reaction $^{14}N(p,\gamma)^{15}O$ has been studied to 70 keV and the reactions $^{6,7}Li(p,\alpha)^{3,4}He$ to 30 keV. A systematic study of electron screening effects was performed.

The acquisition of the 3MV tandem accelerator opened new perspectives of studying astrophysical relevant nuclear reactions, using the high sensitivity of the AMS line.

In the short term the work to develop a calibrated PIGE setup will be concluded and extended to a new acelerator line connected to the 3MV tandem accelerator, creating new perspectives in applied work in Environment, Materials and Health Sciences and Geology.

Researchers (*)
A.P. JESUS, Full Professor, FCT/UNL, Group Leader
J.P. RIBEIRO, Associate Professor, FCUL

Collaborators
R. MATEUS, Technical Assistant

Students
J. CRUZ, Ph.D. student, FCT/UNL
M. FONSECA, Ph.D. student, FCT/UNL
M. MORENO, Ph.D. Student, FCT/UNL
H. LUÍS, Research scholarship

(*) Also member of CFNUL.

Experimental Study of Nuclear Reactions for Astrophysics

J. Cruz[a,b], A. P. Jesus[a,b], Hélio Luis, Micaela Fonseca, J. P. Ribeiro[b,c]

Objectives

Nuclear reactions occur in stars at very low energies (Gamow peak), with extremely low cross sections decreasing exponentially with energy, showing effects as electron screening; experimentally, their study pushes to the limit existing techniques. During this year the work related to LUNA collaboration, namely the reaction $^{14}N(p,\gamma)^{15}O$, was concluded. Also the experimental study of the reactions $^{6,7}Li(p,\alpha)^{3,4}He$ was finished. The on-going work is related to the study of the electron screening effect (collaboration with Bochum) and to the preparation of the AMS line of the new tandem accelerator.

Results

Lithium is one of the most interesting and puzzling elements in the field of nucleosynthesis. Its most abundant isotope, ^{7}Li, has the rather unique status of requiring three entirely different nucleosynthetic processes, which are not completely understood.

The reaction $^{7}Li(p,\alpha)^{4}He$ is the major reactions of Li destruction, having thus a crucial contribution to Li abundances. Even though there are several different cross sections measurements for this reaction, they lead to different astrophysical S-factors at relevant energies.

The recent analysis of our data, fig. 1 and 2 lead to a S(E = 0) factor of 3,6 ± 0,1 MeVb for $^{6}Li(p,\alpha)^{3}He$ and 60 ± 1 keVb for $^{7}Li(p,\alpha)^{4}He$.

Future Work

Continuing our goal to measure nuclear reactions relevant to nuclear astrophysics, the aim of future work is the optimization of the AMS technique to detect and quantify ^{6}Li and ^{53}Mn, in order to measure off-line d(alpha,gamma)^{6}Li and $^{51}V(3He,n)^{53}Mn$ reactions. So far the effort has been focused on assembling and making the AMS line operational after the transfer from Australia

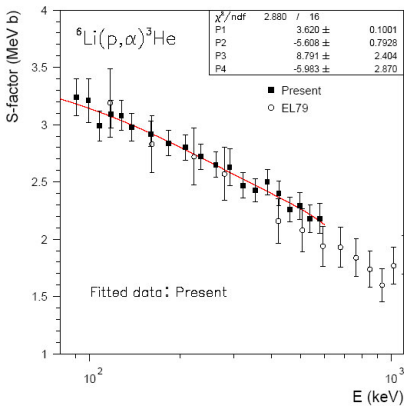


Fig. 1: Astrophysical S-factor for the $^{6}Li(p,\alpha)^{3}He$ reaction for bare nuclei electrões.

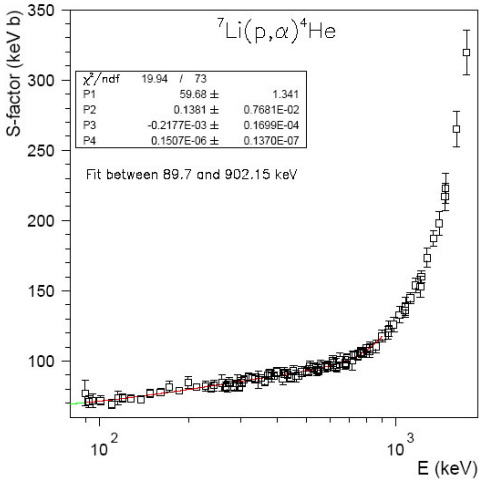


Fig. 2: Astrophysical S-factor for the $^{7}Li(p,\alpha)^{4}He$ reaction for bare nuclei electrons.

[a] Departamento de Física da Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa
[b] Centro de Física Nuclear da Universidade de Lisboa
[c] Departamento de Física da Faculdade de Ciências da Universidade de Lisboa

Calibration of a PIGE Set-up

Micaela Fonseca[1,2], R. Mateus[2], A. P. Jesus[1,2], Hélio Luis[1,2], J. P. Ribeiro[2,3]

The aim of this work is the extension to further light elements of previous work [1-4] 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 the depth of the sample was implemented for thick and intermediate samples. For that purpose some reaction excitation functions were measured in the same analytical conditions. The energy steps needed to define accurately the excitation function were used as energy intervals for the integration procedure.
After the work done for F, Li, B and Na, the excitation functions for ^{27}Al(p,p´□)^{27}Al and ^{25}Mg(p,p´□)^{25}Mg, were obtained to introduce as input. Thick target gamma yields for several samples containing Al and Mg were measured to be compared with calculated yields.
Application of this technique, for F, Li, B and Na analysis of biotite inclusions of granites was performed (fig.1) showing Li concentrations several orders of magnitude above the usual ones, what may be related with the degradation of some ornamental granites.

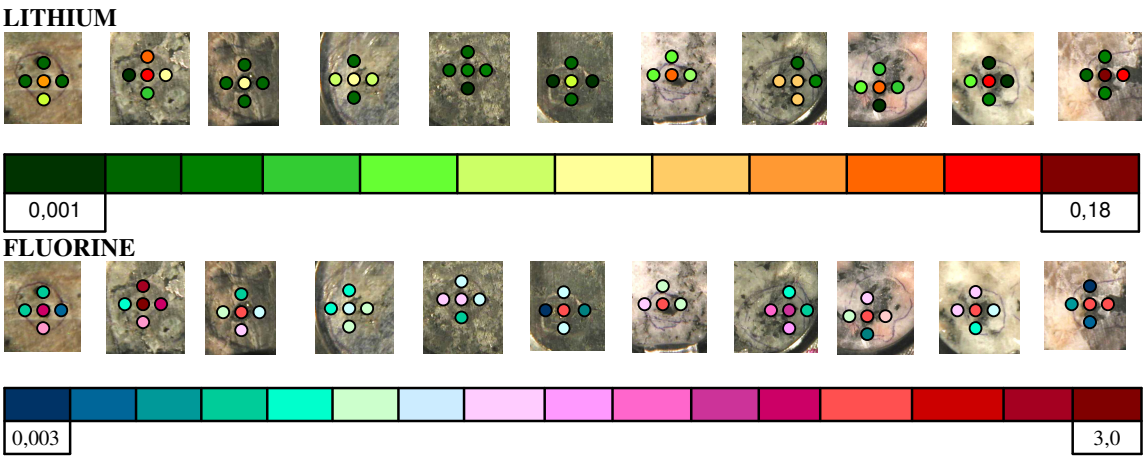


Fig. 1: Massic fractions in percent units of Li (above) and F (below) for several granite samples. The analysis was done on the shown points, being the central points biotite inclusions.

References

[1] R. Mateus, A.P. Jesus, B. Braizinha, J. Cruz, J.V. Pinto, J. P. Ribeiro, Nucl. Instr. Meth. B 190 (2002) 117-121
[2] R. Mateus, A.P. Jesus, J.P. Ribeiro, Nucl. Inst. and Meth. B 219-220 (2004) 519-523
[3] R. Mateus, A.P. Jesus, J. Cruz, J.P. Ribeiro, Nucl. Inst. and Meth. B 219-220 (2004) 307-311
[4] R. Mateus, A. P. Jesus, J. P. Ribeiro, Nucl. Inst. & Meth. B229, 302-308 (2005)

[1] Departamento de Física da Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa
[2] Centro de Física Nuclear da Universidade de Lisboa
[3] Departamento de Física da Faculdade de Ciências da Universidade de Lisboa

Condensed Matter Physics

Fernanda Margaça

The Group's main field of research is the development and characterisation of materials with new or improved properties. To this end, radiation is used as a tool to investigate the structure and to induce structural modifications in special samples. Special polymeric materials are currently investigated in collaboration with groups from the Universities of Aveiro and Coimbra, the University of Sophia, Bulgaria, Laboratoire Léon Brillouin (CEA-CNRS-Saclay), KFKI, Budapest, and the Budapest Neutron Centre. During 2006 the main effort was put into the processing and characterization of hybrid materials and co-polymers prepared by gamma irradiation using the ^{60}Co source of UTR.

The systems studied were: (i) hybrids prepared from mixtures of a polymer (PDMS) and various alkoxides, with emphasis in the thermal characterization of various samples prepared using irradiation methods; (ii) development of new copolymers (HEMA grafted on LPDE thin films) suitable for bioapplications. Here, sample preparation conditions were correlated to the grafted material structure and the hydration level achieved by the final product, and preliminary toxicity studies were conducted. Biocompatibility tests (haemolysis and tromboresistance) are being carried out. Work on these systems is resumed in a M.Sc. thesis completed in 2006 and a Ph.D. thesis to be defended in 2007.

The Group is also active in the area of hardware and software instrument development, with emphasis in the design, construction, and testing of systems and components for neutron beam work.

Installation and alignment of the various components and equipments of EPA was resumed in 2006. Detailed test work of the facility has shown that an enhanced signal to noise ratio requires further improvement of the shielding and the installation of a 20 cm long Be filter. The design of a liquid N_2 cryostat to cool this filter is under way. The acquisition of a new detector assembly for the two-axis neutron diffractometer DIDE with 8 linear position-sensitive ^{3}He counters to replace the old "banana" detector with improved count-rate and equivalent angular resolution, awaits a funding decision. A rotating chopper time-of-flight diffractometer, ETV, is operational. Development of the Converging Multi-channel Collimator (CMC) based on an original concept was temporarily interrupted due to the shortage of manpower especially technicians. The design of a prototype having been completed in 2004, it is intended to proceed with the construction and testing of the device during the coming year.

Collaboration with other research groups and a policy of open access for external users to facilities operated by the Group including students are placed high in the ranking of priorities. One student resumed the work for an MSc degree during 2006.

The Group's work is supported by funds from FCT, IAEA, ITN and income from services.

F. Carvalho, senior researcher and founder of the group, has reached retirement age in January 2006. Although he continues to contribute to current activities the long due implementation of a plan of selected recruitment of scientific personnel has become more pressing.

Researchers
F.G. CARVALHO, Senior Researcher [1]
F.M.A. MARGAÇA, Princ. Researcher
A.N. FALCÃO, Princ. Researcher
L.M.M. FERREIRA, Aux. Researcher
C.M.M. CRUZ, Aux. Researcher (20%)
J.S. NEVES, Aux. Researcher (20%)

Students
M. CARRAPIÇO, B.I. Grantee, POCTI [2]
SUSANA GOMES, B.I. Grantee, POCTI

Technical Personnel
D. SILVA, Laboratory Assistant

Collaborators
I.M.M. SALVADO, Dep. of Glass and Ceramics Engineering, UIMC, University of Aveiro
M.H. GIL, Dep. of Chemical Engineering, Faculty of Sciences and Technology, Coimbra University

[1] retired
[2] left in March

Thermal analysis of PDMS-TEOS-PrZr Hybrid Materials Prepared by γ Irradiation

F.M.A. Margaça, S.R. Gomes, A.N. Falcão, L.M. Ferreira and I.M.M. Salvado[1]

Objectives

The purpose is to investigate the thermal behaviour of hybrid materials prepared by gamma irradiation of the mixture of the precursors PDMS, TEOS and PrZr.

Results

Hybrid materials have been prepared by γ-irradiation of a mixture of polydimethilsiloxane, PDMS, and the alko-xides, ALC, tetraethylortosilicate, TEOS, and zirconium propoxide, PrZr. This is a new method [1] of prepa-ration of hybrids which are currently obtained via the sol-gel process. The sol-gel hybrids have been widely used in different fields, ranging from medical uses to electronics. The applications are a consequence of the final properties of the materials which are known to depend strongly on the processing conditions. The thermal stability of the prepared materials has been investigated by Differential Scanning Calorimetry and Thermal Gravimetry Analysis.

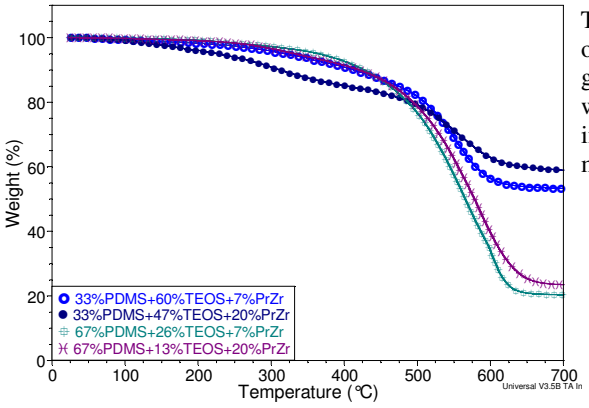


Fig.1: Thermograms of hybrid samples.

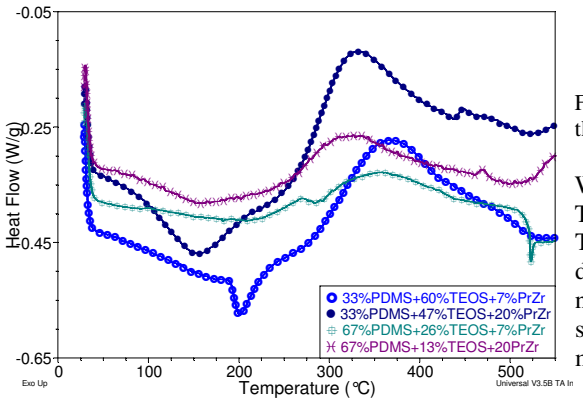


Fig.2: DSC plots of hybrid samples.

DSC and TGA curves show that the thermal behaviour depends on the relative organic/inorganic content. In fact, two distinct behaviours are found depending on whether PDMS/ALK > 1 or < 1, with ALK = alkoxide.

The endothermic peak in the DSC curves is also observed in purely inorganic gels prepared from TEOS and PrZr by sol-gel, as shown in Fig. 3.

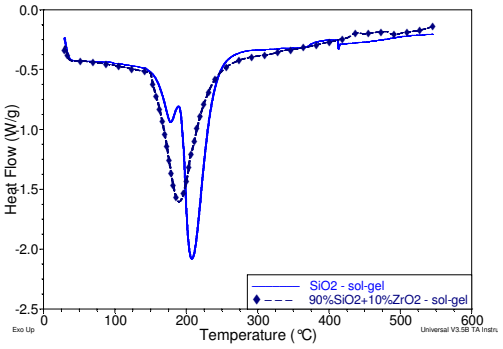


Fig. 3: DSC plot for SiO_2 and 90%SiO_2+10%ZrO_2 materials prepared by sol-gel, without any polymer.

This provides evidence of the presence of inorganic oxide regions in the hybrid materials prepared by gamma irradiation of the precursors. Furthermore it was found that the temperature of the exothermic peak in DSC curves depends on the ratio of the number of molecules TEOS/PrZr.

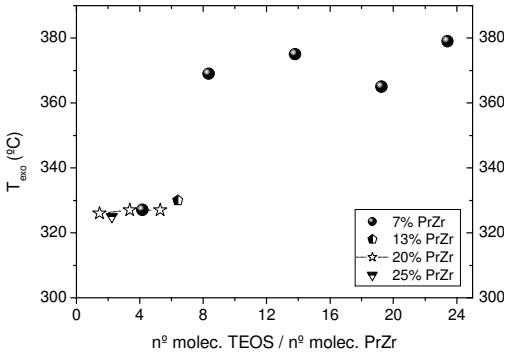


Fig. 4: Variation of the DSC exothermic peak temperature with the ratio no. molecules TEOS/PrZr.

When the number of molecules TEOS/PrZr < 8, T_{exo} ~ 325 ºC. For a higher ratio value T_{exo} > 360ºC. This indicates that the inorganic oxide regions can develop into two structures, depending on the relative number of molecules TEOS/PrZr. A more stable structure develops whenever the ratio of the number of molecules TEOS/PrZr > 8.

Published work

S.R. Gomes, F.M.A. Margaça, I.M. Miranda Salvado, L.M. Ferreira, A.N. Falcão, *Nucl. Instr. & Meth. B* 248 (2006) 291-296.

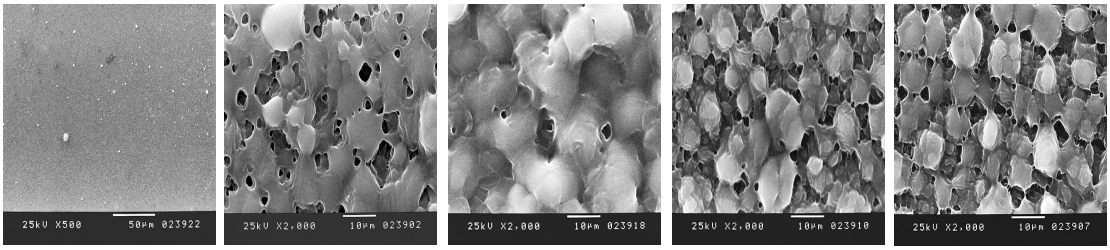
[1] Dep. of Glass and Ceramics Engineering, UIMC, Univ. Aveiro

Elemental and Topographic Characterization of LDPE Based Copolymeric Films Obtained by Gamma Irradiation

L.M. Ferreira, A.N. Falcão, M.H. Gil[1]

The selection of materials for bioapplications requires proper considerations of mechanical, physical and biological properties, and very rarely a single natural or synthetic material presents all the adequate properties. In our studies, using 2-hydroxyethyl methacrylate (HEMA) as grafting monomer, we have optimized the preparation of new grafted copolymeric Low Density Polyethylene (LDPE) based films by means of ^{60}Co gamma irradiation. The films so developed show, at a macroscopic scale, a homogeneous graft distribution (independent of the grafting degree) reaching hydration levels up to 95%. Their characterization was done using Nuclear Microprobe (NM), Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). These techniques proved to be very important for the elemental and topographic characterization of the film. Elemental analysis performed by NM using PIXE (Proton Induced X-ray Emission), allowed evaluation of the toxicological risk in the possible uses of the new films. Trace contamination of elements heavier than Si (Ca, Cl, Fe, K, P, S; Si and Zn) were found, but their concentrations do not pose toxicological risk. AFM and SEM techniques revealed the topography and 3D porous structure of the polyHEMA grafted surface that grows over the LDPE matrix film. The observed porous distribution configuration and their dimensions (Ø = [0.405µm - 5.517µm] assure oxygen permeability. Morphological analysis was important to inform about polyHEMA grafted chain scission processes, which seems to occur with increasing radiation dose above a certain threshold. Further work involves biocompatibility tests (haemolysis and tromboresistance studies) of the prepared films as well as the application of the developed technique to pre-configured polyethylene based supports.

Figure: SEM micrographs of LDPE film (500×) and PE-g-HEMA copolymeric films (2000×).

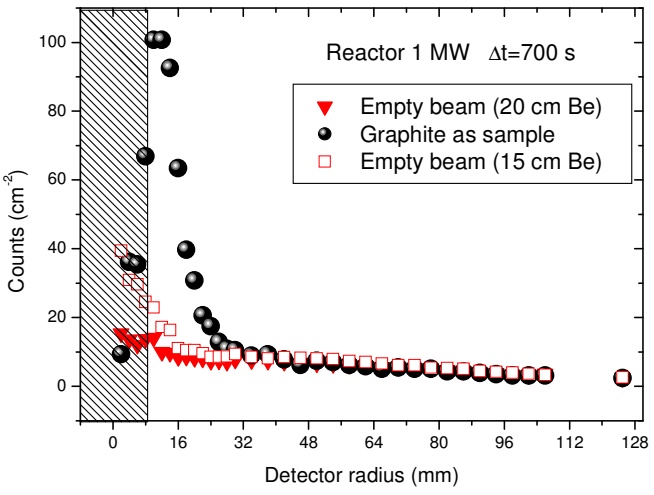


LDPE film matrix (non irradiated)	PE-g-HEMA film (25h; 237%)	PE-g-HEMA film (30h; 403%)	PE-g-HEMA film (35h; 166%)	PE-g-HEMA film (40h; 163%)

[1] Department of Chemical Engineering, Faculty of Sciences and Technology, Coimbra University.

Neutron Spectrometers at the Portuguese Research Reactor

F.M.A. Margaça, A.N. Falcão, J.S. Neves, C.M.M. Cruz, D.M.P.S. Silva, F.G. Carvalho



Installation of the out-of-pile components of the EPA instrument was resumed. A software program for data handling was developed. Test work progressed as concerns the measurement of signal-to-noise ratios under different shielding configurations and instrument operating conditions. The need to use a cooled beryllium filter to reduce the noise was confirmed. The influence of the Be filter in the background associated with the beam is shown in the figure for two different filter lengths. The difference is observed in the region nearer to the beam stop (\\\\) that corresponds to the lower Q region of the measurement. The cooling of the filter will improve the useful intensity by a factor of 3, keeping the background unaltered. Further improvement on the detector shielding is required.

Radiation Technologies: Processes and Products

M. Luísa Botelho

Radiation Technology: 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 the response to a requested service, as a collaborator in a research project or in the transmission of knowledge. The group activities focus on the delineation, development, validation and application of technologies and processes in various fields, such as Environment, Food and Pharmaceutics. As a fundamental part of the validation studies, Risk Analysis is being applied as a process management tool either in production lines of studied products (e.g. food, devices and pharmaceutics) or in environmental control (e.g. hospitals rooms and pharmaceutical industries).

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 the 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 on employing ionising radiation technologies to new processes and applications on Agriculture, Food, Pharmaceutical, Wastewater Treatment and other areas. In order to improve our understanding of the Radiation effects on the 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 microorganisms) and as well as fingerprinting methods to assess the biodiversity 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 two IAEA projects, one ADI/FCT project, one LPM/MDN PIDDAC project, one re-equipment FCT project, Industrial contributions and one IEFP/FSE grant.

Researchers
M. LUÍSA BOTELHO, Aux. Researcher, Group Leader

Students
A. BELCHIOR, M.Sc. student, ITN grant
F. PINTO, undergraduate student, ESTSL
H. PEREIRA, undergraduate student, ESTSL
L. ALVES, BIC grant, ITN grant
R. CLEMENTE, undergraduate student, AESBUC grant
R. MELO, Ph.D. student, ITN grant
S. CABO VERDE, Ph.D. student, ITN grant
T. SILVA, BIC gran, LM grant

Technical Personnel
H. MARCOS, system operator, ITN
V. FOLGADO, laboratory technician, IEFP/FSE grant

Processes and Products Validation

S. Cabo Verde, L. Alves, A. Belchior, H. Pereira, R. Clemente, S. Trabulo[1], *J. Reymão*[2], *E. Cruz*[2], *M. Gaspar*[2], *S. Simões*[1], *M.L. Botelho*

Objectives

As defined by the FDA, validation" means "Establishing documented evidence which provides a high degree of assurance that a specific process will consistently produce a product meeting its predetermined specifications and quality attributes." Based on these guidelines two studies were developed: 1) one had as main objective the **validation** of a **sterilization process** of antibiotic liposome formulations for future implementation in the end of the production line. This work was performed under a consortium research project – Biostrat – between Bluepharma S.A. and INETI to develop new formulations of drugs with an antimycobacterial agent. 2) one other study, a service requested by a Pharmaceutical Industry (Delta Laboratórios), aimed at the **validation** of a finished **pharmaceutical product** through the quantitative determination of the active substance, Bleomycin Sulfate, and the evaluation of the uniformity of content of single dose.

Results

1) In order to find out if gamma radiation could be applied as a **sterilization process of antibiotic liposome formulations** was developed an experimental design integrating physical, microbiological and chemical methods. The physical studies relied on dosimetric systems according to ISO/ASTM standards, namely Fricke and Polymethilmetacrilato dosimeters for calibration (local and irradiation geometry) and routine purposes. The microbiological studies focused the detection of the critical points in the future production line in order to minimize the contamination and in the determination of the sterilization dose (D_{min}) based on ISO standards to delineate future chart controls for the bioburden. The physical-chemical studies were developed in INETI to find out the maximum acceptable radiation dose (D_{max}) that preserves the functions of the liposomes, and were based on the following parameters: antibiotic and lipid concentrations, mean size diameter and polydispersity index of the vesicles and zeta potential. The whole irradiation process was completed in the ^{60}Co facility (UTR) under exploitation of CHIP, S.A. and located in ITN. This validation consisted in the test and documentation of protocols that could guarantee not only the efficiency of the irradiation process but the maintenance as well of the functions of the irradiated product. The products used and tested in this study are still in development and in an experimental phase. Therefore, even though the ISO 11137:2006 lays as reference and guideline to all the irradiation procedures, none of the methods described in ISO were applied outright. Instead, the overall study for the foreseen radiation sterilization of the product was done using the main parameters that underlie ISO 11137:2006 such as, maximum acceptable dose (D_{max}) for product, possible sterilization dose (D_{min}) following the Good Manufacturing Practice in the production line and the foreseen dose uniformity in the process (D_{max}/D_{min}). The evaluation of bioburden in every step of liposome production lines point out to the identification of the extrusion and the columns passage as critical points. These results linked with the ones obtained in bioburden characterization led us to suggest a periodical control of the water system as a corrective action. The bioburden determination before and after irradiation at incremental doses (1 up to 5 kGy) suggested that product's microbial population resistance follow the standard distribution described in ISO 11137:2006 and can attain a low bioburden average. Consequently, future batches produced in the studied production lines that present a bioburden of ≤ 3 cfu per product unit could be irradiated at doses (D_{min}) between 12 and 15 kGy to achieve a Sterility Assurance Level of 10^{-6}. The maximum acceptable dose (D_{max}) in the whole irradiated batch (23 up to 49 kGy) has to be lower than 23 kGy to guarantee the product properties, having a dose uniformity cautious approach of $D_{max}/D_{min} \leq 1.5$ or 1.9, respectively, valid for the current irradiation geometry in UTR.

2) The experimental procedure used in the **validation of Bleomycin Sulphate for injection** was based on the specifications and control methods referred in European Pharmacopeia. The diffusion method using as test organism the strain *Mycobacterium smegmatis* ATCC 607 was performed as a microbiological assay to quantify the concentration (potency) of the active substance, Bleomycin Sulphate. Based on the estimated product potency it was calculated the content of active ingredient in each of the product units (n = 10) by subtracting the weight of the container from the respective gross weight. The followed methodology also included the calibration and control of the rooms and equipments used, namely by: 1) the biomonitorization of the air in the assay room and in the Biohazard safety cabinet equipment; 2) the control of the released pharmaceutical product in the assay room and in the Biohazard safety cabinet equipment and 3) the verification of the air flow velocity of the Biohazard equipment. The results validity was checked by statistical parameters (Shapiro-Wilk test, Bartlett test and Analysis of Variance). The obtained results demonstrated that the analysed samples of Bleomycin Sulphate satisfy the specifications required for the product release in the national market.

[1] Bluepharma S.A, Pharmaceutical Industry.
[2] Innovation, Technology and Engineering National Institute - INETI.

Chemical Evaluation

R. Melo, J. Branco[1], S. Cabo Verde, L. Alves, A. Belchior, T. Silva, V. Folgado, M.L. Botelho

The application of ionising radiation as a tool to optimize the wastewater treatment is foreseen. The efficiency of the radiation impact was measured based on Total Suspended Solids (TSS), Chemical Oxygen Demand (COD), and Biochemical Oxygen Demand (BOD) parameters. The samples used for the study were untreated swine and dairy wastewater, and were undertaken punctually, representing the worst scenario. An increase of the COD and a decrease of TSS were observed after irradiation for the two kinds of wastewater tested. These could be explained by the radiation-induced effect that degradates the organic pollutants that leads to an increase of the chemical species in solution (decrease TSS), resulting in a higher COD for the same absorbed doses. The overall results point out to a decrease of BOD with the increase of the irradiation doses. However, at 7 kGy, for the swine wastewater, there was a punctual increase of BOD which could be connected with the survived microbiota presented in the sample. The Kjeldahl Nitrogen and total phosphorous were also measured as they are potential toxics to the ecosystem. The obtained results are inconclusive, more studies are in progress. A lab scale agricultural wastewater treatment system will be build up, in a near future, to simulate an overall picture of an integrated treatment to foresee better the technical and economical benefits of the design.

[1] Department of Chemistry, ITN.

Microbiological evaluation

S. Cabo Verde, L. Alves, A. Belchior, T. Silva, R. Clemente, M.L. Botelho

The impact of ionizing radiation on microbiota and cells, is studied using different approaches. The range of the irradiation action is measured by inactivation curves where the samples are submitted to several doses and dose rates. The survivors' strains are phenotypical and biochemical characterized and compared with the strains retrieved from non irradiated samples. This permits to establish an integrated view of the changes in the microbial community associated with the absorbed dose applied to the sample as well as for the use of ionizing radiation as tool in the sterilization process. The developed work in this context are the validation of the radiation sterilization of a kettle filter for the industry *Lobo International, Ltd*, Cambrigde/ England and other projects under the title: "Processes and products validation". Untreated swine and dairy wastewater studies were carried out aiming to use ionizing radiation as an optimization tool of the wastewater treatment. We studied the impact of the ionizing radiation on the effluents' microbiota. Studies were also carried out to a genotypic level applying molecular biology fingerprinting techniques (MSP-PCR, RADP-PCR and the 16S- PCR digestion) to isolates bacterial DNA in order to access their genetic similarity and possible genetic alterations induced by gamma radiation. These studies are under progress.

Physics evaluation

A. Belchior, P. Vaz[1], J. Alves[1], R. Trindade[1], M.L. Botelho,

Under REEQ/996/BIO/2005, the upgrading of an irradiation facility (PRECISA 22 ML) is foreseen. To assess the dose distribution inside the irradiation facility, Monte Carlo methods were applied. These methods in radiation transport calculations and particle transport simulations allow a comprehensive knowledge of the spatial dose distributions and the optimization of the irradiation process. The computational tools used to perform these studies were MCNPX and Penelope codes. Taking into account the construction of a pilot plant for wastewater treatment, the studies were performed regarding three different levels inside the irradiator. The results showed dose rate uniformity in the level more distant to the source. The level near the source showed significant differences between dose rate values, including the maximum dose rate of approximately 35 Gy/h. The validation of the simulation results obtained was performed by chemical dosimetry methods, namely by Fricke solution. Studies are underway in order to estimate the uncertainties and to further improve the agreement between experimental and simulated values, including studies using physical dosimetry. Since, dosimetry plays an important role in an irradiation process, a continuous collaboration with CHIP, S.A. is of crucial importance. As result, it was performed a routine dosimeter calibration, Red-Perspex, batch JB 4034, using ceric cerous as a reference dosimeter.

[1] Department of Radiological Protection and Nuclear Safety, ITN

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 of gas discharges;
3. Development of software for control;
4. Design of electronic instrumentation for nuclear applications;
5. Instrumentation and technical assistance.

Modelling of radiation fields, calculation of neutron physic parameters

The MCNP code is being used to calculate the pertur-bation of the neutron thermal flux by a sample in the presence of a moderator.
Monte Carlo calculations have been carried out in the field of the project POCI/FP/63433/2005. ITN participa-tion on the n_ToF (PS213) experiment at CERN (fourth year) and "n_ToF phase 2" EUROTRANS Project (IP EUROTRANS, 516520).

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 of gas discharges

The study of the electron kinetics in Ar-X [<2%] (where X is H_2, N_2, O_2 or H_2O) mixtures with application on GDS (Glow Discharge Optical Emission Spectroscopy) was started.

Development of software for control

Maintenance and optimization of EPA control software at the RPI.

Design of electronic instrumentation

- Two high power SCR controlled DC power supplies and a dual digital ampere-hour meter for using at the isotope enrichment by electrolyse in current flow at the DPSRN;
- New step motor controller provided with a counter and a digital display for the EPA Beam-Stopper at the RPI;
- Development of an electronic circuit to be used in "The Perturbed Angular Correlations experiments" at the RPI.

Instrumentation and Technical Assistance

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.
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

The Group is involved in the following collaborations:

1. n_TOF collaboration, a consortium of 40 laboratories in Europe and USA;
2. IST;
3. Research Institute for Solid State Physics and Optics, Budapest, Hungary.

Researchers

J. MANTEIGAS, Auxiliary Researcher, Group Leader
C. CRUZ, Auxiliary Researcher
I.F. GONÇALVES, Auxiliary Researcher
J. NEVES, Auxiliary Researcher
N. PINHÃO, Auxiliary Researcher (20%)
F.G. CARVALHO, Coord. Researcher (15%)

Students

L. CABEÇA MARQUES, Ph.D. Student
C.M. CARRAPIÇO, graduation student, FC/UA
A. CARRILLO TRIGO, BIC/FCT
C. SANTOS, M.Sc., FCT/UNL

Technical Personnel

T. JESUS, Electronics Technician
N. INÁCIO, Electronics 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 the installation of the "Ion Beam Laboratory – TANDEM 3 MV" at the Physics Sector.

(ii) Maintenance and optimization of the "EPA Control Software" installed at the RPI.

(iii) Technical support (development of electronic circuits) to be used in "The Perturbed Angular Correlations experiments" at the RPI.

(iv) Development and maintenance of electronic equipment to RPI, Physics, Chemical, UTR and DPRSN Sectors

Summary of the more relevant services/quipment rendered in 2006

Activity	Qty	Client	Price (€)
Laboratory equipment for the determination of radioactive element traces by electrodeposition	1 1 1	RPI - IRELAND NATS – OMAN IAEA – Sri Lanka	1 394,22 € 1 566,24 € 1613,69 €
Personal Radiation Dosemeter Equipment	4 1	ATOMEDICAL ESC. SUP. TEC. SAUDE	2420,00 € 726,00 €
Equipment Manufacturing	2 31	ITN/DPSRN CRIOLAB	1250,00 € 393,25 €
Technical assistance to *- Source Containers*	2 1	PORTUCEL/SOPORCEL – CACIA Siderurgia Nacional – Seixal	1512,50 € 326,70 €
Measuring and control of source activities	25 5	PORTUCEL/SOPORCEL – CACIA Siderurgia Nacional – Seixal	3587,65 € 635,25 €
Prices including TAX (VAT)		TOTAL AMOUNT:	15 425,50 €

Participation of ITN in the n-TOF experiment (PS213) at CERN (fourth year) and n_TOF phase 2

P. Vaz, I.F. Gonçalves, C. Cruz, J. Neves, C. Carrapiço, C. Santos, L. Ferreira, L. Távora[1]

A complete and precise knowledge of cross-sections for neutron induced processes is required for multiple applications, such as, the design of innovative Accelerator Driven Systems (ADS) and Energy Amplifier (EA) systems for the transmutation of nuclear waste and energy production, radioisotope production for medical and industrial applications and several topics in Astrophysics, Nuclear Physics and Nuclear Technology. Precisely measured neutron energy is required for the determination of the resonant structure of these cross-sections. The most suitable method to achieve such high resolution measurements is the use of short neutron pulses with a broad energy distribution, the energy of the neutrons being determined on the basis of their time-of-flight (TOF).
The n_TOF Collaboration, a consortium of 40 institutions in Europe, U.S.A., Japan and Russia, has carried out successfully between 2001 and 2004 three experimental campaigns at the neutron time of flight (TOF) spectrometer at CERN, using the CERN/PS accelerator complex. In this facility, a proton pulse of 7×10^{12} protons of 20 GeV impinges on a lead target every 2.4 seconds. After collimation, a neutron flux of the order of 10^5 neutrons/cm^2/pulse is available to perform cross section measurements in the detectors station located 185 m downstream the target area.
The n_TOF phase2 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 n_TOF beam-line and a new experimental area (EAR-2) using a shorter flight path (20 meters), with lower backgrounds and count rates in the detectors, making possible the extension of measurements to higher energies and the availability of a higher neutron flux (a factor of 100).
A team of researchers of ITN has been involved in Monte Carlo simulation activities, data analysis and development of electronics for the BaF_2 calorimeter. ITN is strongly involved in collaboration with CIEMAT-Madrid and INFN-Bari in the following areas: Monte Carlo simulation(I) - full and detailed simulation of the geometry of the new experimental area, computation of the particle fluxes, assessment of the backgrounds, with the usage of the state-of-the-art Monte Carlo codes MCNPX and GEANT-4; Monte Carlo simulation studies (II) - continuation of the studies to simulate the response of the BaF2 calorimeter, calibration and efficiencies on a module-by-module basis; Data analysis (I) - continuation of the analysis of the following data sets: ^{197}Au, ^{237}Np, ^{240}Pu, initiated during 2005, using the BaF_2 calorimeter; Electronics developments for the DAQ and the BaF_2 calorimeter.

[1] Centro de Instrumentação / U. Coimbra

Electron kinetics in gas mixtures used for Analytical Glow Discharge Optical Emission Spectroscopy

Z. Donkó, M. J. Pinheiro, N. R. Pinhão, P. Hartmann

Glow discharge optical emission spectroscopy is a widely used method for quantitative analysis of the composition of materials. The method makes possible the investigation of metals, polymers, glasses and ceramics. The molecular gases present in the discharge as impurities – being sputtered into discharge from the investigated samples or being impurities of the background gas (typically nitrogen, hydrogen, oxygen and water vapor) – can falsify the emission spectra of the investigated samples making impossible the accurate quantitative analysis. Due to this effect many laboratories are working nowadays on the possibility to add to the noble gas small, but controlled amount of molecular gases, to investigate their effect on the emission spectra and to evaluate the necessary corrections to the measured spectra. The research on the effect of these molecular gases on the GDOES glow discharges is a actual subject. The aim of the present work is a study of the electron kinetics and transport properties in these glow discharges to understand how the added molecular gases affect the transport of electrons and their energy distribution. The energy distribution of the electrons can significantly influence the gas ionisation, the excitation of some spectral lines and their intensity, which contains the basic information from the point of view of analytical investigations. Thus calculation of the electrons velocity distribution function is of fundamental importance.

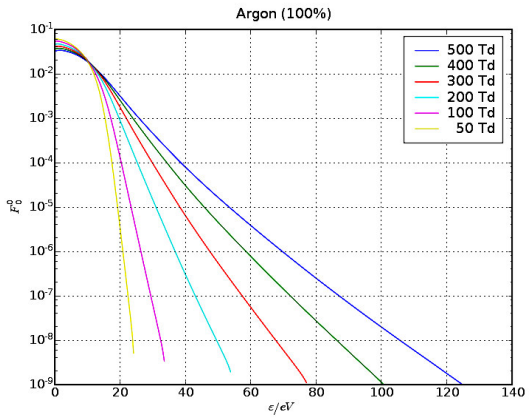


Fig.: Electron energy distribution function in argon as a function of the reduced electric field (Função de distribuição em energia dos electrões em argon em função do campo eléctrico reduzido)