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 featuring an ion microprobe with an external beam facility, a 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 decades allowed the group to achieve a large expertise in the fields of applications of ion beams to characterization and processing of materials. The recent activities of the group have been focused on the study of advanced materials with high technological impact. Several national and international collaborations allowed a continuous exchange of expertise and mobility of researchers, a key condition to keep the scientific activity of the group at the forefront of research in its field.

The research activities of the group were essentially centred in two kinds of materials: wide band gap semi-conductors, and nanostructures and insulators. Wide bandgap semiconductors are the base of optoelectronic devices operating in the visible wavelength range of the electromagnetic spectrum and are under intense research worldwide. Our work was focused on the optimization of the implantation conditions of magnetic and 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 also being studied in collaboration with the Universities of Aveiro and Grenoble.

The work in insulators is a continuation of ongoing projects or bilateral collaborations. Some of these comprise the modification of the optical and electrical properties of α-Al_2O_3 and laser materials (KTP and RTP), as well as the study of nanoaggregates formed in MgO and rutile by high fluence implantation doping with transition metals. Besides this and due to the potential of ion beam techniques to study thin films and multilayers, important work continued in the characterisation of magnetic thin films for magnetic spin valves, tunnel junctions, and oxynitride coatings, in collaboration with INESC and University of Minho.

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 titanium beryllides, the characterisation of the new Eurofer (ODS) steel and the study of surface erosion and fuel retention of W under ITER conditions.

Integrated in these research activities the group has also been strongly committed with the training of 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 2007 was materialized in:

Publications (peer reviewed journals): 38
Conference and workshop contributions: 5 invited, 16 oral and 19 posters.
Running projects: 24

Researchers(*)

E. ALVES, Princ. (Group leader)
R.C. DA SILVA, Princ.
U. WAHL, Princ.
L.C. ALVES, Aux. (75%)
N. BARRADAS, Aux. (10%)
A.R. RAMOS, Aux. (10%)
A. KLING, Aux. (5%)
K. LORENTZ, Post-Doc. fellow, FCT

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A. RODRIGUES, Project grant
C.P. MARQUES, Ph.D. student, FCT grant
J. VAZ PINTO, Ph.D. student, FCT grant
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RBS analysis of InGaN/GaN quantum wells for hybrid structures with efficient Förster coupling

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

Objectives

There is strong current interest in Förster resonant energy transfer (FRET) from a semiconductor quantum well (QW) to an overlayer of another luminescent material. The FRET process becomes efficient when the two materials are placed at interaction distance of a few nanometres. The additional requirement of large spectral overlap between the energy donor and acceptor can be satisfied by combinations of InGaN/GaN QWs (as donors) and overlayers of either light-emitting polymers or nanocrystalline semiconductor quantum dots (as acceptors), both of which can be tailored to have high absorption in the QW emission region.

Here we study a set of custom grown InGaN/GaN single QW samples, in which the GaN cap layer thickness was varied to modulate the FRET rate in hybrid structures. We used high-resolution grazing-angle RBS experiments to determine the GaN cap layer thickness, varied from 2 to 12 nm, which controlled the interaction distance between the QW and the coupled luminescent medium in hybrid structures. The measured thickness values were used to confirm the dominance of sheet-to-sheet dipole-dipole interactions in QW-polymer hybrid structures.

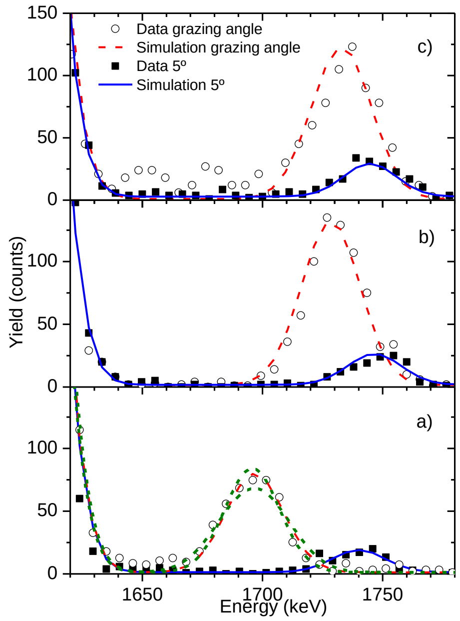

Fig 1. RBS spectra for samples a) A, b) B and c) C. Simulations for the derived parameters are shown. For sample A, simulations x = 0.02 and x = 1 are also shown.

Results

Fig. 1 shows the near-normal and grazing angle spectra for each sample. From the shift in the In peak it is possible to determine the GaN cap layer thckness, which determines the FRET efficiency. The main difficulty is that the problem is ambiguous, as many different solutions lead to acceptable fits. An involved manual analysis can resolve the ambiguity as shown in Fig. 2: the only In QW concentration y consistent with all data is x = 0.07(1) and $t_{GaN,exp}/t_{GaN,nominal}$ = 0.79(5). Using these values we can determine the cap thickness for each layer.

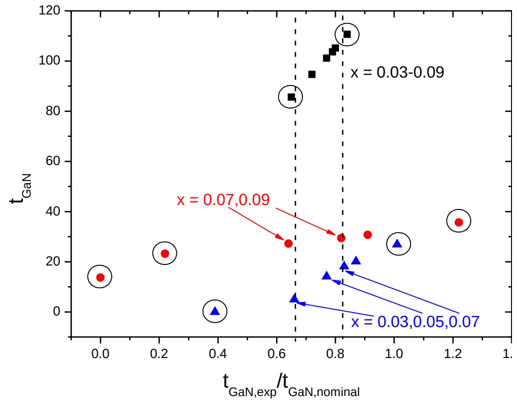

Fig 2. Possible solutions for each sample. The only consistent set implies x = 0.07(1), and GaN cap layer thickness of samples A, B and C:
11.8(8) nm, 3.2(5) nm, 1.9(5) nm.

The results were used to explain quantitatively the FRET process.

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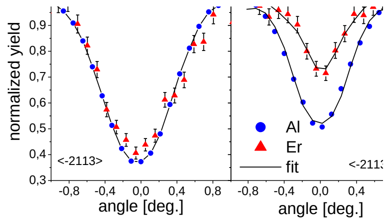
Lattice site location, damage and optical characterization of Eu implanted $Al_XGa_{(1-X)}N$ layers

K. Lorenz, E. Alves, T. Monteiro[1], M. Peres[1], A. J. Neves[1], K. Wang[2], R.W. Martin[2], K. P. O'Donnell[2]

Eu doped GaN has been extensively studied due to the sharp emission in the red spectral region interesting for applications in electroluminescent devices and lasers. The semiconductor band gap can be tuned when using the ternary alloy $Al_xGa_{(1-x)}N$ with different Al/Ga ratios. This can change the excitation mechanisms of the rare earth ions and the efficiency of light emission processes can be optimized by choosing the appropriate $Al_xGa_{(1-x)}N$ host.

$Al_xGa_{(1-x)}N$ films with AlN contents from 0% to 100 % were implanted with Eu ions. The implantation damage and the lattice sites were studied by Rutherford Backscattering and Channelling spectrometry. Al-containing alloys are more resistant to implantation damage than GaN. The Eu ions are incorporated on lattice sites slightly displaced from the substitutional cation-site along defined directions (see figure).



The displacement increases with increasing AlN fraction probably because of the decreasing lattice parameter leaving less free space to accommodate the large RE ion as well as defects. Experiments performed with different implantation geometries indicate that the displacement is due to the interaction with defects caused by the implantation. Photoluminescence (PL) spectra show Eu related luminescence lines in the red spectral region for all samples after annealing. The PL intensity strongly depends on the composition with best results for ~30% AlN content. Excitation spectra show the AlGaN band gap and two excitation bands below gap: X_1 peaks at 3.26 eV in GaN and up-shifts linearly by 0.28 eV as x increases to 1. For $x > 0.6$, a second band, X_2, emerges, showing a similar energy shift. We identify $X_{1,2}$ as core-exciton-like complexes of Eu emitting centers.

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[2] Department of Physics and Applied Physics, University of Strathclyde, Glasgow, G4 0NG, Scotland, UK

Structural and optical characterization of AlInN ternary alloys

K. Lorenz, N. Franco, E. Alves, S. Pereira[1], I. M. Watson[2], K. Wang[3], R.W. Martin[3], K. P. O'Donnell[3]

In addition to a band-gap covering a very wide energy range (0.7 eV to 6.2 eV) the ternary semiconductor AlInN has the advantage that it can be lattice-matched to GaN. $Al_{1-x}In_xN$ layers were grown by MOCVD on GaN buffer layers at temperatures between 760 ºC and 840 ºC to give InN contents between 13% and 24%. While for growth temperatures ≥ 800 ºC the AlInN films grow coherently on GaN, with good crystal quality and homogeneous InN concentration, the sample grown at 760 ºC shows an increase of InN content with depth, a relief of strain towards the surface and a deterioration of crystal quality. AFM studies suggest that the relaxation is accompanied by an onset of three-dimensional growth. The pattern of compositional grading is the opposite to that often observed in InGaN/GaN bilayers with relaxed near-surface InGaN, where InN incorporation is inhibited in the compressively-strained interfacial region and increased in the relaxed surface region. In AlInN, compressive strain seems to facilitate the InN incorporation. Our results imply a relaxation mechanism for AlInN in which strain relief takes place mainly via the change of InN content towards the value of lattice matched material (17-18 %). Photoluminescence (PL) measurements show a clear red-shift of the $Al_{1-x}In_xN$ emission peak with increasing InN fraction and comparison of the emission wavelengths with PL excitation data reveal strong Stoke's shifts.

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A stable In–V_N complex in AlN and GaN: a new hypothesis to explain exciton localisation in nitrides

K. Lorenz, E. Alves, J. Schmitz[1], J. Penner[1], R. Vianden[1]

The fact that especially In-containing III-nitride emitters are relatively insensitive to the large densities of defects (mainly threading dislocations) found in standard $Ga_xIn_{1-x}N$ LEDs and laser diodes, has been the subject of a lively discussion. InN rich nanoclusters, compositional or strain inhomogeneities are possible explanations. Channelling measurements showed that close to 100% of implanted In ions occupy substitutional cation sites in GaN and AlN. However, Perturbed Angular Correlation measurements showed that after annealing only ≈50% of the In probes occupy relatively undisturbed substitutional sites at 293 K while the remaining fraction traps a nearest neighbour point defect. Above 293 K this fraction decreases strongly until all In probes are found in undisturbed substitutional sites. The effect is completely reversible. A model involving an indium–nitrogen vacancy complex is suggested to explain this behaviour. Possibly this complex can act as radiative recombination centre or as seed for phase segregation during growth.

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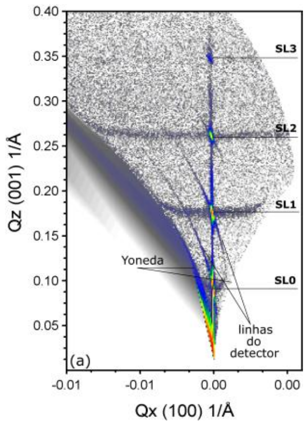
Properties of Ge islands embedded in multilayer and superlattice structures

S. Magalhães, E. Alves, J. P. Leitão[1], A. 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.

In this work we compared Ge quantum dot heterostructures with a planar Ge/Si multilayer. The islands were evidenced using X-ray dispersion techniques, ion beam techniques and photoluminescence. It was found that in the case of the Ge quantum dots samples, the dots created strain phenomena significantly different than the planar homogenous samples, showing the dots presence. The inset figure shows features in a XRR reciprocal space map that are a fingerprint of a correlated vertical structure (the quantum dots). Also, the comparison of the Ge minimum RBS yield from the scans along tilted directions show that, due to the larger Ge lattice constant, the scattering probability increases consistent with the presence of the dots.



The photoluminescence measurements for single layer and multilayers samples indicate the possible presence of islands, located in the range hυ < 0.8 eV. It is well known that the buried Ge layers create strain fields for the subsequent layers which results namely, in the reduction of the critical thickness for the 2D-3D growth transition.

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Structural characterization of oxidized NbO_xN_y coatings under air annealing

E. Alves, N. Barradas, J.M. Chappé[1], S. Lanceros-Méndez[1], F. Vaz[1], M. Fenker[2], H. Kappl[2]

In the present work the oxidation resistance behaviour of NbON multilayer films was studied. The depositions were carried out by DC magnetron sputtering with a reactive gas pulsing process. The nitrogen flow was kept constant and the oxygen flow was pulsed. Pulse durations of 10 s produced multilayered coatings with a period of λ = 10 nm. Three different films with increasing duty cycles have been deposited.

Rutherford Backscattering Spectrometry (RBS) was used to study the chemical composition variations for different annealing temperatures (as-deposited, 400 ºC, 500 ºC and 600 ºC) combined with X-ray diffraction (XRD) to identify the crystalline phases formed. At 400 ºC, for all films a very thin layer starts to form at the surface with enhanced O concentration. The composition of the deeper part of the samples remains unchanged. At 500 ºC, the oxide scale grows, encompassing about half the film thickness. At 600 ºC, the process is finished and a single layer is formed with reduced Nb and increased O concentration. Fourier-Transform Infrared (FTIR) spectroscopy results confirmed the increase of this surface oxidation, while XRD revealed that crystallization of Nb_2O_5 occurs at 600 ºC.

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Intrinsic p type ZnO films deposited by R.F. Magnetron sputtering

E. Alves, Jinzhong Wang[1],Elvira Fortunato[1],T. Monteiro[2]

In this work, ZnO films were deposited on c-plane sapphire substrate in Ar gas by R.F. Magnetron sputtering method. Furthermore, the films were annealed at 400 °C in reducing ambient. The properties of the as-grown and annealed films have been characterised by means of X-Ray Diffraction (XRD), Rutherford Backscattering Spectrometry (RBS), Elastic Recoil Detection Analysis (ERDA), Hall measurement and Photoluminescence (PL) spectra, respectively. XRD studies indicate that after annealing, the crystal quality of ZnO films increases and the strain in the films changes. From RBS and ERDA, we can see that although there is no H_2 introduced in the sputtering chamber, H has been found in the as-grown ZnO films. After annealing, the amount of H in the film increases. Compared with the as-grown ZnO films, the ultra exciting intensity obviously decreases and new optical active centres in the blue/violet (~3.0 eV) and red (~1.9 eV) are enhanced in the PL spectrum of the annealed sample. Hall measurements indicated that the as-grown film reveals p-type conductivity. The p-type conductivity improves with annealing, but in a long term (9 days) the conductivity changes from p- to n-type.

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Effect of ITER-relevant material mixing on fuel retention and material characteristics

L.C. Alves, N.P. Barradas, E. Alves, Graham Wright[1]

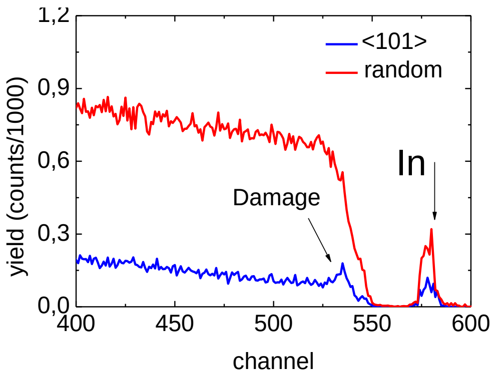
The major goal of the study was the full characterisation of the surface composition and morphology, and fuel retention of W targets exposed to plasma fluxes similar to the ones expected in the ITER divertor (> 10^{23} $m^{-2}s^{-1}$). Tungsten samples were exposed to plasma fluxes in PSI-2 and studied with ion beam techniques and electron microscopy. Fuel retention in the samples and its depth distribution was quantified with Elastic Recoil Detection Analysis (ERDA) and Nuclear Reaction Analyses (NRA).
The W targets exposed in Pilot-PSI were analysed ex-situ with ^{3}He(d,p)α Nuclear Reaction Analysis (NRA) and Thermal Desorption Spectroscopy (TDS). Initial NRA data shows a D depth profile that is peaked at the surface and significant D retention (0.01 at.%) at a depth of ~3 μm after only 40 s (10 discharges) of total plasma exposure time. This demonstrates the trapping of D that has diffused away from the ion implantation zone towards the bulk. The effects of surface polishing/roughness and pre-annealing targets before plasma exposure was investigated through the comparison of D retention as determined by NRA and TDS analysis. The results show that a W target with a surface roughness of <1 μm has nearly 6 times more D retention in the first 3 μm of the surface than an "as received" W target.

[1]FOM-Institute for Plasma Physics Rijnhuizen, Association Euratom-FOM, Netherlands

Ion beam studies of InAs/GaAs self-assembled quantum dots

E. Alves, S. Magalhães, N.P. Barradas, N.V. Baidus[1]*, M.I. Vasilevskiy*[1]*, B.N. Zvonkov*[2]

Self-assembled InAs/GaAs quantum dots (QD's) emit in the telecommunication wavelength range (1.3-1.55 µm) revealing an enormous potential to become the active elements of low threshold lasers and light emitting diodes. However, the luminescence is dramatically quenched at room temperature (and even below) due to the defects in the GaAs matrix which open non-radiative recombination paths.
In this study we combine Rutherford Backscattering Spectrometry/Channelling (RBS-C), High resolution X-ray diffraction (HRXRD) and Photoluminescence (PL) techniques to correlate the structural and optical properties of the InAs/GaAs QD heterostructures. The heterostructures were grown by Atmospheric Pressure Metal Organic Vapour Phase Epitaxy, feature a combined InGaAs/GaAs capping layer and exhibit sizable PL in the vicinity of 1.5 µm. Channelling measurements reveal a good crystalline quality along the main axial directions with minimum yields in the range of 4% to 6% through the entire capping layer. An increase on the dechannelling rate is observed in the region where the InAs quantum dots were buried (see figure). The channelling results also give evidence for the presence of defects preferentially oriented in the (110) planes. Detailed angular scans in a structure with a 25 nm cap allowed the study of the In position with respect to the GaAs matrix and a perfect alignment was found. This proves that the growth interruption and surface treatment using tetrachloromethane during the capping layer deposition, improve the crystal quality of the heterostructure. This helps to overcome the PL quenching at room temperature.



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[2] N. I. Lobachevskii State University, Nihznii Novgorod, Russia

Study of SiGe alloys with diferent germanium concentrations implanted with Mn and As ions

S. Magalhães, V. Batista, N. A. Sobolev[1]*, E. Alves*

In this work we studied the structural properties of SiGe alloys with different Ge molar compositions co-implanted with manganese and arsenic ions. The ions were implanted at room temperature to fluences of 1×10^{15} cm^{-2}, 5×10^{15} cm^{-2} and 1×10^{16} cm^{-2} and energies of 170 keV (Mn) and 200 keV (As) in order to achieve the overlap of the implanted profiles. The alloys were studied with Rutherford Backscattering Spectrometry/Channelling (RBS/C) and X-Ray Diffraction (XRD) techniques. After implantation the implanted region (150 nm) turns into amorphous according with RBS/C. The evolution of the lattice parameter was studied using XRD. The annealing at 550 ºC induces the recrystallization of the amorphous layer for the sample implanted with the lower fluence and the full recovery is complete after annealing at 700 ºC. The samples implanted with higher fluences didn't reveal any noticeable recovery. The evolution of the Mn and As profiles during the annealing at 550 °C do not reveal significant changes.

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In-situ XRD Studies of thermal stability of pure silica and Ti-MCM-41 materials

N. Franco, E. Alves, C. Galacho[1], P.J.M Carrott[1]

In this work we present a study on the thermal stability of silica and titanium containing ordered mesoporous materials with MCM-41 structure, synthesized at ambient temperature and pressure. Calcined grades were analyzed *in-situ*, in the form of compacted powder, to assess its influence on the order-disorder transition temperature. The temperature was raised up to 1000 ^{o}C under vacuum (~10^{-5} mbar) and flowing N_2 (~10^{-3} mbar). An intense X-ray beam collimated by a Göbel mirror was used to follow *in-situ* the temperature dependence of the unit cell dimension in θ-2θ configuration. During the annealing, in steps of 100 ^{o}C, the unit cell parameter decreases, as well as the diffracted signal leading to its extinction at around 1000 ºC. The results show that under vacuum, this transition is reversible and the diffraction peaks (100), (110) and (200) of the two-dimensional hexagonal lattice appear and are slightly shifted to higher angles after cooling to room temperature. The same result, although not so pronounced, was observed when the measurements were done in flowing nitrogen gas.

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Stability of GaN Films Under Intense MeV He Ion Irradiation

C.P. Marques, E. Alves, O. Ambacher[1], M. Niehus[2], E. Morgado[3], R. Schwarz[3]

We have exposed MOCVD-grown GaN films to a 1 nA beam of 1.5 MeV $^{4}He^{+}$ particles produced by the Van de Graaff accelerator at ITN. The material quality was tested by measuring dark conductivity and steady-state as well as transient photoconductivity at room temperature, in coplanar layout. Photocurrent spectra taken below the band gap reveal a broad defect density-of-states distribution. After 5 ns irradiation with laser pulses from a frequency-doubled Nd:YAG laser, the induced photocurrent shows a very slow decay over several orders of magnitude. Compared to the decrease of photosensitivity in thin undoped a-Si:H films under He^4 irradiation – a decrease surprisingly similar to c-Si – we observe that degradation of GaN also sets in at about 10^{12} cm^{-2}, but decreases much more slowly as indicated by the smaller negative exponent in the photocurrent-fluence power law plot. After about 3×10^{15} cm^{-2} the mobility-lifetime-product decreased by half an order of magnitude. This indicates a much higher radiation resistance of GaN when compared to amorphous or crystalline Si.

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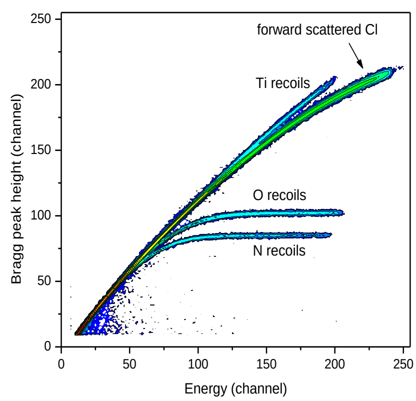
[3] Instituto Superior Técnico, Physics Department, P-1049-001 Lisboa, Portugal

Surface analysis of oxynitride compounds with ion beams

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

Titanium nitride and oxynitride compounds exhibit interesting properties for applications in fields ranging from protective/decorative coatings to solar panels. The properties of these compounds are related to the oxide/nitride ratio and can be tailored by tuning this ratio. Furthermore the thermal stability is other important issue with regarding potential applications. Thus, accurate composition measurements are fundamental to understand the behaviour of these structures. Ion beam based techniques (IBA) are unique for this purpose. The composition was determined by Rutherford Backscattering Spectrometry (RBS) throughout the entire thickness of the films. To get information on the profile of light elements (O, N) and detect the presence of hydrogen on the films, Heavy Ion Elastic Recoil Detection Analysis (HI-ERDA) was performed (see figure).



The results indicate a nearly constant stoichiometry through the entire analysed depth. The oxygen fraction in the films increases with gas flow, reaching a value of x ~ 0.33 for a reactive gas flow mixture of 6.25 sccm. During growth mixed zirconium nitride and oxide phases form. The annealing of the samples in the temperature range of 400 °C to 900 °C, in controlled atmosphere and in vacuum, leads to the formation of new phases. When Zr atomic content is higher than 80% the heat treatment in controlled atmosphere reveals the annealing of defects and the formation of m-ZrO_2 and t-ZrO_2. When oxygen content of the films varies from 6% to 14% the GIXRD reveals the development of t-ZrO_2 at 600 ^{o}C or above.

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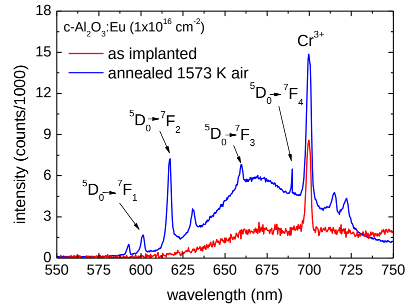
Ionoluminescence studies of Eu implanted Sapphire

C. Marques, L.C. Alves, R.C. da Silva, A. Kozanecki[1], E. Alves

Sapphire single crystals were implanted at room temperature with 100 keV europium ions up to fluences of 1×10^{16} cm^{-2} aiming at study of damage and Eu ion location after implantation and upon annealing under oxidising or reducing atmosphere up to 1300 °C.

After implantation an intense red emission indicating the presence of Cr (a natural contaminant) in the samples is observed, along with F-centres. Thermal treatments in air or in vacuum anneal most of the implantation related defects and promote the redistribution of the europium ions. The characteristic emissions due to 4f intra-band transitions in these rare-earth ions become observable (see figure). Detailed lattice site location studies for various axial directions are underway to allow correlating the damage recovery and incorporation of the Eu ions into well defined sites with the intensity and energy of the ion beam induced luminescence.



[1] Institute of Physics Polish Academy of Sciences, 32/46 Lotników Al., 02-668 Warszawa, Poland

Microstructural Studies of Mg doped $SrTiO_3$ Films

A.R.L. Ramos, E. Alves, O. Okhay[1], A. Wu[1], P.M. Vilarinho[1], I.M. Reaney[2], J. Petzelt, J. Pokorny[3]

STO based materials are important for high dielectric permittivity applications and tuneable microwave devices. Recent results have shown that in-plane strain from the substrate can produce room-temperature ferroelectricity in epitaxial STO. The high ε_r at room temperature in these films (nearly 7000 at 10 GHz) and its sharp dependence on electric field are promising for device applications. However this strain-induced enhancement in T_c is attained through the utilization of a (110) $DyScO_3$ substrate and has not been reproduced on silicon based substrates, as required for device applications. Hence, an alternative way to adjust the dielectric response of STO thin films through chemical substitutions deserves further study. The manipulation of the dielectric properties for specific applications is well known in STO single crystals and ceramics, but not in polycrystalline thin films. A-site substitutions in STO lattice with isovalent Ca, Ba and Pb ions induce a low temperature ferroelectric-type anomaly. In spite of predictions, no polar state was reported for Mg doped STO. However, in a previous work of the authors, $Sr_{1-x}Mg_xTiO_3$ (SMT) films displayed increased tuneability at room temperature, not observed in equivalent bulk ceramics, pointing to modification of the lattice polarization. Moreover it was demonstrated that the solid solubility limit of Mg in STO films prepared by sol gel and by pulsed laser deposition (PLD) was higher than in STO ceramics. In order to clarify the role and solid solubility of Mg in STO thin films prepared by sol-gel and deposited on Si/SiO2/TiO_2/Pt substrates, a systematic study of the structure and microstructure was conducted using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), Rutherford Backscattering Spectroscopy (RBS) and Raman. Results show that the incorporation of Mg and the solid solubility limit of Mg in the A-site of STO lattice of sol gel thin films on silicon platinised substrates is higher than in ceramics and is dependent on the annealing temperature.

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Ion implantation and ion beam analysis of MOD deposited oxide films

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Dilute magnetic oxide semiconductors are semiconducting oxides substituted with magnetic or other transition elements. The importance of these systems has increased in recent years in view of spintronics and photocatalytic applications. In this work oxide films of TiO_2 and V_2O_5 were deposited by metal organic decomposition (MOD) technique. The thickness, composition, orientation of the film on single crystal substrates (sapphire, Si, MgO) and residual C concentration were measured by Rutherford Backscattering Spectrometry in Channelling mode (RBS/C) and Nuclear Reaction Analysis (NRA). X-ray diffraction and Raman spectroscopy were used for analysis of the structure of the oxide films. The stoichiometric oxide films of appropriate thickness were subsequently doped with elements such as Fe, Co and V either using a suitable metal organic solution or by ion implantation. In ion implantation, the ions are distributed in the sub-surface region of the film. On the other hand, impurities incorporated from solution are expected to be distributed over the entire thickness of the film. The effect of doping on optical and photocatalytic properties is being studied and compared for solution doped films with those doped using ion implantation.

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Ion-implanted magnetic nanolayers of wide band gap semiconductors for spintronics applications

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The project investigates the possibility to fabricate diluted magnetic semiconductors by means of ion-implantation of transition metals into single-crystalline starting materials such as the wide band gap semiconductors GaN and ZnO, and some selected semiconducting oxides such as $SrTiO_3$ and TiO_2.
In first exploratory experiments single crystals of ZnO, GaN and $SrTiO_3$ were implanted with 60 keV ^{56}Fe at fluences of 1×10^{15} cm^{-2} and 5×10^{15} cm^{-2}. RBS/C experiments showed that the implantation damage in ZnO and $SrTiO_3$ can be removed to a large extent using air annealing above 1000°C, while in GaN it is more persistent, especially at higher implantation fluences. Characterizations of the magnetic moments of the samples by means of SQUID have so far only been carried out for samples annealed at 900°C, where they revealed ferromagnetic behaviour in the ZnO and GaN samples and in the 5×10^{15} cm^{-2} implanted $SrTiO_3$ sample. Some of the samples were in addition implanted with small fluences (10^{13}-10^{14} cm^{-2}) of radioactive ^{59}Fe (45 d), followed by emission channelling studies of the lattice location of this isotope as a function of annealing temperature. The majority of Fe was found on substitutional Zn sites in ZnO, substitutional Ga sites in GaN, and at or close to substitutional Ti sites in $SrTiO_3$. The emission channelling experiments also indicated that following annealing up to 900°C the implanted Fe atoms are still located in defect-rich regions which are strained or show considerable mosaicity.

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Investigation of changes in the luminescence and structural properties of nano-SiGe/SiO_2 multilayers due to annealing processes

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Semiconductor nanoparticles embedded in an oxide matrix are highly interesting for applications in luminescent devices compatible with CMOS technology. A promising method for the production of this kind of structures is the deposition of amorphous SiGe nanoparticles embedded in SiO_2 using Low Pressure Chemical Vapor Deposition at low temperatures, followed by a thermal treatment to crystallize them. These structures exhibit luminescent emission peaking in the blue-violet at 400 nm. Since the luminescence in single layers is limited by the number of nanoparticles that can be placed in a plane, multilayer structures is of high interest to increase the light output. The dependence of luminescence and structural properties (Ge diffusion, nanoparticle diameters) of the multilayer systems on the layer thickness and annealing conditions has been studied using TEM and grazing incidence RBS. The studies revealed that SiO_2 buffer layers with a thickness of at least 12-15 nm are required to suppress the Ge diffusion which is detrimental to the formation of luminescent nanoparticles. The highest luminescence yield was observed after rapid thermal annealing at 900 ºC for 60 s for multilayer structures containing nanoparticles with diameters of about 3.0-4.5 nm and separated by 35 nm thick oxide buffer layers.

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Oxidation studies of beryllides using ion beams

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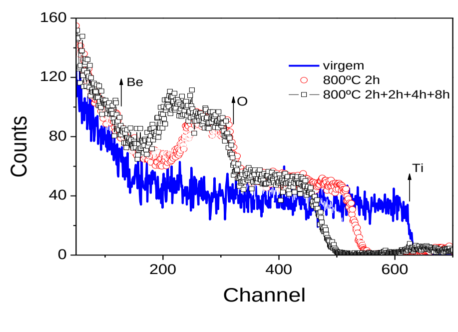
To increase the tritium-breeding ratio in the future nuclear fusion reactor, beryllium is expected to be used as a neutron multiplier. Studies have been performed for the use of metallic beryllium in the form of a pebble bed. However, pure beryllium becomes brittle and swells under neutron irradiation, making its use in the form of beryllides a possible alternative. Aiming at a detailed study of its oxidation behaviour, Be-Ti intermetallic compounds with nominal composition Be-5at%Ti and Be-7at%Ti produced at JAERI, were submitted to different air annealings at temperatures of 800 ºC, for periods of up to 16 h. Rutherford Backscattering Spectrometry (RBS) and Particle Induced X-Ray Emission (PIXE) were used with H^+ and He^+ microbeams (~3 µm) in order to access changes in surface topography and monitor the oxide layer formation. Both alloys reveal intra-grain regions with high concentration of impurities (O, Fe and Ni) and Ti depletion and that oxidation occurs preferentially at the Ti depleted (Be rich) regions.
Furthermore in Ti rich zones, oxidation is not due to Ti but to Be oxidation that occurs after Be diffusion to the sample surface (see figure). Results also show that the oxide layer formed in the Be-7at%Ti is larger than the one measured for the Be-5at%Ti sample and that even after 16 h annealing that layer continues to grow.



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Defect induced magnetism: magnetism in Ar-implanted ZnO and rutile

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The finding of ferromagnetic order in systems that do not include magnetic elements such as HfO_2, along with band structure calculations indicating that cation vacancies may be associated with magnetic moments in materials like CaO and HfO_2, led to the proposal of ferromagnetism based on lattice defects. The defects are hold responsible for the formation of magnetic moments at the molecular orbitals surrounding vacancies and for the formation of impurity bands mediating long range ferromagnetic ordering. This triggered work focused on the role of lattice defects as at least partly responsible for the observed magnetic signal.
Within this context, ZnO and rutile single crystals were implanted with Ar ions with energy of 100 keV and fluences up to 1×10^{17} cm^{-2} and 2×10^{17} cm^{-2} respectively. Ferromagnetic behaviour was observed at room temperature after implantation. Although trace amounts of transition metal impurities were identified in the virgin ZnO crystals, it was shown that they are magnetically inert and cannot account for the observed magnetic behaviour, which was thus assigned to the presence of implantation-induced lattice defects. The ferromagnetic behaviour is suppressed in ZnO after consecutive annealings in air at 400 ºC and 500 ºC. The fact that it disappears after the annealing at 500 ºC can be explained by the annealing out of the implantation defects, confirming the importance of lattice defects towards the magnetic behaviour of ZnO. On the contrary, annealing the as-implanted rutile at 800 ºC in Ar atmosphere for 1 h led to enhancement of the ferromagnetic behaviour. This surprising finding is currently under investigation.

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Structural and magnetic properties of oxides implanted with transition metals – TiO_2 implanted with Co, Ni and Fe: influence of the dopant in the anisotropic magnetic behaviour

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We studied the behaviour of the transition ions Co, Ni and Fe introduced in TiO_2, by ion implantation. Single crystals of rutile TiO_2 were doped with magnetic ions Co, Ni or Fe, using ion implantation with fluences in the range of 5×10^{16} cm^{-2} to 2×10^{17} cm^{-2} and energy of 150 keV. The structural and magnetic properties of such samples were studied after implantation and upon thermal treatments in order to understand the role of the dopant and its concentration. As-implanted samples present different magnetic behaviours that are related with the atomic concentration of the implanted species: samples with lower concentrations display paramagnetic behaviour while for higher concentrations ferromagnetic like behaviour is obtained. For intermediate concentration a superparamagnetic regime is found, indicating the formation of nm-sized magnetic aggregates during implantation. After annealing treatments the samples display anisotropic ferromagnetic behaviour at room temperature that is correlated with the rutile structure and dependent on the implanted species. Enhanced electrical conductivity exhibits also anisotropy at low temperatures, following the same general trend as in reduced rutile. No magneto-resistive effects were detected, indicating that there are no polarization effects of the charge carriers. It is suggested that vacancies accommodate at the interface between the aggregates and the TiO_2 host.

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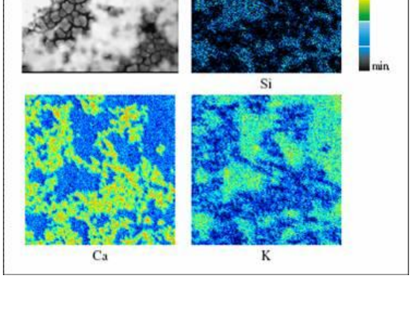
Characterization of potash-glass corrosion in aqueous solution: the influence of Mn, Fe and Cu ions

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

We continued the investigation of 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 56 mol.% SiO_2, 24 mol.% CaO and 20 mol.% K_2O, and with 1 mol.% of Cu, Mn or Fe oxides added, were prepared. The corrosion products were studied by analysing the glass surfaces after being in contact for different periods with static water or using a stirrer.
The experimental conditions used reproduced well the corrosion processes found in ancient glasses of similar composition weathered through five centuries. Silica rich-layers and Ca-carbonates are always found in the exposed surfaces and more than one such layer develops during the longer immersion periods (see figure). 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+) and coordination.



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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 project aimed at measuring (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 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.

The following tasks were performed during 2007:

1. Reproducibility tests for the $^{14}N(p,p_0)^{14}N$ cross sections measured during the first year using thin films.
2. Benchmarking of evaluated/measured (p,p) cross-sections in the 500-2500 keV energy range for C, N and Si using bulk samples.
3. Continuation of the measurement of the (p,p) elastic cross sections for Li in the 500-2500 keV energy range using bulk samples.

Advanced data analysis for IBA

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

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 other hand to automate the data analysis. In 2007 the highlight was the conclusion of an intercomparison exercise of the main codes dedicated to the analysis of IBA data, made with support of the IAEA. The results confirmed that available IBA software packages are, within their design limitations, consistent and reliable, and that, in some complex cases, NDF has further capabilities and higher accuracy. The work on integrating PIXE in the NDF package was continued. Seven papers were published in 2007 in international journals.

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Characterisation of Roman and modern slag at S. Domingos mine

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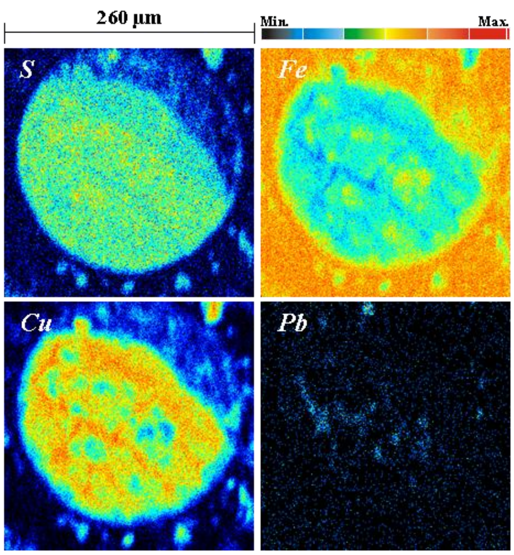
Located in the Iberian Pyrite Belt, the S. Domingos mine has been exploited since Roman times. The exploitation generated a large amount of wastes and residues that cause strong environmental impact. The purpose of this work is to study the slag chemical stability under natural weathering and evaluate the possibility of slag re-processing in order to economically recover some of the contained metals.

The selected samples were analyzed using several techniques, namely, optical microscopy, SEM-EDS, EPMA, µPIXE, ICP-MS, INAA and image analysis. This work indicates that, in spite of the good mechanical properties of the slag for aggregate use, care should be taken since they may release considerable amounts of metals (see figure). A re-processing of the slag is advised as the amount of some valuable metals in the sulphides and sulphosalts may be of considerable economical interest (Cd 100-400 ppm; In 100-300 ppm; Sn 700 ppm; Sb 200 ppm; Ag 100 ppm; Au 300 ppm).



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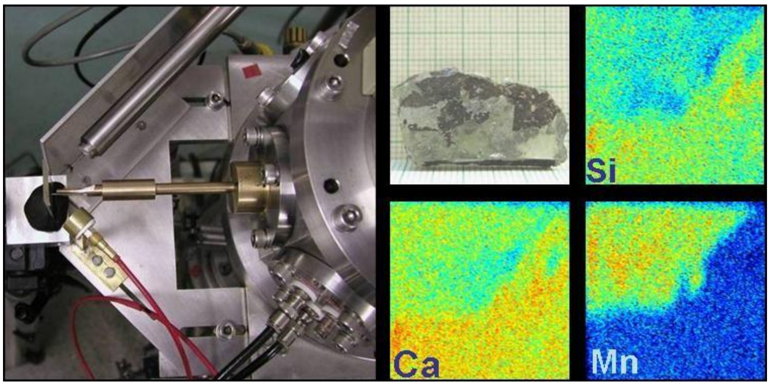
External microbeam line developments*
P.A. Rodrigues, L.C. Alves, R.C. da Silva

Further developments were achieved with the acquisition and installation of new equipment such as a laser device and video cameras for precise positioning of the target, and a new X-ray detector with fine energy resolution capabilities. These enabled to initiate the study of a group of archaeological Roman glass fragments.



Due to their poor state of conservation, namely delaminating of the glass surface, the use of external beam instead of in vacuum analysis was compulsory. Joining the microbeam capabilities (~70 μm) with the possibility of producing a beam scan, sample surface images were obtained allowing to clearly identifying corroded and clean regions, as corroded areas present increased contents of Mn and Fe (see figure).

This allowed a more representative analysis of the glass bulk composition and the possibility of comparing several fragments as part of the same object, as well as giving clues to their provenance and period of manufacture. The project will be completed with the design of an external target holder comprising a 3-d motorized displacement table with 6 degrees of freedom, 3 continuously driven mm-wise translations for coarse positioning and 3 step-wise micrometer translations for fine positioning.

* Project POCTI/CTM/60685/2004

Upgrade of X-ray laboratory at Physics Department
N. Franco, E. Alves

The main activity of the x-ray laboratory at ITN Physics Department is concentrated on the characterisation of semiconductor materials, in collaboration with several research groups. Modern semiconductor materials used for device fabrication are based on thin multilayer structures and the continuous reduction of the device size puts a lot of pressure on the characterisation techniques, demanding beams with high spatial resolution as well high angular resolution. Thus, the laboratory upgrade with a new high resolution beam line was mandatory and the Bruker-AXS B8Discover X-ray diffractometer showed to be the ideal diffractometer that fulfils these demands. Although, after installation several issues related to beam stability emerged, such as primary beam oscillation and too long warming up times, the problems were solved by 6 months long hard work between ITN and German technicians from Bruker-AXS. The D8Discover shows to be a great advantage in materials characterisation adding new X-ray techniques to the laboratory, e.g. GID (Grazing Incidence Diffraction (planar)), as well allowing decreasing the response time to the collaborators.

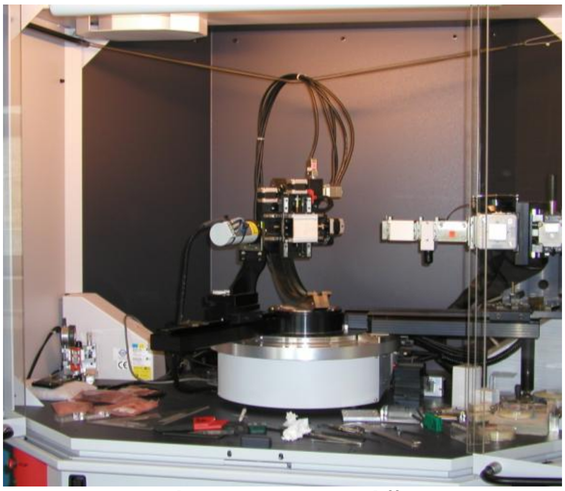


Fig. 1 – Bruker-AXS D8Discover diffractometer