10th International Workshop

on High-Resolution Depth profiling (HRDP-10)

6 - 10 November 2022

Flinders University, Adelaide

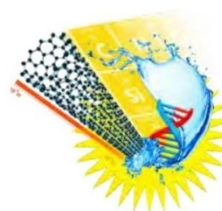## South Australia

Book of Abstracts

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History of the HRDP Workshop

International Workshop on High-Resolution Depth Profiling – 10
November 9 – 10, 2021, Online Meeting

9th International Workshop on High-Resolution Depth Profiling
June 25 – 29, 2018: Uppsala University, Uppsala, Sweden

8th International Workshop on High-Resolution Depth Profiling
August 7 – 11, 2016: London, Canada

8th International Workshop on High-Resolution Depth Profiling
August 7 – 11, 2016: London, Canada

7th International Workshop on High-Resolution Depth Profiling
July 8 – 11, 2013: Singapore

6th International Workshop on High-Resolution Depth Profiling
June 27 – 30, 2011: Paris, France

5th International Workshop on High-Resolution Depth Profiling
November 15 – 19, 2009: Kyoto, Japan

4th International Workshop on High-Resolution Depth Profiling
June 17 – 21, 2007: Radebeul, Germany

3rd International Workshop on High-Resolution Depth Profiling
May 23 – 26, 2005: Maine, United States

2nd International Workshop on Ion Beam Techniques for the Analysis of Composition and Structure with Atomic Layer Resolution
September 24 – 27, 2002: Kyongiu, Korea

Ion Beam Techniques for the Analysis of Composition and Structure with Atomic Layer Resolution
June 26 – 30, 2000: Oxfordshire, United Kingdom

Time schedule

Invited presentation (35 + 5 minutes)

Contributed presentation (15 + 5 minutes)

Sunday, 6 November 2022

16:00-18:00   Welcome Reception

Monday, 7 November 2022

9:00   Opening

9:05   R. Heller, F1

RUTHELDE – An Open-Source Simulation Algorithm for Automated Fitting and Uncertainty Determination of RBS and MEIS spectra

9:45   J.H. Song, F2

Appropriate Screening Function For 100 keV 4He$^+$ Calculated by Numerical Methods

10:05   E. Ntemou, F3

Electronic excitations by keV ions transmitted through single crystalline self-supporting foils

10:25   F.F. Selau, F4

Energy-loss straggling of proton and helium in elemental solids: the importance of the charge-exchange and bunching effects

10:45   Break

11:10   H. Trombini, F5

MEIS technique and PowerMEIS^3 code: a powerful combination for material analysis

11:50   A. Alharbi, F6

Determining the Stopping Power of Low Energy Ne$^+$ Projectiles in Organic components Using Neutral Impact Collision Ion Scattering Spectroscopy

12:10   W. J. Min, T7

Advances in TOF-MEIS for quantitative-ness, semi-automated analysis and inline wafer handling

12:30   Lunch

13:30   A. Le Brun, T8

Nanoscale Structural Characterisation of Biomimetic Bacterial Membranes Using Neutron Reflectometry

14:10   E. Wanless, T9

How does neutron reflectometry aid our understanding of polymer brush coatings?

14:50   Primetzhofer,T10

In-situ and in-operando profiling of light elements in energy materials using coincidence techniques

15:10   Break

15:40   R. Wilhelm, T11

Ultimate surface sensitivity of nano-engineering – slow highly charged ions as a toolbox

16:20	Panel 1
17:00	Closing

Tuesday, 8 November 2022

9:00	Committee meeting
10:00	M. Schlossman, T12
	X-ray studies of molecular and ion ordering at the liquid-liquid interface in solvent extraction
10:40	Break
11:10	E. Ntemou, T13
	Status of the Time of Flight Medium Energy Ion Scattering (ToFMEIS) system at Uppsala University – Acceleration of ultrashort pulsed beams of keV ions for materials science
11:30	R. Holeňák, T14
	Versatile applications of a 3D transmission setup using keV ion energies
11:50	H. Feltham, T15
	Quantifying radiolysis effects for in-situ Rutherford Backscattering Spectrometry (RBS)
12:10	G. Andersson, A16
	Electronic Structure of Titania Surfaces Modified by Metal Clusters
12:30	Lunch
13:30	Y. Yin, A17
	Alternative Elemental Profiling Methods for Corrosion Study of Ferrous (and Nickel) Aloys
14:10	M. Asiri, A18
	Ruthenium Clusters as Co-catalysts for Photocatalytic Water Splitting
14:30	A. Almutairi, A19
	Exploring the Properties and Stabilization of Nanoscale Overlayer/Metal cluster Architectures
14:50	S. Adhikari, A20
	Dye Anchoring Modes of Ru-based N719 dye investigated using FTIR and ARXPS.
15:10	Break
15:40	K. Komander, A21
	Investigating hydrogen storage materials with ^{15}N-ion beams
16:20	Panel 2

| 17:00 | Closing |

Wednesday, 9 November 2022

9:00	I. Koeper, A22
	In-depth analysis of tethered bilayer lipid membranes
9:40	G. Dartora, A23
	Thermal growth of SiO2 in SiC using CO_2
10:00	H. Lim, A24
	Utilization of graphene for analyzing liquid interfaces by SIMS and MEIS
10:20	N. Kishi, A25
	Operando measurement of ^7Li in all-solid-battery using $^7Li(p,\alpha)^4He$
10:40	Break
11:10	R. D. Kolasinski, A26
	Ion and neutral time-of-flight spectroscopy for deciphering hydrogensurface interactions
11:50	Anand Kumar, A27
	Ion specific effects within adsorption/desorption of inorganic ions at liquid surfaces
12:30	Lunch
13:30~22:00	Conference outing and conference dinner

Thursday, 10 November 2022

9:00	D. Moon, A28
	Ion Beam Analysis of Live Cancer Cells in Solution and Nanostructured Materials and Devices
9:40	L. Goncharova, A29
	Detection of hydrogen using medium energy ions
10:20	R. Holeňák, A30
	Development of advanced in-situ instrumentation for materials studies using medium-energy ion beams
10:40	Break
11:10	T. Ozawa, A31
	Development of Channeling 15N-NRA for structure analysis of hydrogen in nanofilms and subsurfaces
12:10	Panel 3
12:30	Conference closing
12:50	Lunch

Program High Resolution Depth Profiling 10 (HRDP-10)

6th – 10th of November 2022, Flinders University, Tonsley campus, Adelaide, Australia

TON_T1_G.32_Tonsley Theatre 2

Sunday 6 November 2022

Welcome reception 16:00 - 18:00

Monday 7 November 2022 — Chair: G. Andersson

Time	Type	Speaker	OL
9:00		Opening	
9:05 – 9:25	I	R. Heller, F1	OL
9:45	O	J.H. Song, F2	
10:05	O	E. Ntemou, F3	
10:25	O	F.F. Selau, F4	OL
10:45		Break	
11:10 – 11:30	I	H. Trombini, F5	OL
11:50	O	A. Alharbi, F6	
12:10	O	W. J. Min, T7	
12:30		Lunch	

Monday 7 November 2022 — Chair: G. Andersson

Time	Type	Speaker	OL
13:30 – 13:50	I	A. Le Brun, T8	
14:10 – 14:30	I	E. Wanless, T9	
14:50	O	Primetzhofer, T10	OL
15:10		Break	
15:40 – 16:00	I	R. Wilhelm, T11	OL
16:20 – 16:40		Panel 1	
17:00		Closing	

Tuesday 8 November 2022 — Chair: D. Moon

Time	Type	Speaker	OL
9:00 – 9:40		Committee meeting	
10:00 – 10:20	I	M. Schlossman, T12	OL
10:40		Break	
11:10	O	E. Ntemou, T13	
11:30	O	R. Holeňák, T14	
11:50	O	H. Feltham, T15	OL
12:10	O	G. Andersson, A16	
12:30		Lunch	

Tuesday 8 November 2022 — Chair: R. Kolasinski

Time	Type	Speaker	OL
13:30 – 13:50	I	Y. Yin, A17	
14:10	O	M. Asiri, A18	
14:30	O	A. Almutairi, A19	
14:50	O	S. Adhikari, A20	
15:10		Break	
15:40 – 16:00	I	K. Komander, A21	
16:20 – 16:40		Panel 2	
17:00		Closing	

Wednesday 9 November 2022 — Chair: Y. Yin

Time	Type	Speaker	OL
9:00 – 9:20	I	I. Koeper, A22	
9:40	O	G. Dartora, A23	OL
10:00	O	H. Lim, A24	
10:20	O	N. Kishi, A25	
10:40		Break	
11:10 – 11:30	I	R. D. Kolasinski, A26	
11:50 – 12:10	I	Anand Kumar, A27	
12:30		Lunch	
13:30		Conference outing and conference dinner	
~ 22:00			

Thursday 10 November 2022 — Chair:

Time	Type	Speaker	OL
9:00 – 9:20	I	D. Moon, A28	
9:40 – 10:00	I	L. Goncharova, A29	OL
10:20		R. Holeňák, A30	
10:40		Break	
11:10 – 11:30	I	T. Ozawa, A31	
11:50 – 12:10		Panel 3	
12:30		Conference closing	
12:50		Lunch	

I: Invited presentation (35 + 5 minutes)
O: Contributed presentation (15 + 5 minutes)
OL: online contribution

Themes

- Fundamentals (F)
- Techniques (T)
- Applications (A)

Times are for Adelaide, Australian Central Daylight Time (GMT+10:30)

Panel session 1: detecting hydrogen
Panel session 2: measurements at elevated pressure
Panel session 3: combining techniques

Zoom sessions:

Monday morning

https://us06web.zoom.us/j/82818919471?pwd=VmNnVWdJYm0zU213N1RGZEVzRXBOQT09

Meeting ID: 828 1891 9471

Passcode: HRDP-10

Monday afternoon

https://us06web.zoom.us/j/82002545052?pwd=ZDNhK0FEaHlLMmJGemdlRm5qSEJDZz09

Meeting ID: 820 0254 5052

Passcode: HRDP-10

Tuesday morning

https://us06web.zoom.us/j/83190730523?pwd=NjFjWjQ4a0p1aUphOFhTeXRETXU2QT09

Meeting ID: 831 9073 0523

Passcode: HRDP-10

Tuesday afternoon

https://us06web.zoom.us/j/89095223700?pwd=dTJRZEwrN1JUVHhJc25QMFZFWFdYdz09

Meeting ID: 890 9522 3700

Passcode: HRDP-10

Wednesday morning

https://us06web.zoom.us/j/89307713241?pwd=WWREQmc5clZBcmRRZjNEYU1vT2Nidz09

Meeting ID: 893 0771 3241

Passcode: HRDP-10

Thursday morning

https://us06web.zoom.us/j/89307713241?pwd=WWREQmc5clZBcmRRZjNEYU1vT2Nidz09

Meeting ID: 893 0771 3241

Passcode: HRDP-10

Locations

Marion hotel welcome reception From Tonsley.
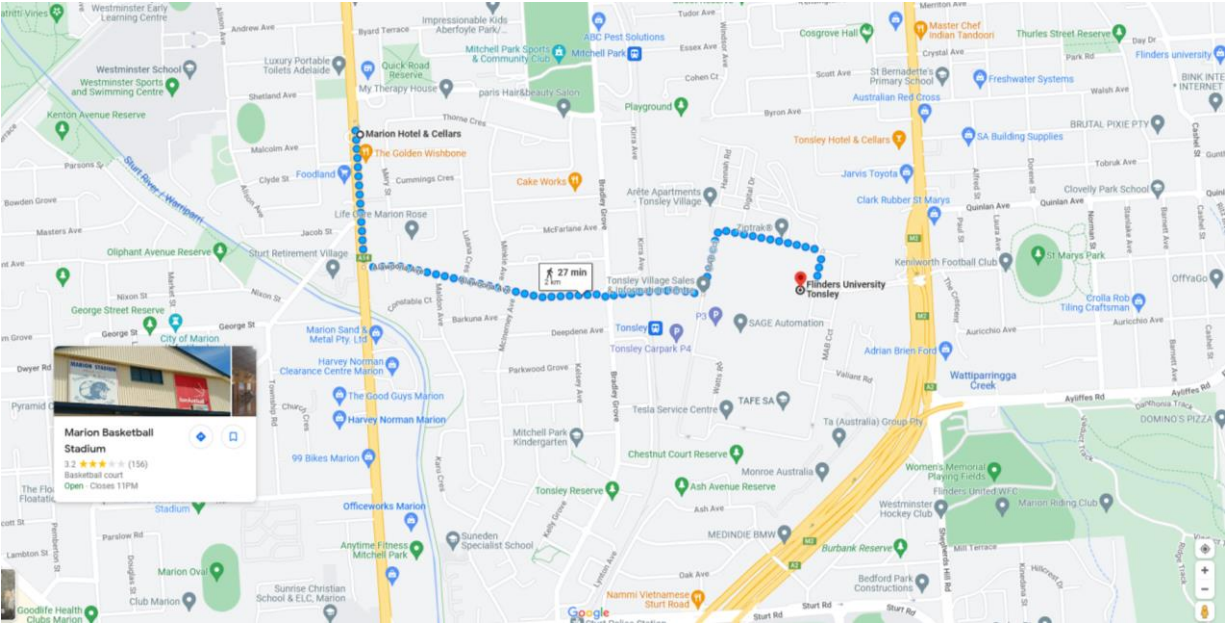
Map Tonsley, overview
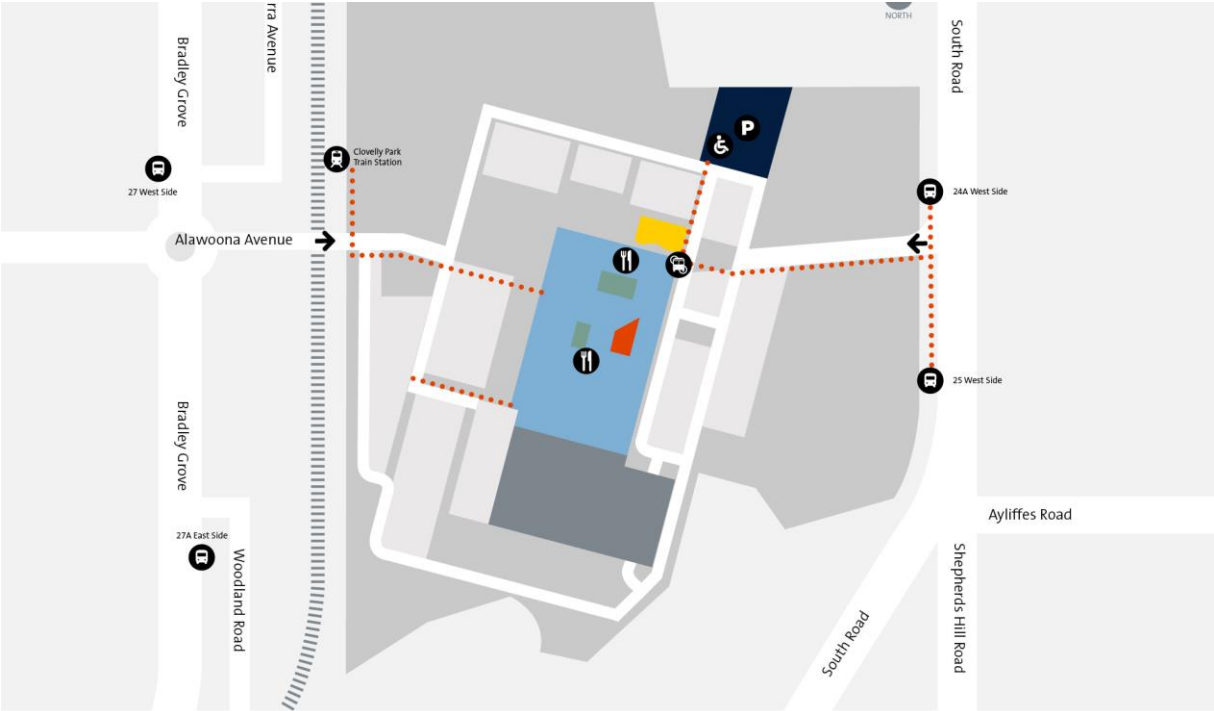
Map Tonsley, building

Ground floor with room for the HRDP-10: G.32_Tonsley Theatre 2

TONSLEY BUILDING PLAN (GROUND FLOOR)

Concierge
Lifts
Toilets
Male Toilets/Showers
Female Toilets/Showers
Parenting Room
Disabled Toilet / Shower
Prayer Rooms Male and Female
Secure Bike Storage
Tonsley Theatres
Meeting Rooms
Wayfinding Touchscreen
Display Screen
Kitchenette
Back of House Areas
Entry/Exit

Abstracts

RUTHELDE − An Open Source Simulation Algorithm for Automated Fitting and Uncertainty Determination of RBS and MEIS spectra

R. Heller[1], N. Klingner[1], N. Claessens[2], J. Meersschaut[2]

r.heller@hzdr.de (corresponding author)

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[2] *IMEC, Kapeldreef 75, 3001 Heverlee, Belgium*

Recently, we applied evolutionary optimization namely differential evolution to fit Rutherford backscattering data [1]. We derived and present an algorithm that is capable to find, with very high precision, the sample composition profile that best fits the experimental spectra in an autonomous manner. The code not only allows precise fitting of the target model but also to determine the uncertainty of the fit parameters. Thus it becomes feasible to predict the expected accuracy of an RBS / MEIS experiment for given experimental conditions (e.g. , scattering geometry, accumulated charge, etc.) prior to the actual measurement. Vice-versa the tool allows to determine what experimental conditions would be required in order to achieve a certain accuracy in the measurements.

In this presentation we will summarize the mechanisms of the code and show certain examples of target model and uncertainty calculations. Further, we present the corresponding open-source software package [2] and demonstrate its capabilities and limits.

References.
[1] R. Heller, N. Klingner, N. Claessens, C. Merckling, J. Meersschaut, Journal of Applied Physics, 2022, submitted
[2] https://github.com/DrReneHeller/Ruthelde

Appropriate Screening Function For 100 keV 4He+ Calculated By Numerical Methods

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HB Solution Corporation, Daejeon 305-500, Republic of Korea

Backscattering equipment has been developed on a wide ion energy range. One of these, TOF-MEIS achieves high resolution for thin film using a high stopping power/Ion Energy ratio meanwhile keep maintaining compact. However, the medium energy ion (100 keV $4He^+$) generates a more complicated phenomenon than RBS that used 1~10 MeV. One of them is regard to screening effect that as energy decrease, would be on the rise.

The screening function of potential energy for atoms could be described by the Thomas-Fermi model that modified to various empirical forms.[1,2] We suggest what is more appropriate Screening function form, have good agreement for backscattering analysis below at 100 keV $4He^+$ ion.

There are various potential energy expression forms consisting of screening effect, but generally, only a few types are used for analysis. For the convenience, Ion scattering processes are calculated by assumed symmetric, but nevertheless, Potential energy regarded that have good agreement with experiments such as Molière, ZBL potential, do not have analytical integral form without approximation.[3,4] We calculated these Integrated Cross Sections through two numerical methods and compared them. One is known as Gauss-Mehler quadrature method [5,6], the other is applications of Andersen potential. We compared the scattering cross section obtained by two methods for some elements and concluded they resulted in same value.

(a) Gauss − Mohler Quadrature   (b) Applications of Andersen potential
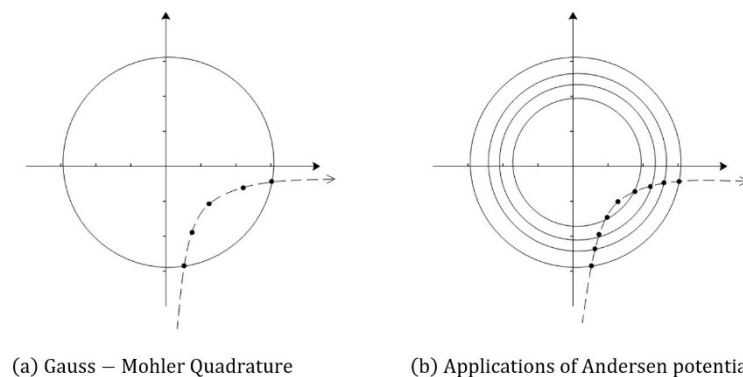
Figure 1. Schematic diagram for two numerical methods. (a) described Gauss-Mehler Quadrature that integral of the path of scattering ion. (b) described applications of Andersen potential method that approximate potential.

After all of these processes, Energy Spectrum of Ion Backscattering at Medium Energy is simulated using Rutherford, Andersen, Molière, ZBL potential. Following Energy spectra show yield difference depending on the screening function model, which could be related to concentration analysis of materials. Therefore, suitable screening function must be selected for correct concentration or quantity analysis.

(a) **Ni Simulation**, Ion : 4He, Thickness 15 nm, density : 8.85 g/cm^3, Slab Intv : 10 Slab
Straggling : Yang, Dose : 300 nC, Scattering Angle : 129.07°

(b) **Au Simulation**, Ion : 4He, Thickness 15 nm, density : 19.3 g/cm^3, Slab Intv : 10 Slab
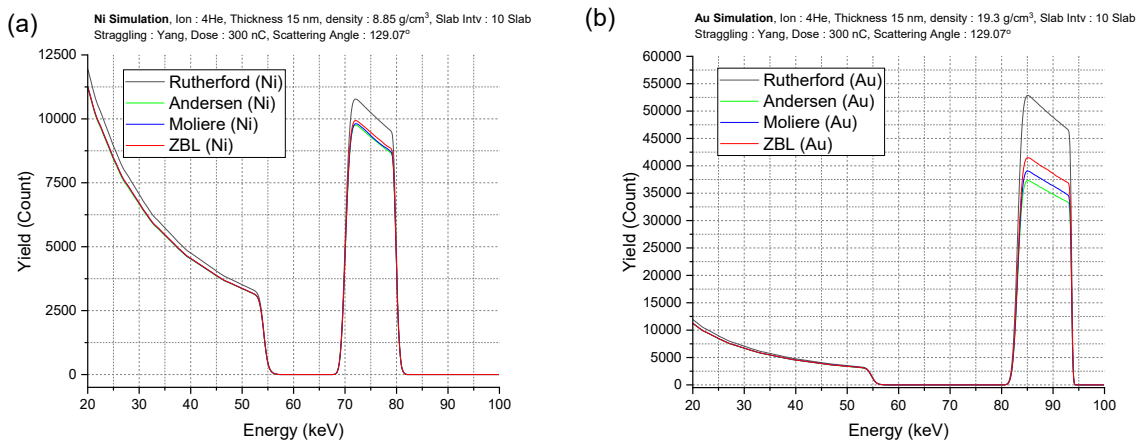Straggling : Yang, Dose : 300 nC, Scattering Angle : 129.07°

Figure 2. Simulated Energy spectra in each screening potential. (a) is Ni Thin film simulation, and (b) is Au Thin film simulation for Rutherford, Andersen, Molière, ZBL.

To suggest which form is more appropriate Screening function for nearby 100 keV 4He$^+$ ion, with experimental Energy spectrum, we measured Ni, Au Film on Si substrate both by 100 keV 4He$^+$ and 1 MeV 4He$^+$. The backscattering spectra of 100 keV 4He$^+$ are obtained by using TOF-MEIS (MEIS-K120, HB-Solution), and that of 1 MeV are by RBS (NEC, KIST). The screening function is determined appropriate for MEIS when the areal density result of MEIS by using screening function is closest to that obtained from RBS.

References.
[1] Interatomic Potentials. I. M. Torrens. Academic Press, New York. (1972) pp 35-87
[2] Comparison of Theoretical And Empirical Interatomic Potentials. D.J. O'Connor, Nucl. Instrum. Methods Phys. Res. B15 (1986) pp 14-19
[3] Higher order momentum approximations in classical collision theory. C. Lehmann and G. Leibfried. Z. Phys. 172 (1963) pp 165-487
[4] Eiffential Cross Section and Related Integrals For The Molière Potential. G.P. Mueller. Radiat. Eff. 50 (1980) pp 87-92
[5] The Numerical Evaluation of The Classical Angle of Defflection And of The J.W.K.B. Phase Shift. F.J. Smith. Physica 30 (1980) pp 497-504
[6] A Database Method For Binary Atomic Scattering Angle Calculation. Nucl. Instrum. Methods Phys. Res. B83 (1993) pp 413-418

F3

Electronic excitations by keV ions transmitted through single crystalline self-supporting foils

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The energy dissipation of ions moving through solids depends on the ion velocity as well as the atomic number of the ion and the target nuclei. In the high-velocity regime, the energy loss is well described by the Bethe and Bloch theory. However, at low velocities (around and below the Bohr velocity, v_0), the situation becomes more complex since trajectory-dependent electronic excitations develop a more dynamic character as formation of molecular orbitals and charge exchange in atomic collisions become increasingly important [1]. These processes are, due to their dependence on the interaction distance between ion and target nuclei, to different extents accessible along different channeling trajectories in comparison to random trajectories in crystalline targets.

When considering electron-hole pair excitations in binary collisions exclusively, in the low energy regime, the specific energy loss is expected to be proportional to velocity for a free electron gas (FEG). However, deviations associated with the excitation thresholds of the target electronic structure and contributions of charge exchange processes have been observed [2]. These deviations are expected to be minimized in random trajectories where the excitation is influenced by the target electronic structure along with the projectile excitation.

Experiments were performed using the Time-of-Flight Medium Energy Ion Scattering System in transmission geometry at the 350 kV Danfysik Implanter at Uppsala University. Pulsed beams of H, He and Ne, with pulse lengths of ~1-2 ns, were directed on Si and SiC single crystalline self-supporting foils with energies between 10 – 300 keV. The transmitted ions were detected by a large solid-angle, position-sensitive detector. As targets, we employed Si (100) and SiC (100) foils with nominal thicknesses of 50 nm and 200 nm (Norcada Inc.).

Energy loss was measured along random and several different channeling trajectories for both Si and SiC, materials with different band gaps (Si:1.1 eV and SiC up to 3.3 eV). For all studied cases, the energy loss in channeling orientation was found lower than in random orientation. The specific electronic energy loss for different ions in Si and SiC in random and channeling geometries was extracted, following the calculation and subtraction of the nuclear energy loss using the Monte Carlo package TRBS. For lower energies, deviations from the velocity proportionality for stopping data were examined for different ions and samples. Data were also compared with SRIM predictions for random geometries. The results obtained in this study provide accurate depth scales for keV ion-beam based techniques and can serve for benchmarking theoretical models for electron dynamics in solids e.g. Time Dependent-Density Functional Theory (TD-DFT) [3].

References.
[1] Disparate Energy Scaling of Trajectory-Dependent Electronic Excitations for Slow Protons and He Ions. S. Lohmann and D. Primetzhofer. Phys. Review Letters 124 (2020) 096601.
[2] Inelastic energy loss of medium energy H and He ions in Au and Pt: Deviations from velocity proportionality. D.

F3

Primetzhofer. Phys. Review B 86 (2012) 094102.

[3] Electron Elevator: Excitations across the Band Gap via a Dynamical Gap State. A. Lim, W. M. C. Foulkes, A. P. Horsfield, D. R. Mason, A. Schleife, E. W. Draeger, and A. A. Correa. Phys. Review Letters 116 (2016) 043201.

Energy-loss straggling of proton and helium in elemental solids: the importance of the charge-exchange and bunching effects

F.F. Selau[1], A. Molling[1], H. Trombini[1,2], R.C. Fadanelli[1], M. Vos[3] and P.L. Grande[1]

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[3]Electronic Materials Engineering, Research School of Physics, Australian National University, Australia

The energy-loss straggling is an important quantity, which describes the energy loss fluctuations of ions traversing the matter [1,2]. Typically, the variance σ^2 and the mean energy-loss $<\Delta E>$ are proportional to the ion path length and therefore the effect of energy-loss fluctuations $\sigma/<\Delta E>$ is more important for short-traveled distances and low-medium projectile energies as far as nuclear multiple scattering collisions are of minor importance. Therefore, the energy-loss straggling is of crucial importance for ion beam analysis with medium energy ion scattering (MEIS).

In this work we have investigated the energy-loss straggling of low and medium energy H and He ions on available simple materials and demonstrate the well-known Yang-O'Connor-Wang [3] empirical formula for the energy-loss straggling in the matter has a clear physical interpretation. This formula predicts, on empirical grounds, energy-loss straggling values that exceed the values of traditional straggling formulas (e.g., by Lindhard and Chu) at energies around 0.3 MeV/amu by a factor of 2–3. This excess is correlated to the bunching effect [4-6], which comes from the inhomogeneity feature of the electron density.
We show that the well-known Yang-O'Connor-Wang straggling formula has captured bunching effects from the experimental data in an empirical way [7]. This formula was further refined in this work to consider the subsequent experimental data. The bunching effect predicted by the CasP code and the experimental straggling excess are similar to each other for both solid and gas targets. The influence of interatomic bunching effects (packing effects) was also investigated for amorphous and polycrystalline solids, and we demonstrated that is of minor importance in contrast to previous estimations [2].

In addition, we quantified the straggling due to charge-changing processes for H and He ions. They are of minor importance in contrast to the one for much heavier ions where the charge-exchange straggling can exceed the collisional straggling by an order of magnitude. Therefore, for the case of H and He ions, the straggling excess captured by the Yang-O'Connor-Wang straggling formula are not due to charge-changing processes and ascribed to bunching effects.

References.
[1]   P. Sigmund, Particle Penetration and Radiation Effects, Vol. 1, Springer-Verlag, Berlin Heidelberg (2006).
[2]   P. Sigmund, Particle Penetration and Radiation Effects, Vol. 2, Springer, Berlin (2014).
[3]   Q. Yang, D. O'Connor, Z. Wang. Nucl. Instr. Meth. B 61 (2) (1991) 149–155.
[4]   F. Besenbacher, J.U. Andersen, E. Bonderup. Nucl. Instrum. Methods 168 (1–3) (1980) 1–15.
[5]   P. Sigmund, A. Schinner. Eur. Phys. J. D 58 (1) (2010)
[6]   F.F. Selau, H. Trombini, G.G. Marmitt, A.M.H. de Andrade, J. Morais, P.L. Grande, I. Alencar, M. Vos, R. Heller. Phys. Rev. A 102 (3) (2020), 032812.
[7]   F.F. Selau, H. Trombini, R.C. Fadanelli, M. Vos, and P.L. Grande. Nucl. Instr. Meth. B 497 (2021) 70-77

MEIS technique and PowerMEIS3 code: a powerful combination for material analysis

H. Trombini[1,2], G.G. Marmitt[3], F. F. Selau[2], I. Alencar[4], M. Vos[5], P. L. Grande[2]

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[2]*Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre-RS, Brazil*
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[5]*Department of Materials Physics, Australian National University, Canberra, Australia*

It is well known that Medium Energy Ion Scattering (MEIS) is capable to determine with sub-nm depth resolution elemental composition and concentration-depth profiles in thin films [1]. Recently, with the advance of computational programs such as PowerMEIS3 [2], more complex materials such as nanoparticles and FinFET-like structures [3,4] could be investigated. Information about these 3D structures includes dimensions, shape, and elemental depth profiles. This characterization comes from the high energy resolution of the MEIS technique and the deep understanding of the energy-loss processes. MEIS also allows us to achieve information on crystalline samples from their high angular resolution exploring the channeling and blocking effects. This feature was already used, for example, to quantify silicon-germanium thin-film strain and showed to be sensitive to the lack of inversion symmetry in crystals (e.g. GaP) which means that MEIS can provide the absolute crystal orientation [5,6]. Another unique feature of the MEIS technique comes when we apply molecular beams. Among several characterization techniques, ion beam analysis is limited to providing the areal concentration in atoms per square cm, i.e., the depth is indirectly obtained after a given value for the density of the layer is selected. With the use of molecular beams, the product between density and thickness can be resolved separately. For this purpose, the Coulomb explosion and vicinage effects must be taken into account [7]. Here we show examples of these MEIS operating modes and highlight their advantages and challenges.

References.
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Determining the Stopping Power of Low Energy Ne+ Projectiles in Organic Components Using Neutral Impact Collision Ion Scattering Spectroscopy

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Using Neutral Impact Collision Ion Scattering Spectroscopy (NICISS), the stopping power of low-kinetic-energy helium projectiles in organic compounds has been determined [1], but not for other noble gas ions. In this study, we used positively charged neon ions with low initial energies of 3, 4, and 5 keV to measure the energy loss in self-assembled monolayers of organic molecules formed on gold-coated surfaces. The loss in energy is calculated by comparing NICISS spectra of a clean gold surface to those of the same surfaces covered with self-assembled monolayers of organic components. With an increase in the film thickness, the energy loss of the projectile increases because the projectile experiences more collisions with the target atoms [1-3].

Angle Resolved X-ray Photoelectron Spectroscopy (AR-XPS) was used to determine the average thicknesses of the films, whereas Metastable Induced Electron Spectroscopy (MIES) was applied to help in understanding the orientation of these molecules through determining the valence electron structure of the topmost layer of the SAMs.

According to the NICISS findings, at low kinetic energies, the stopping power of Ne^+ is higher than that of He^+. Moreover, it was found that when Ne^+-ions are used as projectiles, the difference in energy between the SAM and pure Au decreases with the increase in kinetic energy, which is quite surprising! The interpretation of this occurrence is still ongoing since the potential causes are currently unknown.
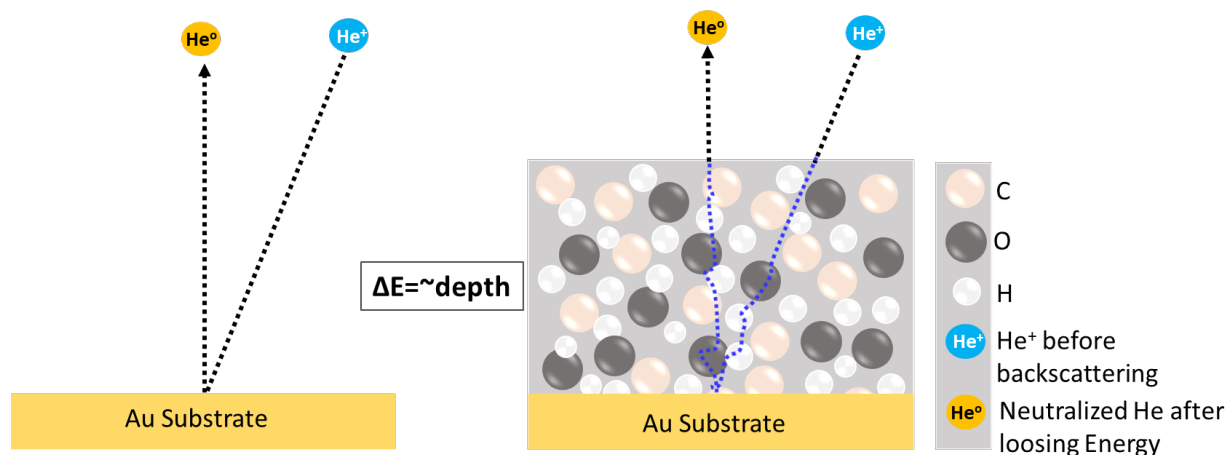

Figure 1: A diagram illustrates the NICIS Spectroscopy principle in a simplified manner. The projectile loses energy as a result of collisions with atoms composing that film. By comparing NICISS spectra with and without the layer (ΔE), the thickness of the film can be estimated.

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Advances in TOF-MEIS for quantitative-ness, semi-automated analysis and inline wafer handling

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HB solution provides commercial TOF-MEIS using 100 keV He^+. It is suitable for thin film analysis below 20 nm thickness. To use MEIS more popularly in many fields including industries, it needs to offer the results that have reliability. Quality data must be acquired in a well-defined measurement environment. The components of the environment are well-defined scattering angle with incident, a calibrated energy analyzer, applied optimize voltage for detector, a low occurring multi-hit etc. For a reliable analysis, the scattering cross-section and stopping power must be appropriately selected.

100 keV He^+ offers relatively high backscattering intensity, high depth resolution by not-too-low stopping power and high system resolution while keeping the equipment size compact. Despite these advantages, the range that nearby 100 keV is traditionally not used for backscattering analysis. Hence, the reliability of the data requires verifying. Several elemental films fabricated on a Si substrate. They were measured in well-defined measurement condition with 100 keV He^+, and were analyzed by several scattering cross sections The each areal density data obtained from MEIS and RBS measurements are compared for finding the appropriate scattering cross-section in which the MEIS data is analyzed closest to the RBS data. Using the selected scattering cross section, we analyzed the height of the corresponding elemental film spectrum with the given stopping power. We additionally measured the stopping power for that element if needed. As a result, more reliable analysis was achieved.

To make the equipment more user-friendly, several development has been done. Automation of the measurement has been achieved by introducing the multi sample holder for stand-alone type TOF-MEIS. In general, 9 samples can be mounted at one sample holder. The measurement conditions such as incident angle, detector (scattering angle), ion dose, sample motion including rotation are selected for each sample. When all measurements are complete, the instrument automatically turns off and checks the data for errors during measurement. After the spectrum check, data can be fitted by semi-automatically with designated simulation model recipe. Analysis of monolayer films is now available.

In addition to the stand-alone TOF-MEIS, an in-line TOF-MEIS for analyzing 300 mm wafers is also under development. The ion beam is focused on a 30 μm beam size to analyze 50 μm x 50 μm Si wafer test patterns. For typical oxide sample measurements, incident angle is set to 0º and the scattering angle to 135º. This set of angles has 4 double-alignment directions, with 4 detectors mounted in that direction. By summing 4 identical data resulted from each detector, the acquisition time is reduced by 1/4. By comparing the measured spectrum with the stored spectrum library, the composition depth profile is selected as the analysis result if the matching rate is good.

MEIS is expected to be used for quantitative analysis in various fields by providing high reliability, and improving user convenience.

Figure 1. (a) Stand-alone type TOF-MEIS (b) TOF-MEIS for in-line analysis

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T8

Nanoscale Structural Characterisation of Biomimetic Bacterial Membranes Using Neutron Reflectometry

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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 structure at surfaces and interfaces for a variety of different applications including 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. The focus of this presentation will be on how neutron reflectometry can be used to study biomimetic membranes assembled onto surfaces.

The presentation will cover different methods that can be used to create different biomimetic membranes that replicate the properties of a bacterial surface and how they can be structurally characterised using neutron reflectometry. Examples of applications will be given including antimicrobial peptide binding [1], drug-delivery [2], and small molecule binding [3].

In addition, the presentation will also cover the capabilities of the two neutron reflectometers that are available for use at ANSTO 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 [4]. 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) [5]. Both reflectometers operate using the time-of-flight principle and are suited for studying a wide variety of surface and interface science.

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T9

How does neutron reflectometry aid our understanding of polymer brush coatings?

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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 [2,3]).

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) methyl ether methacrylate) brushes exposed to mixed electrolytes from across the Hofmeister series.[4,5] Finally, as confined biomacromolecules lubricate natural environments such as knee joints our efforts to use neutron reflectometry to probe confined polymer brushes will be discussed.[6]

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In-situ and in-operando profiling of light elements
in energy materials using coincidence techniques

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Tackling climate change and shortage of natural resources requires a transformation of our global economy into energy-smart, sustainable, cyclic societies. Energy materials for storage and conversion of energy as well as for regulation of energy transport are often complex compound systems critically dependent on light chemical elements such as hydrogen, lithium or oxygen. The subsurface implantation and retention of other light species such as ^{3}H or ^{3}He is critical for plasma facing materials, also those linked to large scale research efforts towards sustainable electricity supply, namely thermonuclear fusion.

For both research fields, in-situ and in-operando methods capable of depth profiling light elements are highly relevant to study, e.g. diffusion and trapping of Li in batteries or fuel retention in a fusion reactor wall. Available techniques like nuclear reaction analysis (NRA) and neutron depth profiling (NDP) commonly work only for certain isotopes and often with poor depth resolution [1,2]. While conventional elastic recoil detection analysis (ERDA) features very good depth resolution for light elements, it commonly suffers from background signals from scattering. Based on coincidence techniques, we present how to perform depth profiling of Li in thin film battery stacks from Li recoils recorded in transmission using 5-10 MeV Li ions and 4-10 MeV He primary ions [3]. We show how to reconstruct the Li concentration profile from Li recoils spectra and demonstrate in-operando measurements of lithium translocation in a full battery stack [4,5]. The advantages and disadvantages of coincidence methods will be discussed together with an outlook on other potential applications.

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Ultimate surface sensitivity of nano-engineering –
slow highly charged ions as a toolbox

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Slow highly charged ions are known for more than a decade to provide a way for surface modification which is based on the deposition of the ions internal energy, i.e. its potential energy. While previous surface modification studies found large (potential) sputtering yields in the range of a 100 to a few 1000 atoms per incoming ion, the spatial energy deposition profile and consequently the sputtered and intermixed volume was not well known [1].

We used freestanding samples of a van-der-Waals (vdW) heterostructure made from a single layer of graphene and single- to trilayers of MoS_2 in order to determine the material removal efficiency down to the atomic level [2]. While doing so, we eliminate all possible contributions to surface erosion from energy deposition into deeper layers and have the opportunity to apply atomically resolved, (almost) non-invasive scanning transmission electron microscopy with elemental contrast and atomic resolution.

We find that graphene efficiently shields the MoS_2 from potential sputtering by taking up most of the neutralization energy. When turning the sample around, the ions can erode the MoS_2 layer but not the graphene underneath. In areas covered with more than one layer of MoS_2, we find at most two sputtered MoS_2 layers using 180keV Xe ions at a charge state of 38.

Our findings clearly indicate that the ions neutralize in only one layer of material, and potential sputtering is limited to 1-2 layers only, leaving material underneath intact. Furthermore, non-susceptible materials like graphene (i.e. metallic layers) remain undamaged apart from single knock-ons from the heavy incoming ion.
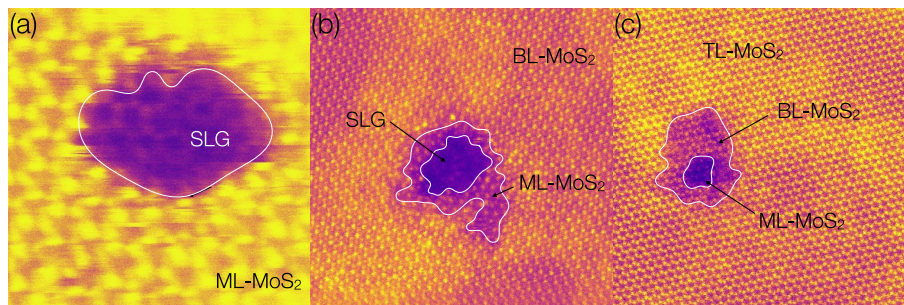

Fig. 1: vdW heterostructure of MoS_2 on graphene exposed to 180keV Xe^{38+} ions. (a) shows a pore in a monolayer (ML) of MoS_2 with graphene (SLG) underneath intact. (b) and (c) show a stepped pore in a bi- and a trilayer (BL- and TL-) of MoS_2, respectively, while a third MoS_2 layer as well as the graphene underneath stays intact.

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X-ray studies of molecular and ion ordering at the liquid-liquid interface in solvent extraction

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Solvent extraction processes are designed to extract a target species of ion from a multi-component aqueous mixture into an organic solvent, then return it to an aqueous phase containing only the targeted species. Ongoing developments of solvent extraction processes are aimed at optimizing the efficiency and kinetics of the separation and recovery of base, rare earth, and precious metals, as well as the reprocessing of spent nuclear fuel and nuclear waste. During solvent extraction, extractants and complexants assist the transport of metal ions across the liquid-liquid interface between an aqueous solution and an organic solvent. Complexation of metal ions with extractants and complexants is believed to take place at or near the organic-aqueous interface, as demonstrated recently by synchrotron x-ray measurements which locate and characterize metal ions and their complexes in the liquid-liquid interfacial region. This presentation will describe recent X-ray studies of model liquid-liquid systems relevant to the extraction of rare earth ions, both in the forward (water to organic) and backward (organic to water) directions. These results suggest a connection between the observed interfacial structures and the extraction mechanism, which ultimately affects the extraction kinetics.

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Status of the Time of Flight Medium Energy Ion Scattering (ToF-MEIS) system at Uppsala University – Acceleration of ultrashort pulsed beams of keV ions for materials science

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Time of Flight Medium Energy Ion Scattering (ToF-MEIS) is a powerful ion beam-based technique that provides information on composition and atomic structure of thin films with high depth resolution. The 350 kV Danfysik Implanter at Uppsala University features a time-of-flight beamline equipped with an electrostatic chopper, a drift tube bunching unit and the associated ion optics delivering a near-parallel beam (divergence < 0.056°) with a beam spot smaller than 1 mm^2. The ultra-high vacuum target chamber is equipped with a precise 6-axis goniometer and two position-sensitive microchannel plate detectors (MCP). The scattered or transmitted ions are detected along with the emitted photons, electrons, recoils and desorbed species. One detector can be rotated around the sample by 180° at a distance of 290 mm (yielding a solid angle of 130 msr) while the second one is mounted at a distance of 1050 mm (yielding a solid angle of 2 msr) from the sample at a fixed scattering angle of 135°. The position sensitive detectors furthermore enable crystallographic studies by acquisition of energy-resolved blocking and channeling patterns [1].

Continuous atomic and molecular beams of a wide range of chemical elements with energies 5-330 keV for singly charged ions are produced at the sources. The chopping of the pulses is achieved by an electrostatic chopper using a horizontal 4 MHz sinusoidal scanning combined with a vertical electrostatic gating, resulting in typical pulse lengths of 1 ns [2,3]. One way to further compress these pulses in time is by using the drift tube buncher. The buncher is optimized for 100 keV H for which a time resolution of 300 ps was achieved [4]. However, only a very limited number of combinations of ions and energies can be tuned in this way. Therefore, the most recent upgrade of the system and the second way to further compress the produced pulses, is by employing a second electrostatic chopper operating at the frequency of 16 MHz. The combination of the two choppers offers a pulse repetition rate from 1 Hz to 1 MHz and a time resolution below 300 ps for a wide range of energies and ion species, approaching intrinsic limitations in time-resolution of our detection electronics (~200 ps).

The energy resolution obtained for 100 keV He by the detector with the shorter flight distance and both choppers is ~0.5 keV resulting in a relative energy resolution ($\delta E/E$) of ~ 0.005. By using the second detector the energy resolution is further increased to ~0.2 keV, resulting in a relative energy resolution of 0.002. The corresponding depth resolution at the surface of amorphous Si is significantly below 10 Å.

The upgrade of the setup leads to increased energy resolution, and along with the additional capabilities of the setup (annealing, charge discrimination and implantation) will facilitate modification and depth profiling studies of superlattices and thin films in the sub-nm range.

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T13

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T14

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

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In this contribution we present a number of applications using 3D transmission experiments at the Medium Energy Ion Scattering facility at Uppsala University [1]. Specifically, we present simultaneous measurements of angular distributions and flight time of primary and secondary particles exiting thin self-supporting foil targets:

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

- A deflection unit allows for studying the equilibrium charge distributions of the transmitted projectiles [3].

- By employing heavier projectiles, recoils can be detected with high sensitivity for light elements and surface structure [4].
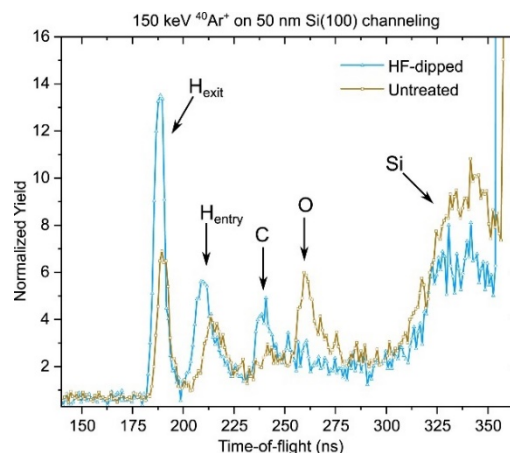
Fig.1: Time-of-flight spectra of recoils created in a silicon membrane by impact of 150 keV ^{40}Ar+.

The presented work furthermore illustrates how a number of ion-beam based techniques benefit from the versatility of the resulting instrument: apart from the relevance of fundamental data for understanding electron dynamics in solids and for quantification in analytical approaches, our results provide a basis for interpretation of prospective transmission microscopy studies. They can also be used to interpret implantation profiles in single-crystalline materials. Recoil detection in the presented approach gives the possibility to perform high-resolution depth profiling of surface and bulk composition for sensitive systems with extremely low incident doses.

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Quantifying radiolysis effects for in-situ Rutherford Backscattering Spectrometry (RBS)

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Studying the growth of metal oxides concurrently with ion beam analysis and electrochemical techniques requires the use of two incompatible resources, an ultra-high vacuum (UHV), and a liquid electrolyte. The UHV must be free of any liquid, as exposed solution will spontaneously boil, generating an environment unsuitable for ion beam analysis. To develop a reliable and reproducible method of studying the oxide growth of metals, an in-situ cell has been designed which isolates the liquid electrolyte from the UHV [1]. To control the growth of the oxide film while measuring the oxide layer thickness, electrochemical anodization can be coupled with ion beam analysis techniques, such as Rutherford Backscattering Spectroscopy (RBS). To utilize electrochemical techniques, a cell (Fig 1.) is designed with a small chamber filled with liquid electrolyte in contact with the metal. In the solution, a micro Ag/AgCl reference electrode and micro Pt counter electrode are embedded, and a small amount of 0.27 M $NaCl_{(aq)}$ is used as the electrolyte solution. RBS is an ion beam analysis technique which traditionally uses a 500 keV – 3 MeV ion beam comprised of H or He ions, collecting information on the energy lost from incident ions backscattered from the nuclei of the target. Using simulations, a layer profile of the material can be constructed with nanometer precision, giving information on layer composition, thickness, and order. RBS provides detailed information for elements with $Z > 14$, making it an ideal tool to measure near surface events on metallic targets, and study oxide growth mechanisms [2].
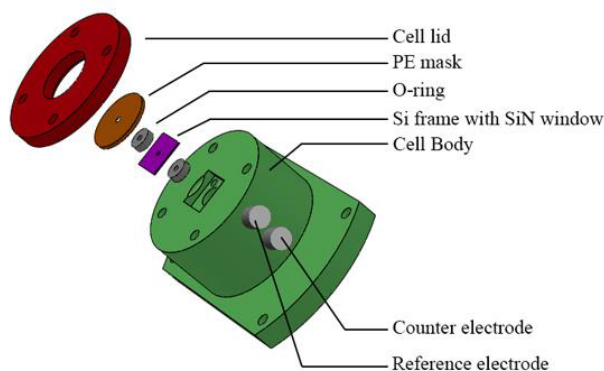

Fig 1. Exploded schematic diagram of in-situ electrochemical cell. Adopted from reference [1].

The cell design is such that liquid electrolyte is isolated from the UHV with 100 nm of magnetron sputter deposited Ti on a 100nm thick SiN window. The 3 μm penetration depth of RBS passes through the entirety of the SiN window, metal, and oxide, with remaining ions being consumed in the liquid electrolyte. Our work aims to study anodic Ti oxide growth mechanism of thin film magnetron sputter deposited Ti on Si (001), with a 1 mm^2, 50 nm thick SiN window. The solution

used is a 0.27 M NaCl$_{(aq)}$ electrolyte, and the applied voltage is between 1 – 10 V vs Ag/AgCl. The growth is studied using the Tandem accelerator at Western University, with an energy between 1 MeV – 2.5 MeV He+, and a backscatter angle of 170°.

The α flux that passes through the sample and into the liquid electrolyte creates issues involving radiolysis product generation leading to enhanced oxide growth rate. Upon interacting with the water in the liquid electrolyte, radiolysis products that affect the rate of oxide growth such as hydrogen peroxide, radical species, and solvated electrons, amongst others are generated [3]. Fig 2. demonstrates the enhanced passive oxide growth of Ti in contact with electrolyte exposed to α flux, compared to the passive oxide generated with no α flux exposure. Fig 3. Without α flux exposure, for a longer period of contact with electrolyte, TiO$_2$ passivates quickly, generating a passive oxide on the surface, inhibiting further oxidation [4,5]. Conversely, the solution exposed to α flux shows a significant increase in oxide thickness, showing no characteristics of oxide passivation, and potentially different mechanism of the oxide growth. This implies that exposure of the solution to α flux induces spontaneous and non-passivating enhanced oxide growth.
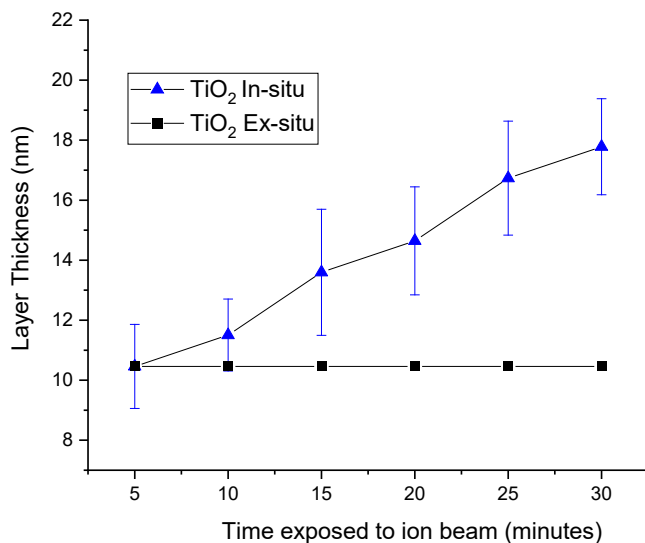
Fig 2. Spontaneous oxide growth of TiO$_2$ with in-situ exposure to liquid electrolyte and α flux, compared to the reference sample (same electrolyte, no flux).
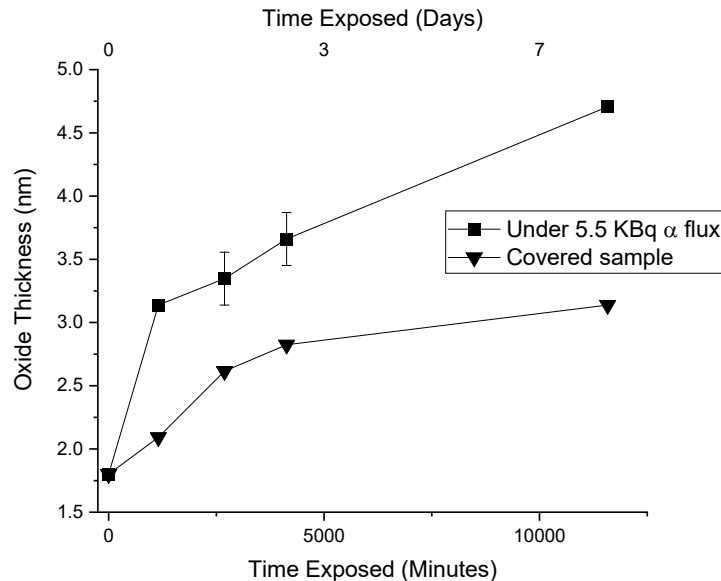
Fig 3. Ex-situ sealed source radiolysis testing of TiO_2 growth in 0.27 M $NaCl_{(aq)}$ compared to sample unexposed to α flux.

After careful quantification of the radiolysis-induces oxide growth rate, we can proceed with further in-situ experiments. This allows us for the isolation of (a) electrochemical-potential induced growth from (b) spontaneous α flux radiolysis product generation growth.

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Electronic Structure of Titania Surfaces Modified by Metal Clusters

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Metal clusters with a size of less than 100 atoms are suitable for modifying the electronic properties of semiconductor surfaces. [1, 2, 3] Metal clusters have been shown to be promising candidates as co-catalysts for photocatalytic water splitting.[4] However, using such clusters as co-catalysts requires implementing processes which suppress their agglomeration on catalyst surfaces. In order to avoid agglomeration of the metal clusters and in order to retain their specific electronic structures, the coverage of the surface with metal clusters has to be kept below 10%. As an alternative, thin layers of metal oxides can be deposited on top of the clusters to reduce their mobility. The main challenges in this field are a) to maintain the size and thus the properties of the metal clusters and determine the size of the clusters and b) to determine the electronic structure of the clusters.

The first challenge described above is considered as one of the main challenges in the field of surface modification with metal clusters can be addressed by introducing defects on the metal oxide surface, specifically oxygen vacancies and using electron microscopy techniques techniques for determining the size of the clusters. The second challenge can be addressed by using experimental techniques which are exclusively sensitive for the electronic structure of the outermost layer. Metastable Induced Electron Spectroscopy (MIES) is such a technique and has been used successfully to determine the change in electronic structure due to the deposition of Au and Ru clusters. Applying techniques such as singular value decomposition, the changes of the electronic structure can even be quantified. [2]

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Alternative Elemental Profiling Methods for Corrosion Study of Ferrous (and Nickel) Aloys

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This work illustrates an alternative depth profiling method upon a particular type of sample surfaces- ferrous and nickel alloys with hard-surfaces, where heavy elements dominate the surface-bulk area. The analysis needs to be performed with a probing depth up to hundreds of micros due to the corrosion layer depth. Therefore, backscattering methods and reflectometry including sputtering are generally not compatible for analysing such samples, unless a high-energy heavy-ion accelerator is applied.

A compatible and cost-effective method of elemental depth profiling upon such alloy surfaces is discussed in the work. The methodology involves a well-polished cross-section surface in parallel to the surface normal of the corroded alloy surface, where the interface layers from the alloy surface to the bulk are exposed for analysis [1]. The technique allows the scanning electron microscopy (SEM) and optical microscopy to be conducted on the cross-section. Energy-dispersive X-ray spectroscopy (EDX) and Auger electron spectroscopy (AES) can be further carried out on the imaged area for identifying the elemental profile by either mapping or line-scan functions.

In our study, the ferrous SS 316L was first exposed to the phase change salt PCM 710- a mixture of sodium carbonate and potassium carbonate to serve as heat transfer fluid for high-temperature concentrated solar thermal plant application. The steels are generally used as PCM contaminant for thermal storage to allow PCM to charge over daytime and discharge over nighttime to produce thermal energy. However upon the thermal cycling simulation of 550-750°C range, severe corrosion has been observed on the SS 316L surface. The cross-section profiling showed a distribution of FeO_x on the steel surface (Figure 1) when exposed to PCM710 in air environment, where Cr was depleted from the outermost layer. Underneath the FeO_x (up to few micros), a Cr and O enriched layer over a depth of about 500-600 micros was formed when the thermal cycling has been conducted up to 500 times. Ni was also seen in the CrO_x layer but at a lower concentration. By contrast, the elemental mapping and profiling of the corroded SS 316L under PCM710 in Ar environment showed the Cr/O layer formed in a layered structure on the surface and Na was additionally observed which overlapped with the distribution of Cr and O. The identification of Na indicated the formation of Na chromite ($NaCrO_2$), which was only seen under Ar environment.

The corrosion mechanism appears to be two-fold: (i) the metal elements are oxidised, even under inert atmospheres and (ii) Mainly Cr as oxides are leached into the PCM resulting in the formation of a pure FeO_x layer which is then subject to spalling into the PCM710 leaving subsequent layers exposed. The processes are dynamic thus the oxidation of Cr, depletion of Cr, oxidation of Fe and spalling off of FeO_x occur simultaneously and continuously. Under inert Ar atmosphere the PCM contributes to the oxidation process. Na is observed through the thickness of the Cr/O layer and chromites are formed due to the decomposition of Na carbonate under Ar,

the phenomenon is only observed in air environment, suggesting this mechanism is only significant in inert atmospheres.
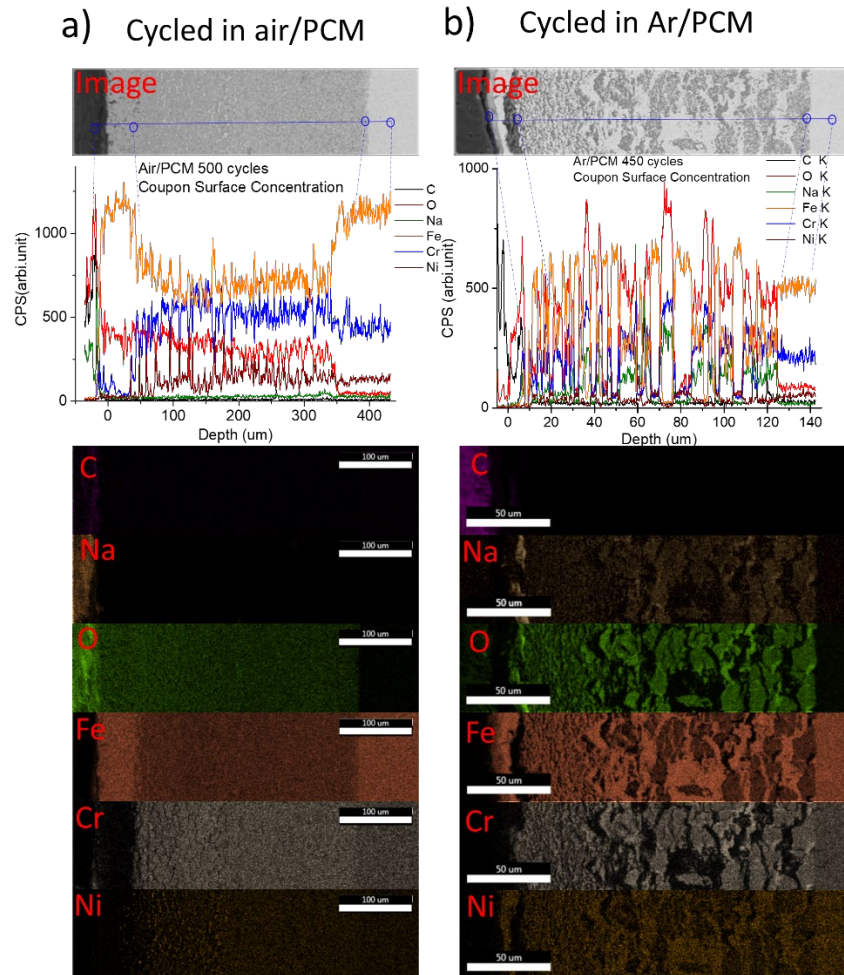
a) Cycled in air/PCM   b) Cycled in Ar/PCM

Figure 1. a) Cross-section analysis including line scan and elemental mapping of SS316L subject to PCM in air environment, 500 cycles; b) Cross-section analysis including line scan and elemental mapping of SS316L subject to PCM in Ar environment, 500 cycles

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Ruthenium Clusters as Co-catalysts for Photocatalytic Water Splitting.

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Fossil fuels have played an essential role in the development of modern society. However, concerns over their contribution to climate change and the destruction of the natural world have led to a demand for a fast transition to renewable sources of energy. The energy that can be provided by splitting the water using sunlight is a promising source of sustainable energy. Photocatalytic water splitting is an appealing approach for using solar energy to produce and store hydrogen, which can be an environmentally friendly renewable fuel. However, only a few semiconductor materials can be efficiently employed for the water splitting process. One of the semiconductors that have shown great potential to be used in photocatalytic water splitting is TiO_2. It was demonstrated that the photocatalytic activity of the prepared materials could be increased by applying noble metals as co-catalysts [1,2].

In this project, we investigated several strategies to study the water dissociation in which the samples were prepared by annealing and sputtering in an ultra-high vacuum (UHV). In order to achieve the objectives of this work, two main techniques based on electron spectroscopy were employed. They have been used to investigate the formation of the samples with or without water adsorption. Firstly, X-ray Photo-electron Emission Spectroscopy (XPS) was employed as a common technique to investigate the chemical compositions of surfaces. Secondly, Metastable Induced Electron Spectroscopy (MIES), the most surface-sensitive technology for analyzing the surface, have been used to measure the electronic structure of the material and to determine the molecular orientation on the topmost atomic layer and the density of state (DOS).

This study examined the effects of sputtering, heating, different disposition times (amount of loading), and water exposure on two samples. RF sputtering TiO_2 thin film and $Ru_3(CO)_{12}$ clusters deposited on RF sputtering TiO_2 thin film have been studied to investigate the water dissociation. The XPS and MIES provided evidence for the water dissection of RF sputtering (TiO_2) thin film by CVD. However, the XPS and MIES results also give evidence for the less water dissociation of $Ru_3(CO)_{12}$ clusters deposited on RF sputtering (TiO_2) thin film by CVD.

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Exploring the Properties and Stabilization of Nanoscale Overlayer/Metal cluster Architectures.

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The deposition of metal clusters can modify the electronic properties of solid surfaces, to achieve a specific and unique electronic surface structure, by variation of the cluster size and elemental composition. However, metal clusters are not particularly stable due to their size and the tendency to agglomerate on surfaces, which results in loss of their remarkable properties. By adding an overlayer of metal oxide using atomic layer deposition, it is expected to prevent the agglomeration and stabilise metal clusters on the surface. For applications in catalysis the overlayer needs to be not thicker than 2–3 monolayers such that the reactant can interact with the overlayer protected cluster. This also introduces a new system of overlayer/clusters/semiconductor material which provides new and unique electronic properties. The applications of this combination are vast, with potential use in catalysis, photocatalysis, medical devices, and sensors.
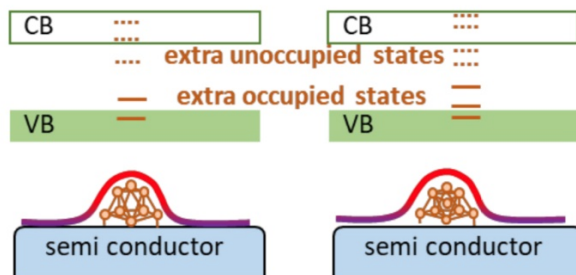

Figure: a thin overlayer on top of the clusters stabilizes the cluster. The combination of substrate, specific cluster and overlayer material will result in unique electronic properties at the specific site of the cluster on the surface.

Dye Anchoring Modes of Ru-based N719 dye investigated using FTIR and ARXPS.

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Immobilization of dye on semiconductor substrate deposited on a conductive glass combinedly make the working electrode. The way the dye anchors on to the titania substrate directly influences the charge injection from the dye molecule to the conduction band of the semiconductor. Thus, dye anchoring plays an important role in determining the cell efficiency and extensively influences the cell stability. This makes the investigation of the characterization of the dye complex adsorption on the titania substrate very crucial as it will help in exploration of the sensitization phenomenon and to optimize their quantum yield.

The present work aims to re-investigate extensively studied Ru-based dye, N719 using FTIR and Angle resolved XPS, to set up a methodology and further apply it in investigating the anchoring in other dyes. FTIR helps in identifying the change in the structure of dye molecule upon adsorption revealing information about the anchoring modes. ARXPS on the other hand helps in determining the depth profile of the dye adsorbed on to the titania. ARXPS being a non-destructive technique is based on simple principle of tilting the sample to increase the sample surface sensitivity [1].

The ageing of dye sensitized solar cell has adverse impact on the cell performance of which one of the crucial factors is change in the dye structure. To understanding how the dye attaches on to the titania substrate and how the dye anchoring changes with ageing give insight into how the change in dye structure with ageing is affecting the cell efficiency and what functional groups are more prone to get affected under stress.

FTIR result suggested, the role of TBA^+ is deprotonation of the carboxylic group hence, COO- anchors to titania via multiple modes, i.e., bidentate chelating and ester bonds. However, the changes in feature of NCS suggested the partial involvement of thiocyanate ligand in the dye attachment. In addition, the depth profile obtained from ARXPS suggested the dye adsorption mostly concentrated onto the surface than depth with COO- at the depth and NCS+S just above Ru with Ru at the depth of 0.7 λ.

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Investigating hydrogen storage materials with ^{15}N-ion beams

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Crystalline early transition metals absorb hydrogen atoms into distinct octahedral or tetrahedral interstitial sites forming compounds existing as multi-phase systems (MH$_n$)[1]. Meeting requirements for reversible solid-state storage for energy applications, such as fast delivery at ambient temperatures and high absorption rates, nanostructures can be used to improve reaction kinetics and reduce the enthalpy of formation [2]. Another class of materials recently gaining attention as potential storage materials are fully amorphous systems based on early transition metals. For both classes of systems, energetic ion beams provide means to assess concentration and spatial distribution in real space.

Real space location of hydrogen sites in single crystalline two-dimensional superstructures is achieved by ^{15}N(6.6 MeV)-ion channelling in combination with ^{1}H(^{15}N, $\alpha\gamma$)^{12}C nuclear reaction analysis [3]. The detection of characteristic γ-emission discloses absolute hydrogen concentration and relative lattice location. Detection of elastically backscattered ions (Fig. a) allows not only alignment towards crystallographic axes, but also exploration of hydrogen-induced lattice expansion [4], vibrational modes and the electronic stopping cross section. Monte-Carlo simulations of ion trajectories and average nuclear encounter probabilities (NEP) verify the exact location of subsurface hydrogen and reveal for the first time thermal vibrational
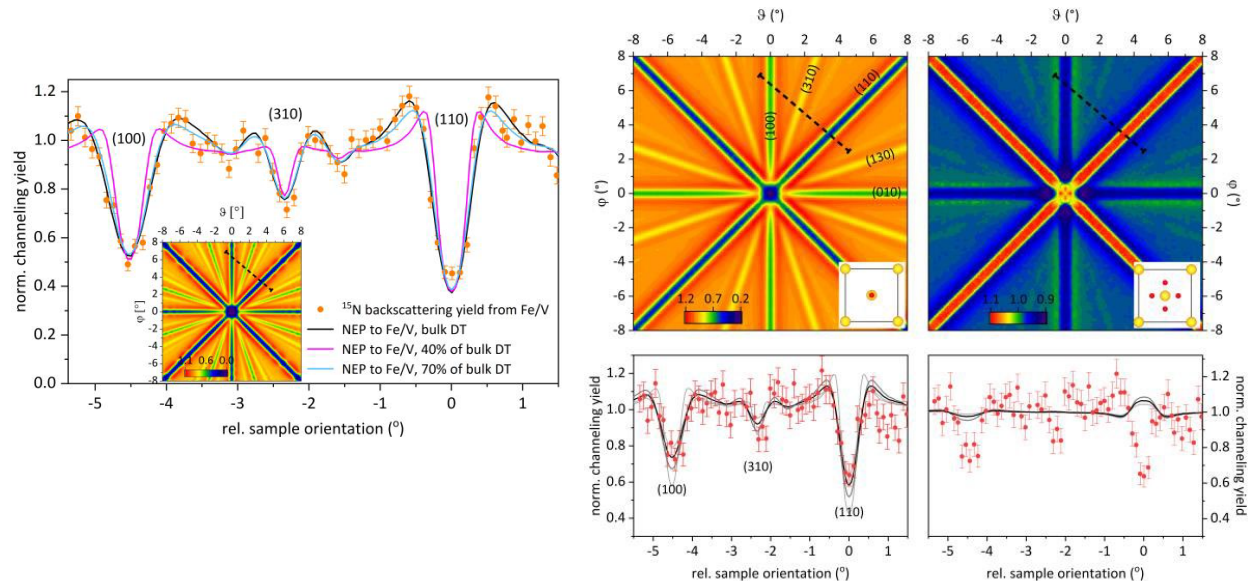

Figure (a): Angular line scan of primary ^{15}N ions of 6.6 MeV backscattering from a Fe/V-superlattice and comparison to simulation of average nuclear encounter probability (NEP) assuming different values for the Debye Temperature (DT) (continuous lines). (inset) Angular map of simulated average ^{15}N-NEP to Fe/V atoms. The dotted line indicates the experimental angular line scan [3]. (b) Upper panels: Simulated NEP for 6.6 MeV primary ^{15}N ions steered to hydrogen atoms in O$_z$ (left) and T$_z$ sites (right) through the Fe/V superlattice. Incident beam angles are varied around the [001] channel. (insets) The location of hydrogen atoms (red) in the V unit cell (yellow) for a projection along [001]. Lower panels: Normalized γ yield (red) from the angular line scan (dashed black line in upper viewgraphs) is compared to the NEP for different thermal vibrational amplitudes of hydrogen (continuous lines). [3]

amplitudes (Fig. b). The effect of elastic boundaries, finite size and proximity on the site occupancy and phase formation of metal hydrides, e.g. vanadium, is studied on the nanoscopic to atomic scale.

In an effort to improve accuracy, we have assessed the accuracy of Bragg's rule predicting the stopping power of transition metal hydrides. This quantity, which is necessary for quantification in the above-mentioned ion-beam based studies has to the best of our knowledge, not been quantified directly for such systems. At the same time, the extraordinarily high solubility of hydrogen in certain compounds based on early transition metals may challenge theoretical or semi-empirical predictions.

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In-depth analysis of tethered bilayer lipid membranes

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Tethered bilayer lipid membranes (tBLMs) are versatile model systems that consist of a lipid bilayer that is covalently attached to a solid surface, making the architecture very robust. A linker between bilayer and surface creates a small reservoir, enabling the transport of water and ions across the membrane. At the same time, the solid surface allows for the use of a wide array of analytical techniques to be applied, enabling in-depth structural analysis of the membrane.

Model membrane are useful architectures when it comes to the study of membrane related processes. A tBLM allows for systematic investigation for example of the binding of molecules to the membrane, the interaction of small molecules with incorporated proteins or the effect of the membrane composition on the function of integrated protein.

Here, we present an overview of how the combination of a range of techniques such as electrochemical impedance spectroscopy, neutron reflectivity, ion scattering techniques, surface plasmon resonance spectroscopy can be used to determine structural features of a membrane with ultra-high resolution.

A range of different tBLM architectures will be presented, including the use of bacterial lipids in order to create mimics for bacterial membranes. These can be used to study the function of antibiotics.

Thermal growth of SiO$_2$ in SiC using CO$_2$

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Silicon carbide (SiC) is a wide bandgap semiconductor with large application in power electronics. What distinguishes SiC from other wide bandgap materials is the possibility to thermally grow silicon dioxide (SiO$_2$) films, and this allows to adapt a good part of the existing silicon metal-oxide-semiconductor (MOS) technology to SiC. Although SiC is already present in the power electronics market, there is the possibility to broaden its application. Currently, the bottleneck for its even larger application is the low channel mobility of metal-oxide-semiconductor field effect transistors (MOSFETs) made on SiC. This is mainly attributed to the poor electrical quality of the SiC/SiO$_2$ interfacial region, which is known to be not as abrupt as the Si/SiO$_2$ counterpart, and in which residual carbon compounds can be found [1].

While most of the currently used routes of increasing channel mobility involve post-oxidation annealing, especially in atmospheres containing nitrogen compounds [2], there are some suggestions that other types of gases, such as CO$_2$, can be used to achieve a similar benefit [3]. Although it is believed that residual carbon compounds are responsible for poor interfacial properties, it is suggested that using carbon-based gases during the thermal oxidation process or post-oxidation annealing can lead to the formation of carbon structures that do not play a great role in electric properties degradation. In this work, we characterize SiC oxidation using CO$_2$ as the oxidant species. Ion beam and spectroscopic techniques were used to get a deeper understanding of the interfacial region between SiC and SiO$_2$.

A systematic oxidation-and-analysis procedure was developed in Si-face 4H-SiC samples. SiO$_2$ films were thermally grown in a static atmosphere quartz-tube reactor using different combinations of temperature, CO$_2$ pressure and oxidation duration. The idea was to simulate several 'snapshots' of the oxide growth process by preparing several samples with different oxidation duration but using the same pressure and temperature conditions. We used channeled Rutherford Backscattering Spectrometry (c-RBS) to determine total oxygen incorporation as well as the amount of silicon atoms that is part of the formed SiO$_2$ films. This allows us to estimate SiO$_2$ film thickness and the silicon-to-oxygen ratio of each sample.

Total oxygen incorporated as a function of oxidation duration for each combination of temperature and CO$_2$ pressure are shown in Fig.1. It is interesting to note that temperature is shown to have a significant role in SiO$_2$ thermal growth on SiC. However, oxygen incorporation for current samples oxidized for 30 min using 950 mBar of CO$_2$ have shown similar oxygen quantities. Besides that, one can notice that the sample with most oxygen is the one whose thermal treatment had the lowest CO$_2$ pressure.

By using c-RBS technique we were able to distinguish between Si atoms present in the crystalline SiC structure from Si atoms present in the amorphous SiO$_2$ thin film grown. Fig.2 presents amorphous silicon quantities as a function of the total oxygen incorporated. It should

be noted that, since the grown film is supposed to be SiO_2, a ratio of 2 oxygen atoms per 1 silicon atom is expected. However, we observed a higher O-to-Si ratio, which suggests that there is an excess of oxygen – or lack of silicon – in the amorphous part of our samples.
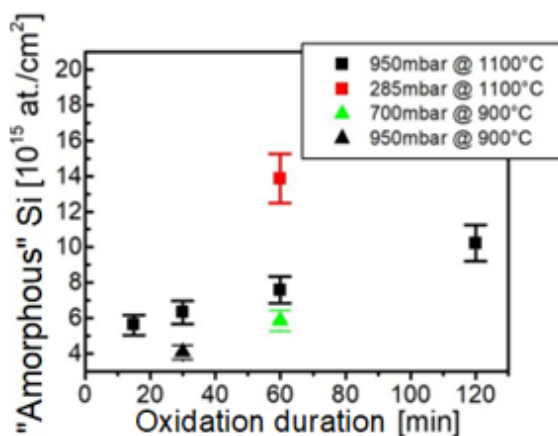

Fig. 1 – Total oxygen incorporation determined by c-RBS technique. Squares and triangles indicate different oxidation temperatures, while colors indicate different CO_2 pressures used in the oxidation process.
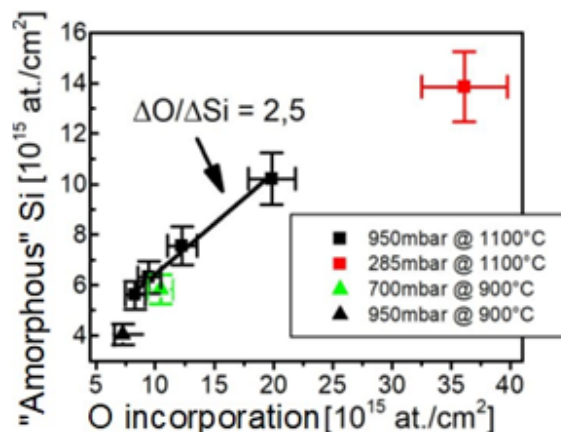
Fig. 2 – Amorphous Si present in samples as a function of total oxygen incorporated. Keep in mind that all oxygen present in samples come from the CO_2 gas used in the oxidation, while all silicon comes from the single-crystalline substrate.

This work is currently in progress and more experimental data will be available by the time of the conference.

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Utilization of graphene for analyzing liquid interfaces by SIMS and MEIS

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Detailed compositional and structural characterization of liquid interfaces is required to better understand interfacial phenomena occurring in electrochemical, colloidal, and biological systems. However, nanoscale characterization techniques using accelerated electrons and ions operate under an ultra-high vacuum environment, which presents a difficult challenge for analyzing liquid interfaces in ambient conditions despite their wise usage in surface and interface analysis. Recent advances in graphene techniques have enabled ambient imaging and spectroscopic analysis of materials and cells in solution using ultra-high vacuum-based analytical tools. We also used graphene to develop novel methods for analyzing liquid interfaces even under an ultra-high vacuum environment. Here I will show technical details on how to handle graphene to make liquid samples stable during analysis in a vacuum for mass spectrometry imaging of wet/live cells using time-of-flight secondary ion mass spectrometry (ToF-SIMS) [1, 2] and for depth profiling of electrical double layer using time-of-flight medium energy ion scattering spectroscopy (ToF-MEIS).

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Operando measurement of ^{7}Li in all-solid-battery using ^{7}Li(p,α)^{4}He

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All-solid-state Li-ion batteries, which would safely increase the capacity of Li-ion batteries, are attracting much attention. At present, a problem that the conductivity is not sufficient for a practical use is remained [1]. In this study, we are trying to observe the behavior of ^{7}Li using ^{7}Li (p, α) ^{4}He NRA (Nuclear Reaction Analysis) [2] and solve the above problem.

NRA was performed using 1 MV Tandetron at UTTAC in Univ. of Tsukuba. We used the 1.5 MeV H$^+$ beam. The detector was mounted in a direction of 150° with respect to the beam direction, and the sample was tilted so that the angle of α emission was 70° from the surface normal. We used two samples for this study. One sample is consisting of stacked layers of Li /Li$_3$PO$_4$ /Au deposited on a Si$_3$N$_4$ substrate with 100 nm thickness. The other sample is Li /Li$_3$PO$_4$ / LiCoO$_2$ /Au. The later sample is only added the positive electrode into the former sample. In order to perform the operand measurement, positive voltage is applied to the Au layer (collector) with respect to the Li layer (the negative electrode). The samples were discharged at the bias voltage below 0.1 V and charged at the bias voltage above 4.0 V. The behavior of ^{7}Li was studied by comparing the NRA spectra obtained at the bias voltages for charging and discharging.

Figure 1 (a) shows the NRA spectra taken on the sample without positive electrode, Li /Li$_3$PO$_4$ /Au. We notice that the Li ions penetrated into the Au layer, and formed the Au-Li alloy layer around 3270 ~ 3320 ch. This implies a self-organization of a positive electrode between the collector and electrolyte layers. On the other hand, the relative yield of Li layer (negative electrode) around 3050 ch decreases to compensate the Au-Li alloy formation. Figure 1 (b) shows the NRA spectra taken on the practical sample, Li /Li$_3$PO$_4$ / LiCoO$_2$ /Au. The voltages for charging, discharging, and recharging (again) loaded on the Au layer, are shown. In contrast to the case of the former sample, we cannot find any drastic changes in the NRA spectra through the measurements, while there are subtle changes in both the positive and negative electrodes. We are able to say that this more practical battery is structurally stable during the charging and discharging cycle. In order to focus our attention into the slight changes found in the practical battery, we will use a ^{6}Li-enriched target in the deposition of a particular layer.

Fig. 1 the NRA spectra of (a)the NRA spectra of Li /Li$_3$PO$_4$ / Au/ Si$_3$N$_4$ and (b) The NRA spectra of Li /Li$_3$PO$_4$ / LiCoO$_2$/Au/ Si$_3$N$_4$

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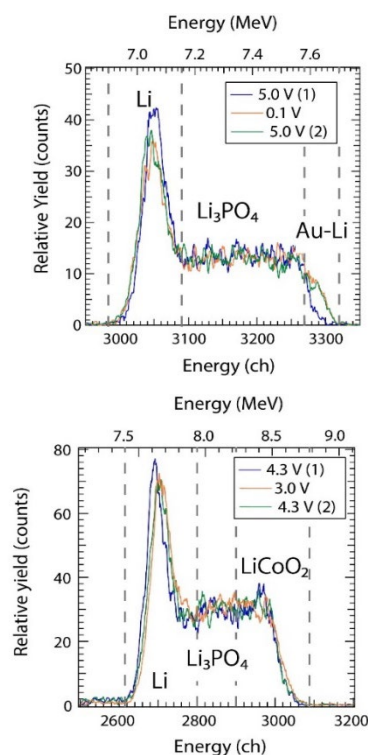[2] A. Sagara et al., Nuclear Instrument and Methods in Physics Research B 34 (1988) 465-469.

Ion and neutral time-of-flight spectroscopy for deciphering hydrogen-surface interactions

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In this study, we use low energy ion scattering (LEIS) and direct recoil spectroscopy (DRS) to provide isotope specific information about the atomic-scale behavior of hydrogen on surfaces. During these measurements, we dose the surface with atomic or molecular hydrogen beams while probing the surface with low energy ions (typically < 3 keV He+ or Ne+). We then measure the recoiled adsorbate signals as a function of angle of incidence or surface temperature to analyze both the chemisorbed hydrogen concentration and its binding configuration. In our recent work, we have pursued the use of multi-angle scattering maps, which involve acquiring scattered and recoiled particle fluxes over a large angular sector. When coupled with binary collision or molecular dynamics simulations, this approach allows us to measure the height of the hydrogen layer above the surface to within < 0.02 nm [1]. We have applied these techniques to a variety of materials, ranging from model systems to technical surfaces.

Like most surface analysis techniques, both LEIS and DRS are generally used at low pressures typical of ultra-high vacuum systems, usually $<10^{-4}$ Pa. In this study, we consider modifications to these techniques to extend this range, with the eventual goal of using these techniques to study surfaces exposed to hydrogen environments at elevated pressures. To demonstrate our approach, we have constructed a prototype instrument for time-of-flight (TOF) spectroscopy consisting of a differentially-pumped ion source and flight tubes. For these measurements, we relied on a pulsed alkali ion source with customized ion optics to probe a variety of targets. This equipment was attached to an ultra-high vacuum chamber where the scattered and recoiled particles are sampled at angles of 65° and 160° relative to the incident ion beam, enabling detection of both forward and back-scattered particles simultaneously. Initial characterization of 10 keV Li+ scattered from Au, W, Pd, Ni, and Al surfaces at pressures of 5×10^{-2} Pa and above revealed minimal attenuation of the scattered signal and good mass resolution. A potential advantage of the instrumentation as discussed above is its compact size in comparison with the equipment needed for high energy ion beam analysis (e.g. Rutherford backscattering), making it easier to implement on smaller systems. Preliminary results from these experiments will be presented, including initial studies of chemisorbed hydrogen on different metal surfaces of interest for hydrogen-surface interactions R&D.

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Ion specific effects 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, electrochemical reaction development and as a model system for atmospheric chemistry studies. Since the recent developments in surface-sensitive experimental techniques, many investigations focused only on aqueous surfaces and have shown that adsorption or desorption of ions in aqueous solution follows a specific ion series (direct or indirect Hofmeister series). It is assumed that this behaviour originates from the ion-solvent interaction[1]. As shown in a recent comprehensive investigation, ion specific effects are observed as well in non-aqueous solvents [2]. However, consensus for adsorption or desorption of inorganic ions at surfaces of liquids other than water is limited and thus the origin of ion specific effects has not yet been understood. Therefore, to further unravel the origination of ion specific effect at liquid surfaces, we have employed neutral impact collision ion scattering spectroscopy (NICISS) [3] to obtain concentration depth profiles of various ions in glycerol, formamide, benzyl alcohol and propylene carbonate solution.

From comparisons of different combination of cations and anions concentration depth profiles in various solvents, we have observed different factors influencing ion specificity at solvent surfaces i.e., 1) competing effect of bulk over interface, 2) reversal in specific ion order depending on solvent's identity [4], 3) complexity of counter-ion effect for ionic adsorption at solvent surface and 4) secondary order effect due to difference in solvent permittivity and solvent molecule orientation at the interface.
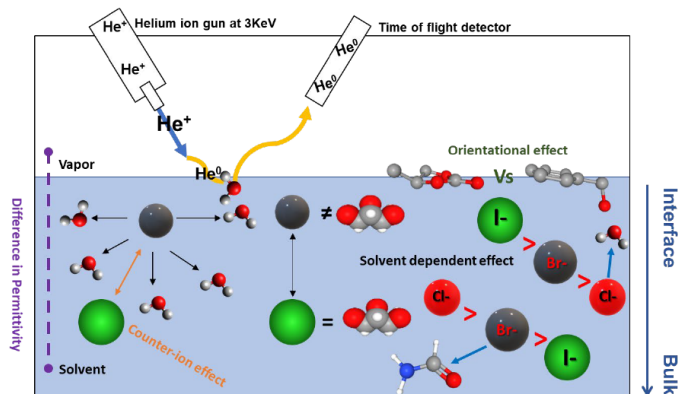
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Ion Beam Analysis of Live Cancer Cells in Solution and Nanostructured Materials and Devices

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Most of nano analysis tools are based on electron and ion beam in ultrahigh vacuum. However, many important phenomena are in the liquid phase such as life phenomena, nucleation, corrosion, etching, and electrochemistry. Filling the gap between the ultrahigh vacuum and the liquid phase has been one of the most exciting challenges. Recently, single layer graphene has been used for electron beam analysis such as liquid TEM analysis and wet cell SEM analysis recently. For last several years, we have been trying to use single layer graphene for ion beam analysis of bio-liquid interfaces.

We showed that live cells in solution can be preserved intact and hydrated even under ultrahigh vacuum by capping with single layer graphene. The cell viability was improved by fabricating a reservoir of cell culture media solution. It is quite interesting that sputtering of molecular ions is possible through a single layer graphene. Raman analysis and HIM observation of sputtered graphene showed the graphene layer is damaged and oxidized but it sustains the layered structure to keep the cells wet. The molecular distributions of cholesterol and various fatty acids on membranes of live A549 cancer cells were observed by TOF-SIMS. [1] Preliminary results will be reported on single protein imaging by multiplex analysis of confocal, SEM, TEM, and SIMS using antibody conjugated nanoparticles

Using recently developed TOF-MEIS, we could analyze compositional and structural profiles of CdSe/ZnS QDs and As-doped FINFET nanodevices [2]. TOF-MEIS could reveal the initial nucleation mechanism of calcium phosphate nanoclusters down to sub 1 nm diameter, which is quite contrary to the classical nucleation mechanism [3].

Further possible applications of TOF-MEIS on various nanoscience will be discussed.

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Detection of hydrogen using medium energy ions

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Medium energy ion scattering (MEIS) is a powerful tool for depth profiling, capable of providing quantitative information on the structure and composition of shallow layers with sub-nm depth resolution near the surface [1, 2]. This method is applicable mostly for impurities with atomic number Z > 6 on light substrates. However, MEIS lacks sensitivity to light elements (H, D, He and B). Thermally driven transport and exchange of hydrogen isotopes in silicon-based metal-oxide-semiconductor (MOS) and other device-related structures is important for device performance and other fundamental studies. The motivation for this work was twofold: (i) importance of light elements quantification to obtain accurate stoichiometry, and (ii) general importance of hydrogen in semiconductor devices (for instance, giant hydrogen isotopic effect on hot-electron degradation mechanism).

There were several adaptations of MEIS in the past three decades to perform elastic recoil detection analysis (ERDA) using electrostatic energy analyzer (ESA) or time-of-flight (TOF) detection system in medium energy range (10-500keV). Copel *et al.* successfully demonstrated detection of hydrogen and boron using time-of-flight approach, with depth resolution of ~10Å [3]. Nishimura *et al* [2] utilized a modified version of ESA with a wide interelectrode distance of 18 mm, covering a broad energy range $W=0.1E_o$, where E_o is the energy of ions detected along the central curvature of the ESA. Both H^+ and H^- detection was demonstrated, with sensitivity of 0.1ML. More recently, Holeňák *et al*. has shown possibility to detect hydrogen using ^{22}Ne and ^{40}Ar pulsed beams as projectile with TOF detector for samples in transmission geometry[4]. For a large solid angles of the detector (0.13 sr), a high-depth resolution below 60 Å and sensitivity below 10^{14} atoms/cm^2 was achieved. Our implementation of medium energy (ME-ERDA) is based on using ~300-500keV N^+ or Si^+ ions as projectiles and detecting negative hydrogen (H^-) recoils using standard ESA detector [5]. We applied this technique to the analysis of H-terminated Si (001), self-assembled monolayers, and 2–5 nm thick HfO$_2$ and HfSiO$_x$ films grown by atomic layer deposition on Si(001).

The key points for detecting recoiled H ions directly in the medium energy ion range are (*i*) to increase the recoil cross-section, (*ii*) to find suitable recoil energy and separation with other elements; (*iii*) to minimize the background due to elastically scattered incident projectiles. We attempt to detect the recoiled negatively-charged hydrogen ions H^-, therefore it is also important to select incident beam with the negative ion fractions as small as possible. Possible candidates (^{11}B, ^{14}N, ^{20}Ne, ^{23}Na, ^{24}Mg, ^{27}Al, ^{31}Si, ^{31}P, ^{32}S, ^{35}Cl) were reviewed based on the equilibrium charge distributions of ions exiting carbon foils [6]. Fig.1(a) shows the recoil cross-section as a function of the recoil angle for 200keV He^+, B^+, N^+ and Si^+ ions incidents on H, with ZBL potential as the interatomic potential. Cross section increases with the recoil angle increase and

higher for larger Z elements, however heavier projectiles, e.g. Au$^+$, were not tested due to significantly higher sputtering yields and modifications of surface morphology. In order to satisfy condition (*ii*), kinematic factor dispersion was examined as a function of scattering angle (Fig. 1(b)), and suitable angles were selected to measure H but still achieve separation between H and heavier elements, e.g. C and Si.
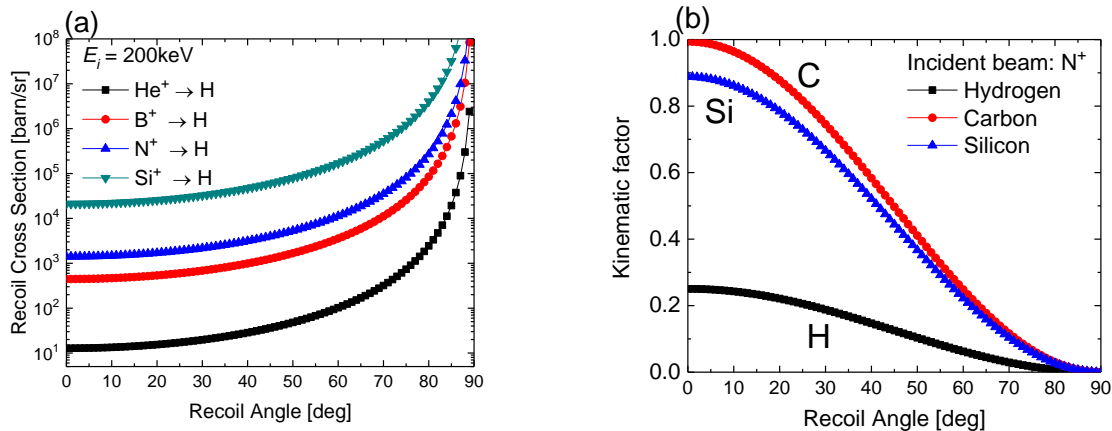

Figure 1. Recoil cross-section (a) as a function of recoil angle for 200keV He$^+$, B$^+$, N$^+$ and Si$^+$ ions incidents on H; (b) Kinematic factor for recoil events from H, C and Si targets for incident N$^+$ beam.

We were able to obtain hydrogen profiles for H-terminated Si(001), layers of 1-propanethiol, 1-octadecanetiol, and hafnium silicate films using 500keV Si$^+$, incident angle of 45° and ESA angles centered at 75°. Selected results for H-Si(001) and 1-octadecanetiol are presented in Figure 2(a) and (b), respectively. Assuming dihydride model for the H-Si(001) surface with coverage of 1.38×10^{15} H/cm^2, sensitivity of 2×10^{14} H/cm^2 is possible with the present setup. We note that damage effects are significant at these conditions, and surface needs to be refreshed under the beam (3.7×10^{14} ions/cm^2 exposures were used).
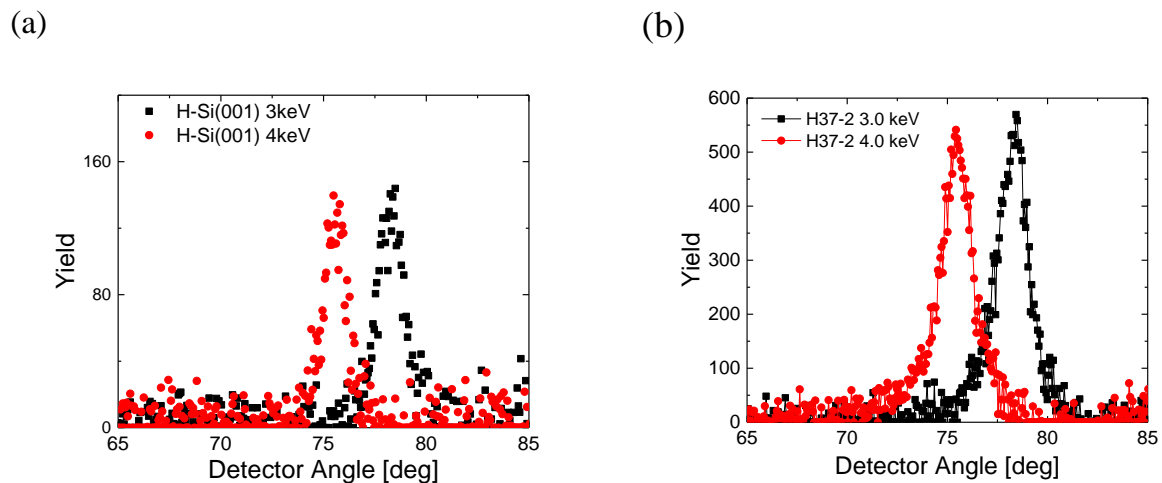
(a)   (b)

Figure 2. Elastic recoil spectrum of H from (a) a HF-etched Si(001) sample, (b) 1-octadecanetiol

comparing angular section measured at ESA energies of 3keV and 4keV. Note that background due to Si ions detected in this scattering geometry was subtracted.

In order to determine the absolute quantity of H on Si by this approach, the charge fraction of H-, (which is dependent on the energy) must be estimated in advance. Quantitative analysis of hydrogen content in these thin films is complicated by the presence of residual hydrogenated species after expose to air and in vacuum system, giving rise to so-called hydrogen surface peak. Comparison between ME-ERDA, ERDA and SIMS results will be discussed, as well as the limitations of such analyses.

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Development of advanced *in-situ* instrumentation for materials studies using medium-energy ion beams

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Ion beams form the basis for unique tools for thin film characterization in terms of composition and structure on nm to µm length scales. In parallel, the ongoing miniaturization makes it necessary to study continuously shrinking structures, challenging the analytical methods employed, and, in case of ion beams, requiring a reduction of the ion energies. With surfaces coming more into the focus for keV-beams, details in sample preparation protocols and materials processing procedures of the highest standards in terms of cleanliness become of increased importance. Thus, *in-situ* preparation of materials is a logical next step for detailed studies of material properties when studying near-surface composition and structure of material systems. Furthermore, such instrumentation permits to follow materials synthesis and modification in real-time.

In this contribution, an *in-situ* sample preparation equipment connected to the Medium-Energy Ion scattering chamber [1] located at the ion implanter of the tandem laboratory national research infrastructure at Uppsala University will be presented. The preparation chamber features a number of surface modification techniques including: e⁻-beam evaporation, magnetron sputtering, ion bombardment surface sputtering, thermal annealing, residual gas analysis, or measurements of optical transmission.

At the current stage of the development, the benchmarking of the instrument was conducted to thoroughly explore the quality of the *in-situ* procedures for a variety of systems, including complex synthesis pathways of e.g. oxyhydrides, studied for their potential for smart windows, but also of thin film systems relevant in electronics, e.g. metal-silicides. The instrumentation also permits *in-situ* preparation of more fundamental systems, as required for basic research in ion-solid interaction, in particular self-supporting amorphous and single crystalline thin film targets.
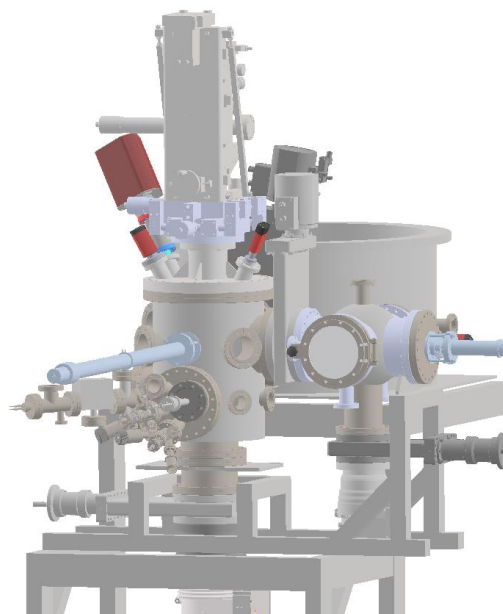

Fig.1: Computer-aided design of the *in-situ* preparation chamber at Uppsala University

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Development of Channeling ^{15}N-NRA for structure analysis of hydrogen in nanofilms and subsurfaces

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Hydrogen (H) has a possibility to modify the physical properties of host materials such as superconductivity and metal-insulator transition, etc. The H amount and its location are crucial for these phenomena. Because the H atom potentially occupy a metastable site in nanofilms and subsurfaces due to the surface effects and the lattice distortion, H in nanofilms and subsurface regions is expected to exhibit anomalous properties. To perform the structure analysis of the H atom in nanofilms and subsurfaces, we have developed an apparatus for Channelling ^{15}N-NRA using ^{1}H(^{15}N, $\alpha\gamma$)^{12}C nuclear reaction analysis combined with Ion Channelling technique at the 1E beam line of Micro Analysis Laboratory (MALT) in the University of Tokyo. A monochromatized ^{15}N^{2+} beam is delivered to samples mounted on a three-axes rotational stage in a UHV chamber with a base pressure below 1×10^{-5} Pa as shown in Fig. 1. By scanning the incident beam angle, we can directly determine the lattice location of the H atom in nanofilms and near surfaces in a depth-resolved manner. We show the results of structure analysis for TiH$_{2-\delta}$ nanofilms and metastable PdH$_x$.

We investigated the H sites in a 100-nm-thick epitaxial TiH$_{2-\delta}$(110) film. We successfully obtained the two-dimensional mapping of ^{15}N-NRA as functions of incident angles. In combination with beam trajectory simulations, we found that 5 at. % of the H atom occupy the octahedral site whereas the H atom are mainly located in the tetrahedral site [1]. We also demonstrated that the lattice location of hydrogen is tuned by the isotope effect.

We analyzed the structure of a metastable PdH$_x$ formed by low-energy hydrogen ion implantation at low temperature. PdH$_x$ was formed in the range of 40 nm of a Pd(100) single crystal. It was revealed that the implanted H atom partially occupy the tetrahedral sites and migrate to the octahedral sites by annealing. The depth dependence of ^{15}N-NRA yield showed that the tetrahedral site occupation of the H atom is enhanced within ~3 nm from the surface. Combined with electrical resistance measurements, we successfully derived the H hopping rate from the tetrahedral to octahedral sites [2]. Whereas thermal over-barrier hopping dominates the H diffusion above 80 K, quantum diffusion is clearly identified at low temperature. From the temperature dependence of the hopping rate, non-adiabatic effects by conduction electrons on the quantum tunnelling are discussed.
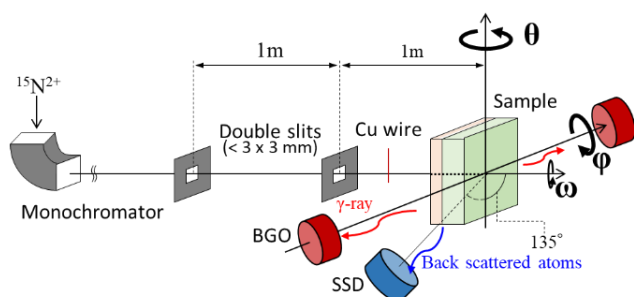
Fig. 1. Schematic illustration of the developed Channeling ^{15}N-NRA apparatus.

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