High Resolution Depth Profiling HRDP-10
Online Meeting November 9 and 10 2021

Day 1 9th of November 2021

Times for the meeting in various time zones

Time zone	Time for meeting
ACDT	Adelaide: 7:00 – 10:15 am
AEDT	Australian East cost: 7:30 – 10:45 am
EST	US East coast: 3:30 - 6:45 pm
PST	US West coast: 12:30 - 3:45 pm
CET	Central Europe: 9:30 pm - 12:45 am
BRT	Brazil: 5:30 - 8:45 pm
KST	Seoul: 5:30 - 8:45 am
SGT	Singapore: 4:30 - 7:45 am

Scanning Transmission Ion Micrsocopy in the Helium Ion Microscope for nanoparticle research

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Studying the interaction of nanoparticles with biological tissue at the nanometer scale in a form as close as possible to the native wet environment is a key challenge in many nano-toxicological questions. The nanomaterial risk identification involves their physico-chemical characterization currently employing a variety of techniques and separate instruments. This makes the characterization an expensive and time-consuming process.

Here, we are developing a new integrated instrument for the ion beam based characterization of nanoparticles. The aim is to improve the efficiency of the nanomaterial characterization workflow by integrating several ion beam based techniques in one single instrument. The npSCOPE instrument is based on the well known Helium Ion Microscope technology [1] combined with cryo-capabilities and detectors for secondary electron imaging, a secondary ion mass spectrometer (SIMS) for chemical analysis [2] and a dedicated scanning transmission ion microscopy (STIM) detector allowing the detection of transmitted ions/atoms to obtain in-situ structural/3D visualization data [3].

After an introduction to the npSCOPE instrument and its capabilities we will introduce the new STIM detector and present first results obtained with it and other STIM detectors on single and polycrystalline samples as well biological specimen. The latter will focus on different kinds of nanoparticle samples relevant in the field of nano-toxicology. Finally I will present the first STIM blocking patterns recorded in the HIM.

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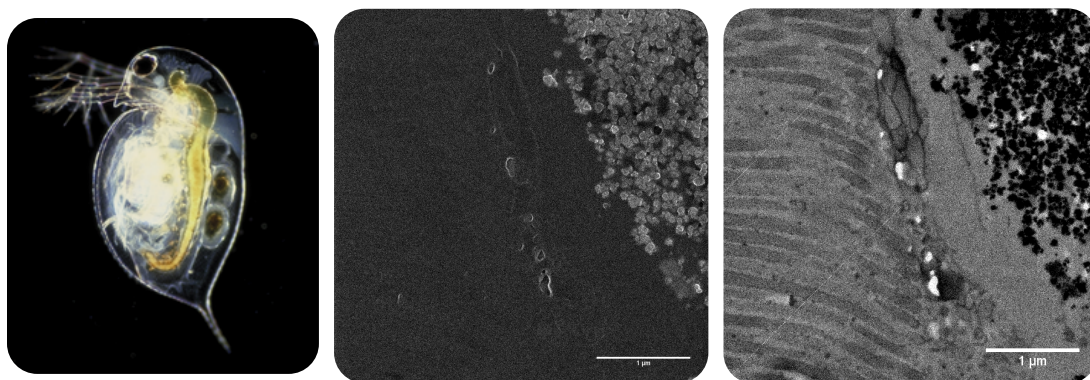
Figure 1: STIM analysis of daphnia (left) gut sections after TiO$_2$ exposure. HIM secondary electron image. STIM bright field image of the same area with remarkable clear visualization of the gut wall.
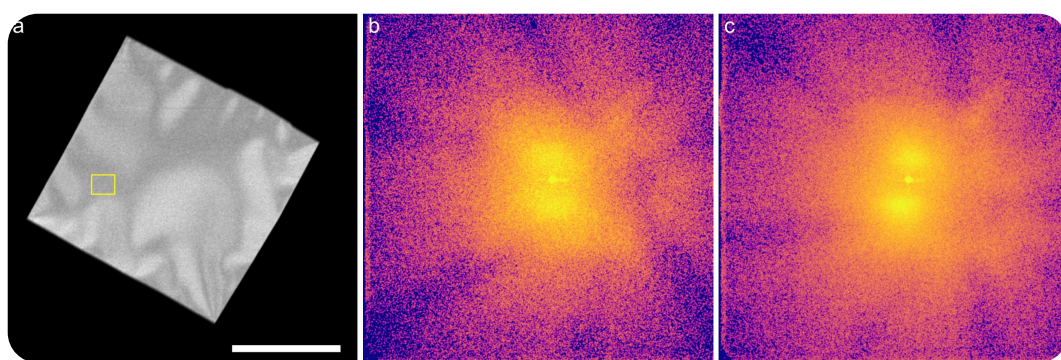

Figure 2: Single crystalline Si membrane (left, bright field image) and STIM blocking patterns obtained from the marked area (middle) and after rotation of the sample (right).

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Deciphering the behavior of chemisorbed hydrogen on surfaces using multi-angle scattering and recoil maps

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Hydrogen-surface interactions are crucial for many applications, ranging from catalysis, plasma effects on materials, and hydrogen energy infrastructure / storage. Under appropriate conditions, low energy ion scattering (LEIS) and direct recoil spectrometry (DRS) can provide unique insight into the both the concentration of chemisorbed hydrogen, as well as its binding geometry. This area of study generally has been elusive for many other surface science techniques, where the presence of hydrogen only weakly affects the measurement. Our research group has been using multi-angle ion scattering and recoil maps for LEIS and DRS analysis of hydrogen-covered surfaces [1,2]. This involves acquiring ion energy spectra over a wide range of polar and azimuthal angles and then compiling this information into a 2-D map of scattered and recoiled particle fluxes. This approach has the advantage of providing much more comprehensive information than is possible through single azimuthal or polar scans and is particularly helpful for deciphering the LEIS/DRS data and fitting it to different models. The mapping techniques appear to be equally suited for general analysis of forward scattering and impact-collision ion scattering spectrometry (ICISS) configurations [3].

Recently our work has focused on extending this mapping approach to recoiled hydrogen. Because the chemisorbed hydrogen often resides in binding sites well above the substrate surface, we typically use a low energy ion beam (< 3 keV) at grazing incidence to probe the surface, and collect recoiled hydrogen in the forward direction (at scattering angles $< 30°$ relative to the incident ion trajectory.) Depending on the configuration of the hydrogen relative to the first layer surface atoms, the recoiled hydrogen flux is enhanced along different crystallographic orientations via DRS. Blocking of the outgoing recoiled hydrogen by other surface atoms (including adsorbed species) provides further structural information. This combination of shadowing and blocking provides sensitivity not only to the binding site of the adsorbed hydrogen, but also its height above the surface. This report will summarize our recent work to apply these techniques to different model systems (including W+H, Be+H, and Al+H), as well as other more complex materials used for hydrogen storage.

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Near surface probe of electric fields by ion induced charge from keV ions for quantum computer devices

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Construction of large-scale quantum computer devices [1] that employ near-surface donor atoms in isotopically pure silicon devices can be done with keV ion implantation. We have developed the method of deterministic ion implantation [2] to position single donor atoms in arrays at the technologically useful depth of ~20 nm so that surface control gates can be used to program and read-out the donor electron and nuclear spins that serve as quantum bits (qubits). The method makes use of on-chip electrodes to record the pulse of ~1000 e-h pairs [3] induced by a single ion impact from the electronic stopping fraction of the ion-solid interaction [4]. By mapping the charge collection efficiency recorded by novel low-noise charge sensitive electronics connected to the on-chip electrodes, together with either a scanned focused beam (FIB) or collimated beam (nanostencil) of keV ions, the technologically useful surface E-fields can be mapped with high precision.
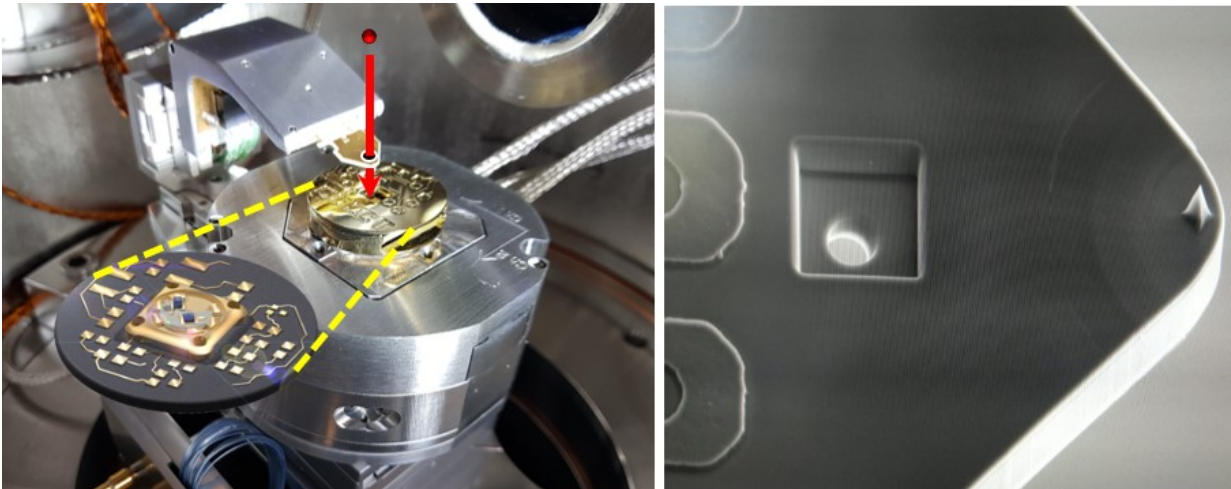
(left) AFM system in target chamber of ion implanter with charge-sensitive electronics and (right) AFM cantilever with the ion beam nanostencil 10 μm in diameter. Stencils as small as 20 nm can be used.

We have discovered, remarkably, that the pulse height defect associated with the stopping of heavy donor atom qubits is much less than predicted from measurements made by continuous beams, showing the method can be applied to exploit the promising attributes of high nuclear

spin donors ^{123}Sb (I=7/2) and ^{209}Bi (I=9/2) building on the foundations already established for ^{31}P (I=1/2) [5]. We also find that a ^{28}Si (I=0) ion beam can be used to deplete the non-zero nuclear spin ^{29}Si (I=1/2) isotope in thin surface layers on ^{n}Si [6] to provide a spin-depleted matrix needed for long-lived qubits in the solid state.
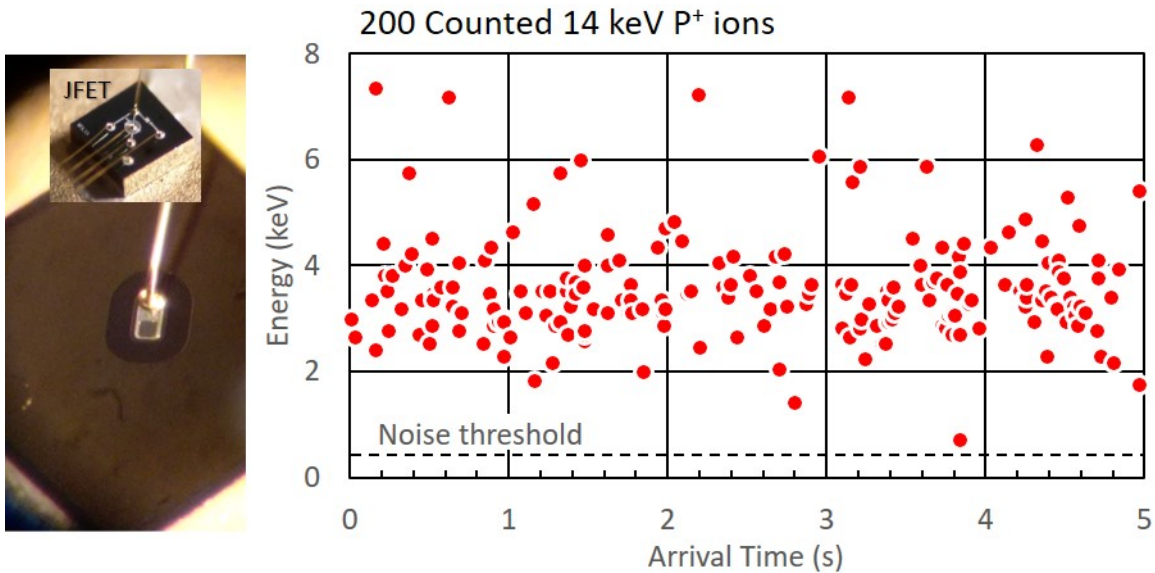
(left) Substrate with on-chip surface electrodes and JFET charge sensor and (right) single ion implantation pulse height signals for 200 ions. The number of electron-hole pairs is given as an equivalent energy using a conversion factor for silicon of 3.6 eV/e-h pair. The noise threshold is 0.5 keV for this system at a substrate temperature of $-10°C$. The vertical scatter arises from the statistics of the ion stopping process.

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Surface Analysis of Transition Metal Sulfides and the Detection of Minority Species

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Transition metal sulfides play a vital role in a number of geological, environmental and technological areas including ore formation, weathering of minerals, minerals processing, biomineralization, corrosion and catalysis. Understanding the physical and chemical properties of their surfaces, and with the environment and microbes is crucial to mining, the environment and nanotechnology. The study of mineral surfaces using advanced spectroscopic techniques is challenging due to the non-perfect nature of minerals surfaces. Surface analysis techniques including X-ray photoelectron spectroscopy (XPS), Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-ray absorption Spectroscopy (XAS) have been used to elucidate the surface properties of minerals and their use is now widely accepted by industry. However, there is still questions regarding the accurate interpretation of photoemission and X-ray absorption spectroscopy. Increased interest in these materials has driven developments in sample preparation and the use of in and ex situ nanospectroscopic techniques. Synchrotron nanospectroscopic techniques including Photoemission electron Microscopy (PEEM) and Scanning Transmission X-ray Microscopy (STXM) have been used for the study of heterogeneous surfaces, providing quantitative chemical mapping, the detection of minority species and analysis in liquids.

Surface Debye temperature measured by LEED and its relationship with defect concentration in epitaxial films

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The study of defects is of paramount importance in thin-film device fabrication. Novel experimental methods are needed to identify and quantify defects during film growth. The Debye temperature (θ_D) of a solid is a representation of the stiffness [1] and so is sensitive to defect concentrations. The θ_D tends to decrease in the vicinity of the surface such that the endpoint value found for the top atomic layer is known as the surface θ_D.

In this collaborative project, we have used a suite of surface characterization techniques to characterize and quantify defects on the surface and in the near-surface region in epi-films compared to single crystals. We applied Rutherford Backscattering Spectroscopy (RBS, random and channeling modes) [2], Positron Annihilation Spectroscopy (PAS) [3], and Low Energy Electron Diffraction (LEED) [4] to study defect density and distribution and calculate surface DT for Si epitaxially grown on sapphire thin films. Figure 1 shows Rutherford Backscattering Spectroscopy (RBS) in a channeling alignment to measure defect distribution as a function of depth, which can be correlated with PAS measurements, giving information about defect densities.

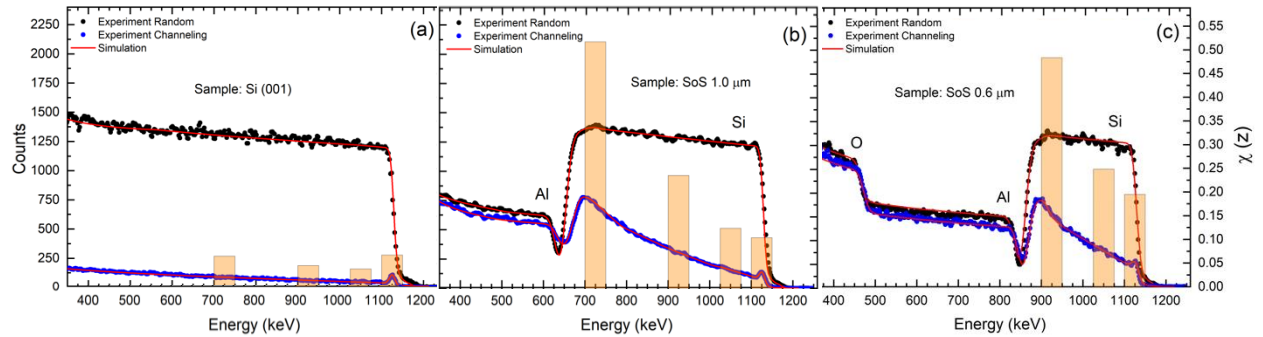**Figure 1:** Random and channeling spectra along with the parameter χ (which is defined as the ratio between the aligned yield by the random yield) on the right scale, of samples (a) Si (001), (b) SoS 1.0 μm, and (c) SoS 0.6 μm.

These results were compared with surface Debye temperatures θ_D calculated from LEED (figure 2) patterns which showed that the larger the concentration of defects in the epitaxial layer, the

lower is the surface θ_D. For example, the surface Debye temperature of bulk Si (001), 1µm Si on sapphire, and 0.6µm Si on sapphire were 333K, 299K, and 260K, respectively. Overall, we found good agreement between estimates of surface θ_D from LEED, defect densities estimate from RBS, and PAS results.
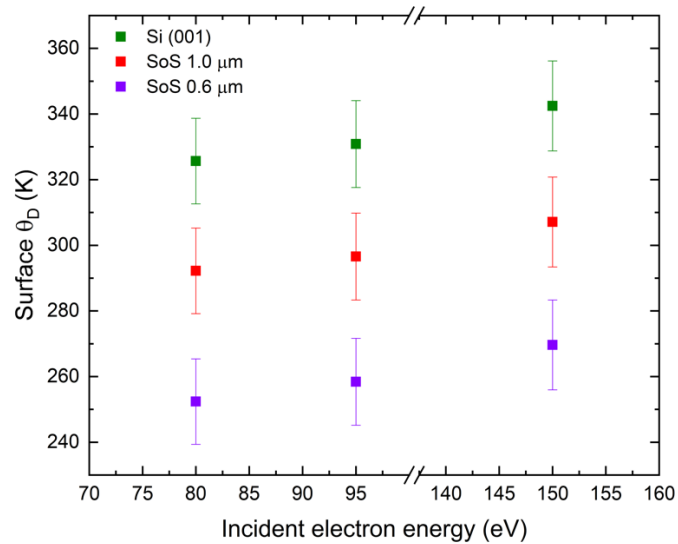
Figure 2: Calculated surface Debye temperature from LEED measurements at 80 eV, 95 eV and 150 eV incident electron energy.

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A study on the aging of embedded Ag nanoparticles by medium-energy ion scattering

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Nanoparticles (NPs) are widely discussed in the literature due to their intrinsic properties, largely attributed to the high area/volume ratio present by these structures. These properties allow for innovative applications in different areas. Silver NPs, especially, exhibit a pronounced localized surface plasmon resonance and strongly modulate local electric field, allowing for applications from biosensors to solar cells enhancing [1 - 4]. However, Ag is an extremely reactive metal and the oxidation processes can interfere with the stability and degradation of the material, causing microstructural changes over time [5]. In this sense, the medium-energy ion scattering (MEIS) can be an indicated technique for characterization. MEIS yields quantitative with deep subnanometric depth resolution data about a sample and can identify shapes, size distributions, composition and stoichiometry [6].

In this work, distributions of silver nano-objects (plate-like NPs – see ref. [7] for a detailed transmission microscopy study) were produced by magnetron sputtering over thin films of 100 nm thick Si_3N_4/Si and covered by a layer of Si_3N_4 to avoid the rapid oxidation (nominal parameters: 3 nm for Ag, 10 nm for Si_3N_4, pure targets, room temperature). This sample was cleaved on slices of about 1 x 0.5 cm². One slice was placed in the MEIS sample holder, and the remaining ones were stored at room temperature and ambient atmosphere in dust-protected cases for about 4300 h. The samples were characterized with the MEIS technique with an He^+ beam, 200 keV, normal incidence, in a 500 kV HVEE ion implanter (Ion Implanter Laboratory – IF/UFRGS).

The results from MEIS measurements, after being analyzed by the PowerMEIS 3 simulation program [6, 8], indicated that the microstructural configuration of the post-deposited sample are spherical NPs with a mean diameter of 6.5 nm, covering about 70% of the layer area. This layer of NPs is buried on approximately 4.8 nm of Si_3N_4. The aged samples presented significant changes. A second Ag peak near the surface indicates a diffusive behavior of the Ag content, although the original peak preserves the typical characteristics of nanoparticles signal. The comparative analysis of the Ag peak areas of the post-deposited and aged samples indicates that the metallic content is conserved, there was only a morphological or chemical (oxidation) change in the sample.

The MEIS results demonstrated the action of time on the sample, which can be crucial for potential applications. This is an ongoing study, which will require analysis in different aging periods, including annealing and inert atmospheres, to compare with the room temperature and

ambient atmosphere case.

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A MEIS study of the thermal behaviour of Cu and Au nanoparticles grown on CeO₂ thin films

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Bimetallic catalysts often outperform monometallic ones in terms of activity and/or selectivity. Generally, their behaviour is strongly dependent not only on the molar ratio of the two elements but also on nanoparticle size and the interaction with the support material.

Medium energy ion scattering (MEIS) has been used to investigate the morphology and chemical composition of Cu and Au nanoparticles deposited onto ultrathin CeO₂ films on Si(111) as a function of annealing temperature, both for samples that were maintained in an ultrahigh vacuum environment and exposed to air. The Cu/Au/CeO₂/Si(111) system was chosen as a model in order to provide an insight into how the catalytic properties of Cu/Au/CeO₂ depend on the presence of discrete Cu and Au particles versus fully intermixed Cu/Au systems.

To extract the depth dependent compositional and structural information of the bimetallic Cu/Au nanoparticles from the experimental MEIS spectra, the PowerMEIS3 scattering simulation software was used. It considers the sample under investigation in terms of voxels organised in a matrix format which can represent any complex structure containing a number of elements. Different type of matrices considered include discrete, alloy and core-shell spherical nanoparticles particles as well as thin films.

Analysis showed that when Cu is deposited after Au deposition on CeO₂/Si(111) at room temperature, the MEIS data is best fitted by assuming the formation of discrete hemispherical particles of Au (of radius 2 nm) and Cu (of radius 1.5 nm) which are stable up to 450K and after annealing to 525K transform into hemispherical alloyed CuAu particles of radius 2nm. After reversing the deposition order, best fits were obtained for a hemispherical core shell structure (of typically 2.7 nm) at room temperature, which after annealing to 375k had an Au rich core and a Cu shell and upon annealing to higher temperatures of up the 600K, morphed into homogeneously alloyed hemispherical particles of radii 3.4nm. Exposure to air of this sample led to Cu segregation to the surface.

Depth Profiling of Metal-Oxide Layers Over Metal Clusters Using High Resolution Electron Microscopy

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Metal clusters deposited onto semi-conducting metal oxide surfaces have been shown to act as co-catalysts for photocatalytic reactions such as water-splitting. [1] It is known that the electronic structure of metal clusters depends on the number of atoms forming the cluster, thus it is important to maintain the specific size of the clusters. Furthermore, a key component of metal cluster based photocatalysts are overlayers, which provide a dual role; (i) to protect the metal clusters from agglomeration and (ii) to reduce the recombination reaction of H_2 and O_2 back into water.

In order to maintain the cluster functionality, it is critically important to control the depth of the overlayer; not too thick but not too thin either. In order to quantify the layer thickness, we have applied high resolution electron microscopy (HAADF-STEM) coupled with elemental mapping (EDX). This presentation will highlight several examples, including our recent work on Cr_2O_3 overlayers on various gold clusters such as Au_{25} and Au_9. [2,3]
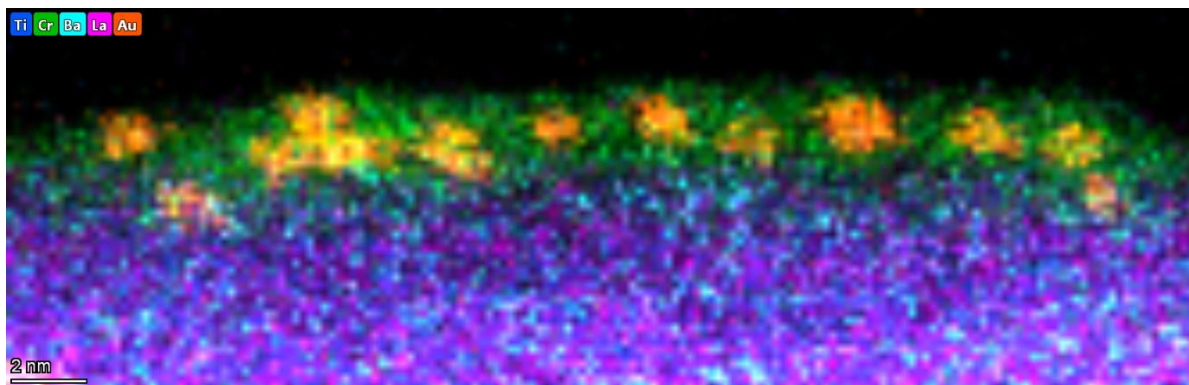
TEM/EDX image of Au_{25} on $BaLa_4Ti_4O_{15}$ with a Cr_2O_3 layer less than 1 nm thick. [2]

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Ion Specificity within Adsorption/Desorption of Inorganic Ions at Liquid Surfaces

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Adsorption or desorption of inorganic ions at solvent surfaces has relevance in complex biological process, physiochemical systems and as a model system for atmospheric chemistry studies i.e., ionic presence in aerosol droplets influences Cl_2 and Br_2 uptakes. Since the recent developments in surface-sensitive experimental techniques, many investigations have shown that adsorption or desorption of ions in aqueous solution follows specific ion series (direct or indirect Hofmeister series) and this behavior is believed to be originated from ion-solvent interaction[1]. The recent discovery of specific ion effect in non-aqueous solutions suggests that water is not a special liquid in the matter of specific ion effects [2]. But consensus for adsorption or desorption of inorganic ions in liquids other than water is limited hence a clear origination of specific ion effect is not understood mainly because ionic interactions nearby liquid surfaces are very small and require high-resolution depth profiling techniques. Therefore, to further unravel the origination of specific ion effect at liquid surfaces, we have employed neutral impact collision ion scattering spectroscopy (NICISS) [3] to obtain concentration depth profiles of various ions in just formamide solutions and formamide solutions with enzymatic process mimicking thermoresponsive free-polymer structures (Poly-propylene glycol).

Various inorganic salts dissolved in formamide and with free-polymer structure are investigated to compare the depth profile onsets of ions. By this comparison we are able to depict the manifestation of ion specificity at formamide surfaces (a non-aqueous solvent) and their salting in/salting out behavior in presence of free-polymer structures[4].

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Validating a simple procedure for thickness evaluation of thin films by medium-energy scattering of hydrogen and dihydrogen cations

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Characterization of solid layers at nanometer scale is a basic requisite in modern materials science, where a variety of experimental techniques are available [1]. Among them, Medium-Energy Ion Scattering (MEIS) has evolved to a versatile, near-surface characterization technique, suitable for depth profiling of nanosctructured materials. However, interpretation of spectra recorded for elemental primary ions, as hydrogen or helium cations, scattered by targets composed of thin solid layers relies jointly on the accuracy of energy loss for the ion-target combination and on the precise knowledge of the target density at such small dimensions. Energy-loss accuracy is critical to convert the detected energy of the scattered ion into the appropriate depth scale. An example of difficulty is the case of platinum films [2], where reappraisals of electronic energy-loss cross sections indicate that current estimations are generally larger than older ones. Another example is the international Round-Robin Test (RRT) for hafnia thin film determination conducted in collaboration with several institutions [3]. The discrepancy in the results was greatly diminished by utilization of fitted-to-data energy-loss cross section. Besides the difficulties with the energy-loss accuracy, in most methodologies based on ion-target interactions, quantitative information is obtained only as the number of scattering centers per unit area. In order to estimate the thickness of a film, one must assume a given value for its density. The breakup of molecular ions, as dihydrogen cations, in matter operates differently. It provides the means to unfold the number of scattering centers per unit area into the product between thickness and density of a thin film [4]. However, additional physical ingredients have to be taken into account and solved numerically for each combination of primary ion and target material [5]. Alternatively, the broadening of scattering-yield edges for concomitant measurements with elemental and molecular ion beams at the same specific energy can furnish information concerning the distance traveled by the ion independently of the energy-loss cross section. Here we propose a simple fitting-of-a-polynomial procedure of scattering spectra for the evaluation of layer thicknesses based on first-order approximation of the repulsive force experienced by the molecule constituents while penetrating the target. Fitting optimization and the necessity of correction factors are evaluated within the investigation of a toy model, i.e. data generated numerically. The procedure is then applied to the thickness determination of a platinum film supported on silicon. Results are in good agreement with measurements performed independently by transmission electron microscopy. Perspectives on the procedure application to more elaborate cases are given.

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High-Resolution Depth Profiling of Diamond-Like Carbon and Tungsten Sandwich Nanostructures Using a Scanning Auger Spectromicroscopy

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The choice of Plasma-facing material (PFMs) for reactor design is critical for the successful utilization of fusion as a power source. Plasma-surface interactions include physical sputtering, chemical erosion, thermal sublimation, re-deposition of eroded material and implantation of plasma species. These interactions can have a negative impact on plasma performance and material lifetime, and hence play an important role in determining the viability of fusion as power source [1]. The current leading PFM, tungsten, shows some degradation under high heat and particle loads, hence continued research into new PFMs is vital. The present study considered a sandwich structure of coatings between Diamond-Like Carbon (DLC) and tungsten as one potential PFM configuration. The tailorable properties of DLC, and multilayered coatings means that this configuration may offer additional benefits as PFM. Initial testing used gold coated silicon wafers as the substate, with DLC as the top and bottom layers and tungsten as the middle layer. Nanometre scale DLC layers were deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD).

High resolution depth profiling is a useful tool for validating the structure of various films and coating configurations. In this study, high resolution depth profiling was performed using a PHI710 Scanning Auger Nanoprobe for the purpose of confirming the coating configuration and estimating the thickness of each layer. Using a floating column ion gun, the sample was sputtered with argon ions accelerated at 500 V and anaylsed with Auger Electron Spectroscopy (AES) between sputtering intervals, 12 – 30 seconds. A total sputter time of 20 minutes was required to observe the 3 layered structure, with the key elements of carbon, tungsten, gold and oxygen being monitored. Determining the thickness of each layer requires the careful consideration of each material, and the relative sputter factor with respect to the calibration material, silicon dioxide. This initial study of the sandwich structure showed its successful deposition and provides some indication of layer thickness. Further calibration of the depth profiling can be comparatively performed with additional techniques, such as atomic force microscopy (AFM) to verify the accuracy of the calculated depth.

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<u>Day 2 10th of November 2021</u>

Times for the meeting in various time zones

Time zone	Time for meeting
ACDT	Adelaide: 7:00 – 10:15 am
AEDT	Australian East cost: 7:30 – 10:45 am
EST	US East coast: 3:30 - 6:45 pm
PST	US West coast: 12:30 - 3:45 pm
CET	Central Europe: 9:30 pm - 12:45 am
BRT	Brazil: 5:30 - 8:45 pm
KST	Seoul: 5:30 - 8:45 am
SGT	Singapore: 4:30 - 7:45 am

Progress in Understanding Low-Velocity Electronic Stopping

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At the latest HRDP workshop in Uppsala we reported that extraction of electronic stopping cross sections from transmission experiments in the velocity range below the Bragg peak requires knowledge of impact-parameter dependent energy loss [1]. Distinct differences were pointed out [2], in particular for heavy ions in gas targets, between reported stopping cross sections and revised values based on impact-parameter-dependent energy losses extracted from the PASS stopping code [3–5].

Since then we turned our efforts toward stopping of protons, stimulated by a wellknown discrepancy between experimental data found in reflection and transmission experiments, as exemplified for protons in silver in refs. [6] and [7], respectively.

As a first step we carried out Monte Carlo simulations of reflected-ion spectra [8], following the procedure applied in studies like ref. [6]. Reflected-ion spectra found from characterizing slowing-down by PASS stopping cross sections reproduced results found in previous simulations [6], whereas significant differences were found when impact-parameter-dependent energy losses were applied.

As a next step we explored the significance of coupling between nuclear and electronic processes. Standard textbook knowledge treats electronic and nuclear stopping as mutually independent. While this is well established at moderate and high beam energies, problems occur in the velocity range below the Bragg peak, which become serious in the energy range below 10 keV/u.

While there must be coupling terms of higher order between electronic and nuclear *stopping* [9], a more serious effect is the influence of *nuclear scattering* on *electronic stopping*.

In standard theory, the elementary excitation event is described as the interaction of an ion in uniform motion passing a nucleus at rest, while all dynamics affect the electrons of the target and/or projectile. Deviations from this picture become exceedingly important with decreasing beam energy, where the change in relative velocity during the interaction cannot be neglected. A simple estimate of this effect can be obtained by replacing the impact parameter by the distance of closest approach. We denote the resulting change in predicted stopping cross section as the RM correction.

Although this simple model is inherent in the Firsov energy loss formula [10], it has consistently been ignored in numerous applications of Firsov's formula in stopping theory. We emphasize that this correction is important in theoretical predictions of both transmission and reflection measurements, and it is missing in most current descriptions of electronic stopping.

We have explored the RM correction applying the PASS code. Here follows a list of results:

- RM-corrected PASS stopping cross sections agree well with data reported from reflection measurements for protons in several materials such as Ni, Cu, Ag, Au [11].

- Monte Carlo simulations including the RM correction lead to good agreement with measured reflection spectra [11].

- RM-corrected stopping cross sections show a conductor-insulator difference, since electronic energy loss in a free electron gas is not coupled directly to an impact parameter [11].

- The RM correction suggests the existence of an isotope effect in electronic stopping at low velocity [11]. Positive experimental evidence has been found [12], but a systematic search would be desirable.

- For transmission experiments, the reduction of the extracted stopping cross section due to the finite width of the detected beam [1] competes with the RM correction. The relative significance of the two corrections is found to depend on the projectile as well as the target.

- Ion-target reciprocity [13] cannot be expected to remain valid in the presence of a sizable RM correction because of different symmetry properties of electronic stopping and nuclear scattering.

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Elucidating the depth profiling of ions implanted into 2D and 3D samples by electron backscattering

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The concentration and depth distribution of heavy ions implanted in low-Z targets can be researched by studying the energy spectra of electrons scattered from the surface. For high-energy incoming electrons, the elastic peak splits up in different components as the recoil losses depends on the mass of the scattering atom. This technique is often referred to electron Rutherford backscattering spectrometry (ERBS). Besides the elastic peak, the measurement can also see the consequences of electronic stopping. Then the technique is usually referred to as reflection electron energy loss spectroscopy (REELS). In this work, Au ions were implanted with 30 and 300 keV in SiO_2 and 30, 100 and 300 keV in Al and analyzed by ERBS/REELS [1,2]. The implanted Au fluence was checked with (ion) Rutherford backscattering using 2 MeV He^+ ions. The range and straggling of the Au distribution after implantation were compared with simulations through SRIM/TRIM and TriDyn codes. Large changes in the REELS spectra are observed after Au implantation, but the nature of the change indicates that they are not due to modification of the dielectric function of the implanted layer, but should be interpreted as changes in the partial intensities that make up the spectrum. Two models are used to describe the results quantitatively. One method assumes v-shaped trajectories (i.e. only a single elastic deflection) and the REELS spectrum can then be calculated in a closed form. The other method is Monte-Carlo based simulation performed with PowerMEIS 3 (available online at http://tars.if.ufrgs.br/pm3) which allows for multiple elastic deflections. Both methods describe the experimental spectra quite well. It was found that the depth resolution of the technique is about 20% of the electron inelastic mean free path. To extend the depth profiling analysis to 3D samples, a FinFET like structure was studied [3,4]. PowerMEIS 3 was used to simulate multiple elastic and inelastic interactions of the electrons with these 3D structures and was indeed able to reproduce these experimental results, including the shadowing effects from the fins. These shadowing effects carry information on the 3D structure as they induce changes in the elastic and inelastic regions of the spectrum. It was shown that the energy dependence of the IMFP is important for the understanding of ERBS/REELS spectra variations as well as the dimensions of the 3D structure.

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Versatile applications of a 3D transmission setup using keV ion energies

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Recent developments of existing instrumentation for Medium Energy Ion Scattering [1] broaden the versatility of the system. In this contribution we present a number of applications using 3D transmission experiments, i.e. simultaneous measurements of angular distributions and flight time of particles exiting thin self-supporting foil targets:

- Analysis of primary ions exiting the thin self-supporting foils allows for mapping of intensity and different energy loss moments [2].

- By employing heavier projectiles, recoils can be detected with high sensitivity for light elements and surface structure.

The presented work furthermore illustrates how a number of ion-beam based techniques benefits from the versatility of the resulting instrument: apart from the relevance of fundamental data for quantification, our results provide a basis for interpretation of prospective transmission microscopy studies. They can also be used to interpret implantation profiles in single-crystalline

Fig.1: 3D surface map of the mean energy loss for 50 keV He transmitted through a 200 nm single-crystalline silicon foil.

materials. Recoil detection in the presented approach gives the possibility to perform high resolution dept profiling of surface and bulk composition for sensitive systems with extremely low incident doses. Finally, the ongoing construction of a preparation chamber will allow for the possibility of complex in-situ synthesis, as well as for an accurate study of near-surface materials analysis under a wide range of conditions.

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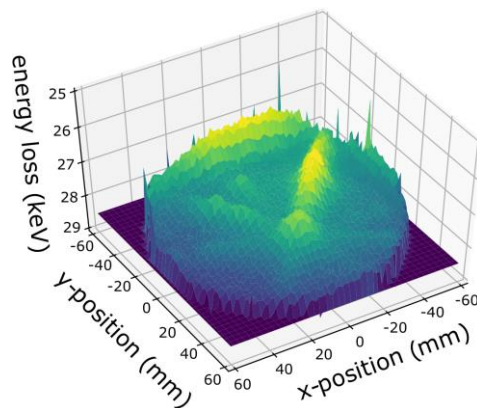
RBS HEDGEHOG – A New 680 msr ultra-high sensitivity RBS Setup

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RBS as one of the most widely used IBA methods requires a rather high beam fluence due to the small backscattering cross-section. Although the lack of measurement statistics can be compensated by a longer measurement time, this can only be applied to macroscopic beam spots and is not possible for sensitive samples or in a micro beam setup. Higher beam currents on the other hand would lead to increased pile-up contribution and thus reduce sensitivity for low abundance trace elements.

Larger detectors are an easy means to increase the covered solid angle, however this is limited in terms of kinematic broadening and decreasing energy resolution due to increasing detector capacitance [1]. Multi-detector setups overcome this limitation and are attracting increasing interest in various laboratories. Geometric constraints, mechanical robustness, the cost of multiple MCA systems, as well as the difficulty of simultaneously analyzing data from the individual detectors make this a difficult but worthwhile endeavor.

In this contribution, we report on our recently commissioned setup - namely, the "RBS hedgehog" located at the 3-MV tandem accelerator of the HZDR' Ion Beam Center. A theoretical design study of the influence of different detector configurations on the kinematic broadening for different energies and ion species is discussed prior to the introduction to the used in-house designed and fabricated PIPS detectors and MCA systems. The setup is equipped with 76 independent RBS detectors arranged in 5 concentric rings with backscattering angles of 165° to 105° covering a total solid angle of 680 msr - equivalent to 34% of the total backscatter angle. The 76 independent MCA systems can handle up to 8 Mega counts per second.

The setup enables ultra-high sensitivity measurements and multiple scattering angles partially resolve the ambiguity of RBS. We present initial experimental results for various samples.

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Photochromic Mechanism and Dual-Phase Formation in Oxygen-Containing Rare-Earth Hydride Thin Films

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The phase formation of a photochromic $Gd_{0.31}(H_{0.55}O_{0.45})_{0.69}$ thin film, grown by reactive magnetron sputtering, is critically evaluated [1]. The average chemical composition was determined by means of multiple ion beam-based techniques following an iterative self-consistent approach [2,3]. Transmission electron microscopy data revealed that oxygen is preferably incorporated into the underdense columnar grain boundaries, when the as-deposited gadolinium hydride film is exposed to ambient conditions. Structural characterization by X-ray diffraction in combination with spatially-resolved composition analysis at the nanometer scale by atom probe tomography (Figure 1) supports the dual-phase formation of Gd_2O_3 and GdH_2. Moreover, the dual-phase formation is accompanied by a significant compressive residual stress of 5.9 ± 1.5 GPa.
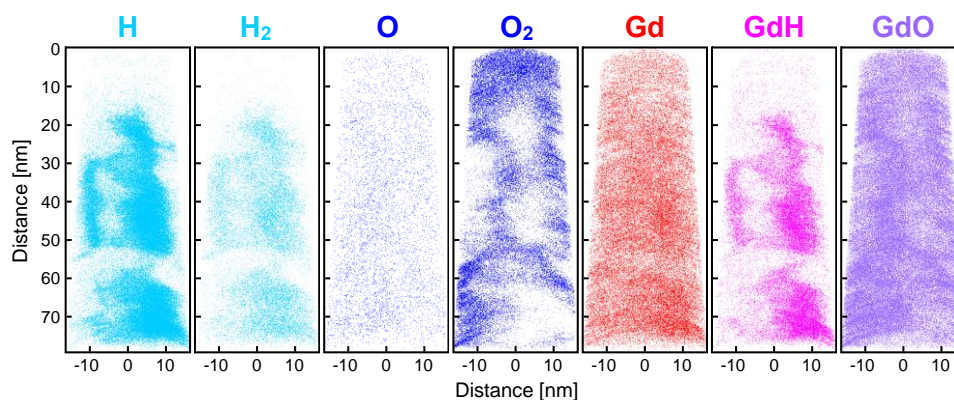

Figure 1. Atom probe tomography reconstructions of detected H, H_2, O, O_2, Gd, GdH and GdO species.

Since the formation of two phases as well as the significant compressive stress state are in agreement with prerequisites for photochromism in bulk yttrium hydride at high pressure, the photochromic mechanism can be understood as photon-induced hydrogen transfer between the two phases. As the microstructures of photochromic $Gd_{0.31}(H_{0.55}O_{0.45})_{0.69}$ and photochromic $Y_{0.33}(H_{0.42}O_{0.58})_{0.67}$ are very similar, it can be learned that the dual-phase formation is not limited to $Gd_{0.31}(H_{0.55}O_{0.45})_{0.69}$ and appears to be relevant for photochromic oxygen-containing rare-earth hydride thin films. It has to be emphasized that the dual-phase formation identified here clearly speaks against the notion of an oxyhydride nature of such photochromic thin films [4,5].

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What can neutron reflectometry reveal about polymer brushes?

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Polymer brush coatings are routinely grown on solid substrates to change surface behaviour to suit particular applications. Many physicochemical techniques can reveal fundamental characteristics of the brush such as thickness (ellipsometry), wettability (contact angle) or stiffness (quartz crystal microbalance with dissipation monitoring). However, it is only neutron reflectometry that can probe the internal brush nanostructure; the polymer depth profile. In many instances key brush properties, such as wettability, lubricity, adhesion and even anti-fouling, are related to this nanostructure. Thus neutron reflectometry is critical to increasing our understanding of brush solvation as a function of depth in different environments such as under pH variation (for polyelectrolyte brushes [1]) or temperature variation (for thermoresponsive brushes [2]).

Subtle conformational changes in thermoresponsive polymer brush depth profiles have been used as exemplar systems to reveal specific ion effects. These brushes undergo a phase transition from well to poorly solvated over a given temperature range, forming an interface with switchable physicochemical properties. Examples will be discussed from our recent studies of poly(*N*-isopropylacrylamide) and poly(oligo(ethylene glycol) methacrylate) brushes exposed to mixed electrolytes from across the Hofmeister series.[3,4] Finally, as natural environments and advanced technologies are often comprised of mixed electrolytes, understanding the interplay of different ions in various solvents is imperative for advancing our knowledge of polymer-salt interactions.[5,6]

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Characterization and properties of SiGeSn alloys fabricated by ion implantation

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Ion implantation is a powerful strategy for fabricating optimized SiGeSn ternaries. The technique allows seamless exploration of multiple compositions of the alloy for properties as new materials for optoelectronics. There is a research trend to optimize new Si photonics materials for the synergic integration of electronics and photonics, to provide a route for developing new infrared detector technologies for optoelectronics applications. We focus on photodetectors for Si photonics and try to mitigate the limitations of Si as a photon detector, by developing optimized $Si_xGe_{1-x-y}Sn_y$ photodetector materials for short infrared wavelength (SWIR) range operation.

A 4×4 matrix of $Si_xGe_{1-x-y}Sn_y$ alloy was fabricated by ion implantation to obtain different compositions of Si, Ge and Sn (Si, $x = 0.7 - 1.0$, Sn, $y = 0 - 0.08$) for operation at wavelengths of $1.2 - 1.5\mu m$. Tunable bandgap semiconductor materials were achieved by controlling the composition. Sn segregation and defects were minimized by annealing at 400°C, 600°C, or 800°C for 30 minutes in forming gas. The composition, depth profile, and effects of annealing were determined by Rutherford Backscattering Spectroscopy (RBS) analysis (with channeling), and data were analyzed to determine the energy gap and wavelength of operation of the samples. Spectroscopic Ellipsometry was used to study changes in optical properties in the 600 - 1200nm range due to alloying; SiGeSn alloy samples exhibit very different optical behavior from the Si reference sample, for instance the lowering of Si penetration depth due to alloying. No strong evidence of Sn segregation was observed from X-ray Photoelectron Spectroscopy (XPS) analysis which was used to study the chemical states of the alloy. RBS revealed more diffusion of Sn and Ge into the bulk at 600°C and 800°C than for the 'as is' and 400°C annealed samples, as well as crystallization of Ge and Si from 600°C anneal temperature was observed. This SiGeSn alloy growth by ion implantation provides an effective way to achieve monolithic integration on a Si wafer, and thus provides an attractive alternative for development of SWIR detectors in a broad wavelength range.

Nanoscale Structural Determination at Surfaces and Interfaces Using Neutron Reflectometry at ANSTO

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Neutron reflectometry is a surface sensitive technique used to probe the structure of surfaces and interfaces perpendicular to the lateral plane in the size range of 1 to 100 nm. The information obtained is a depth profile describing the thickness, composition, and roughness of the different distinct layers within a system. The unique properties of the neutron as a scattering particle offer some attractive advantages such as being able to probe buried interfaces, study samples within complex sample environments, or distinguish separate parts in a multi-component system using selective deuteration or other isotopic labelling. Neutron reflectometry has been used to investigate the structure at surfaces and interfaces for a variety of different applications including probing the location of novel antibiotics and other drugs bound within model membrane systems, the structure of organic solar cell devices from different processing conditions, magnetic structures from magnetic thin films, polymer brush responses to external stimuli, how pharmaceutical formulations interact with different surfaces, etc.

ANSTO has two neutron reflectometers that are available for use to the wider scientific community. There is Spatz which operates in a vertical sample geometry (horizontal scattering geometry) and is suitable for studying gas-solid interfaces and solid-liquid interfaces [1]. Platypus operates in a horizontal sample geometry so as well as being suitable for studying gas-solid and solid-liquid interfaces, the instrument is also suitable for studying gas-liquid interfaces (free liquid surfaces) [2]. Platypus also has a complete polarisation analysis capability for magnetic thin films [3]. Both reflectometers operate using the time-of-flight principle where the neutron beam is pulsed using a pair of spinning disc choppers and the neutron wavelength of the reflected neutrons is determined by the time it takes to travel from the disc choppers to the detector. This makes both instruments ideally suited for kinetic measurements.

This presentation will provide an overview of neutron reflectometry and its capabilities including some examples and applications taken from the reflectometers at ANSTO.

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Recent Activities of MEIS R&D in Korea

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We briefly report recent activities on MEIS research and development in Korea.

First of all, we have been investigating bio and liquid interfaces with MEIS and SIMS using single layer graphene [1]. Electric double layer (EDL) of electrolytes were depth profiled with TOF-MEIS to investigate the change of EDL as a function of the electrolyte concentration and the ionic strength.

Secondly, MEIS has been successfully used to measure the thickness of gate oxides accurately with the traceability to the SI units by mutual calibration methods with TEM, XRR, and XPS. [2,3]

Thirdly, to meet the demand from semiconductor industries for accurate measurement of ultrathin gate oxide thickness for precise process control, we have been developing an *in-line* TOF-MEIS system for direct analysis of 300 mm wafers.

Discussions for continued development of MEIS methodology are expected.

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Investigation of damage build-up in semiconductors by 300keV Ar irradiation using Channeling-Rutherford backscattering spectrometry

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In the semiconductor industry, ion implantation is a well-known technical procedure that is frequently adopted to modify the characteristics of the host material, this method of material modification involves injecting significant numbers of foreign atoms into it, up to several atomic percent [1]. Another method is to use the energy of the ion beams to induce defects into the material, therefore influencing its characteristics. Aside from the defect engineering possibilities opened up by this method, knowing the impacts of such irradiation is critical for understanding damage build-up due to irradiation effects in radiation-rich settings, such as nuclear and space applications. To investigate the response of materials under controlled conditions using ion beams, dedicated experiments utilizing accelerator-based techniques are frequently chosen.

Rutherford backscattering (RBS) of light energetic ions in conjunction with channeling is extensively utilized for defect investigations in crystals for more than 5 decades [2,3]. Crystal defects raise the relative RBS minimum yield due to direct backscattering and dechanneling of ions interacting with displaced atoms. The conventional RBS-channeling (RBS-C) method permits the determination of the number of displaced atoms in crystalline solids as a function of depth. The computer code DICADA (Dechanneling In Crystals And Defect Analysis), developed by Gärtner, is a good tool for simulating the fractional disorder, from the dechanneling of ions due to the influence of defects, as a function of depth [4].

In the present experimental work, RBS-C has been used to investigate the kinetics of crystalline to amorphous phase transitions in semiconductor single-crystals of Si (111), Si (100), GaAs, and 4H-SiC implanted under identical conditions using 300 keV Ar ion radiation at room temperature. Ion irradiation parameters were carefully studied before the experiment utilizing Transport of ions in matter (TRIM) 2013 full-cascade simulations [5]. The ion fluences (ions/cm^2) were calculated and converted to the appropriate displacement per atom (dpa) values. 1 dpa indicates that all atoms have been moved at least once from their respective lattice positions. The RBS-C data was recorded using 2 MeV He$^+$ and depth distribution of damage was evaluated using simulation code DICADA [4]. RBS-C shows that irradiation leads to the formation of a damaged/amorphous layer, which extends towards both the crystal surface and larger depths with increasing fluence for all the semiconductors under consideration.

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Nanoscale Profiling of Organic Layers at Deeply Buried Liquid-Liquid Interfaces Using X-ray Reflectivity and Fluorescence

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Molecular ordering at interfaces between two liquids is relevant for a wide range of scientific and technological areas. X-ray reflectivity has been used to probe the electron density profile of molecular layers at flat interfaces between two immiscible liquids. X-ray fluorescence near total reflection (XFNTR) can supplement these measurements by identifying and quantifying metal ion species within the interfacial region. Here, we discuss some recent work in the application of these techniques to aqueous-organic liquid-liquid interfaces that model processes in the solvent extraction of rare earth metal ions.