Medium Energy Ion Scattering – Technique and Applications

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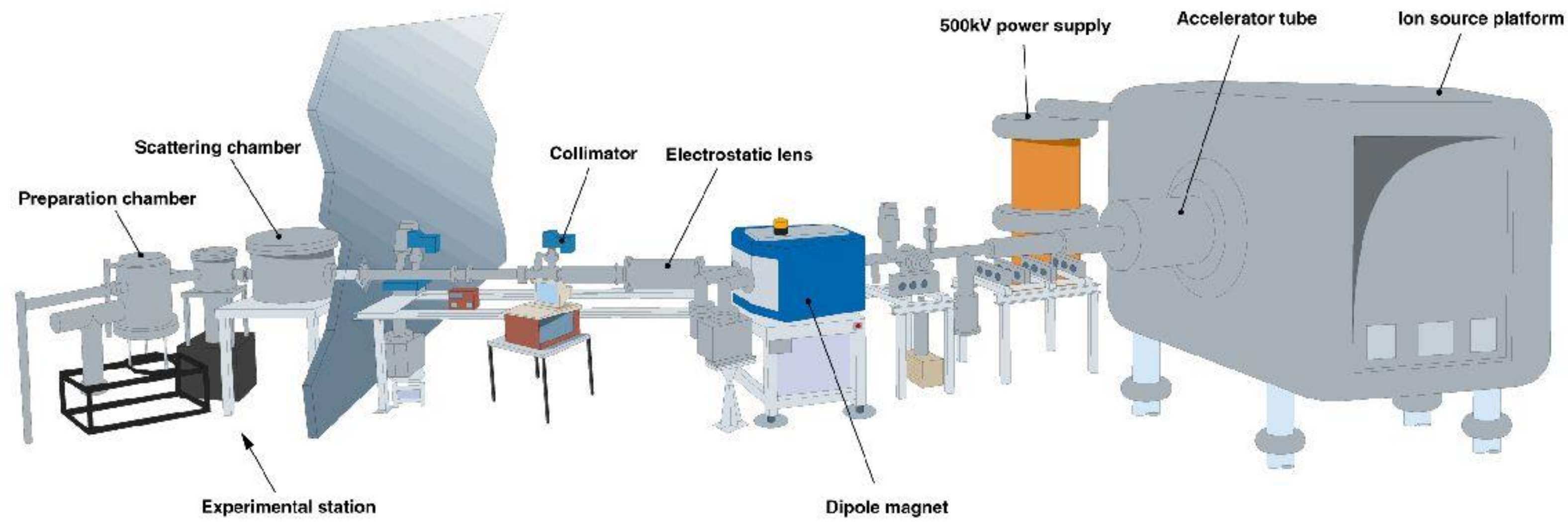
Overview

- The medium-energy ion scattering (MEIS) technique
- Applications of MEIS
  - Surface structure
  - High resolution depth profiling
  - Thin film characterisation
  - Characterisation of nanostructures
- Possible future research areas
- Summary

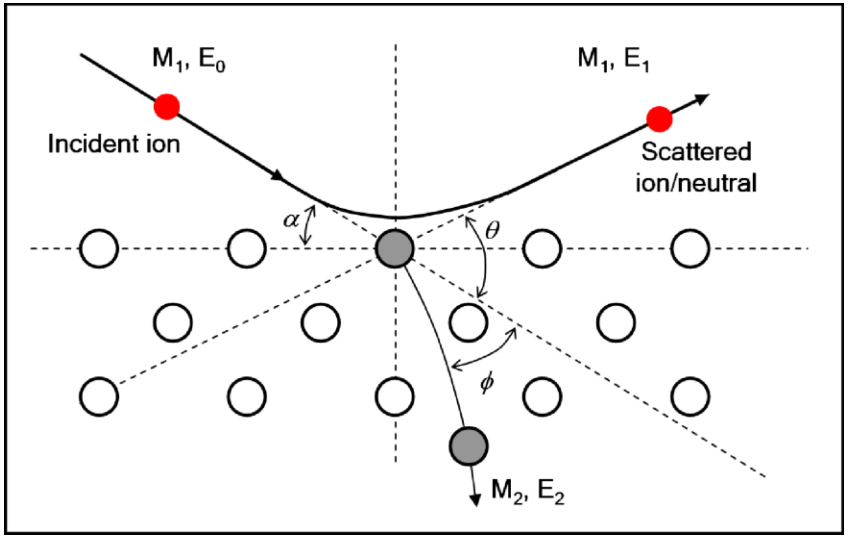
MEIS Technique



Medium energy light ions (50-250 keV H^+ or He^+) used to probe the surface and near surface of materials

- Energy losses during scattering
  - Elastic losses
  - Inelastic losses
- Angular variation in scattered ion intensity
  - Shadowing and blocking

Elastic scattering



$$E_1 = k^2 E_0$$

$$k^2 = \left[\frac{(m_2^2 - m_1^2 \sin^2\theta)^{1/2} + m_1 \cos\theta}{m_2 + m_1} \right]^2$$

- Simple ‘billiard ball’ collisions between ions and atoms
- Conservation of energy and momentum relates ion energy loss to mass of target atom

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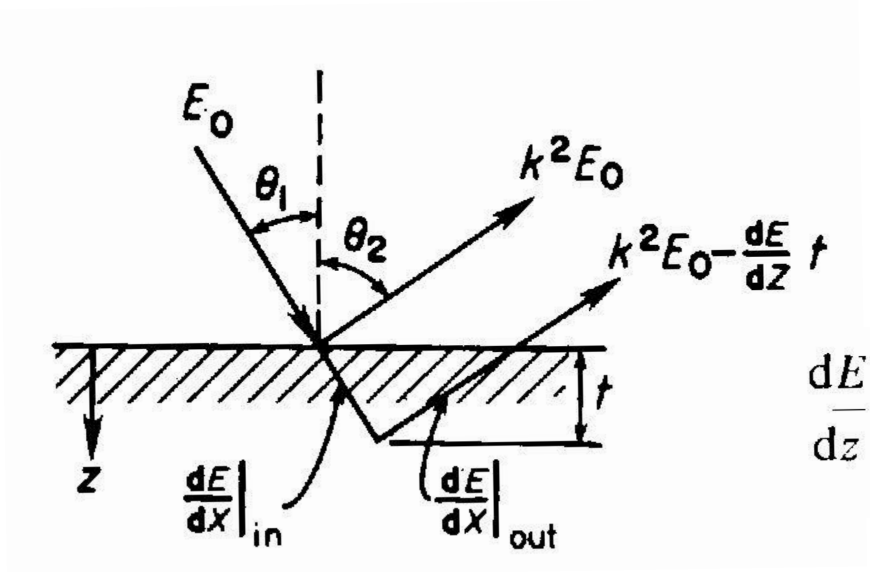
Inelastic Energy Loss



$$\frac{\mathrm{d}E}{\mathrm{d}z} = \left[\frac{k^2}{\cos\theta_1} \left(\frac{\mathrm{d}E}{\mathrm{d}x} \right)_{E_0} + \frac{1}{\cos\theta_2} \left(\frac{\mathrm{d}E}{\mathrm{d}x} \right)_{k_2 E_0} \right]$$

- Inelastic energy losses arise from electronic excitations as ion passes through sample
- Stopping powers well known (e.g. ‘SRIM 2013’)
- Resolution degrades with depth as process is stochastic (energy loss straggling)

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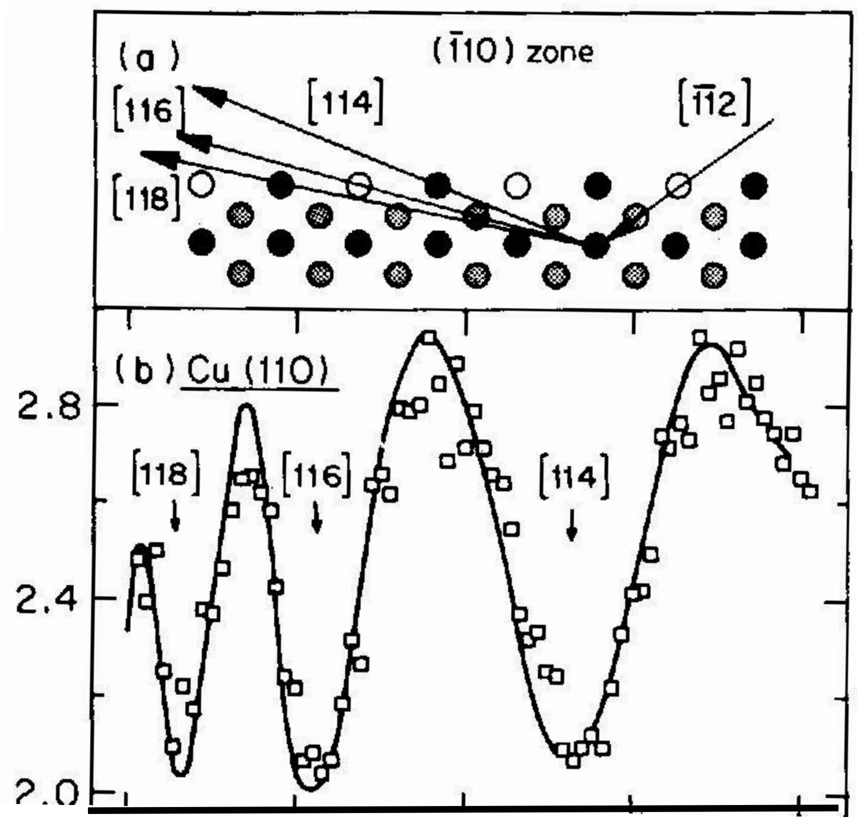
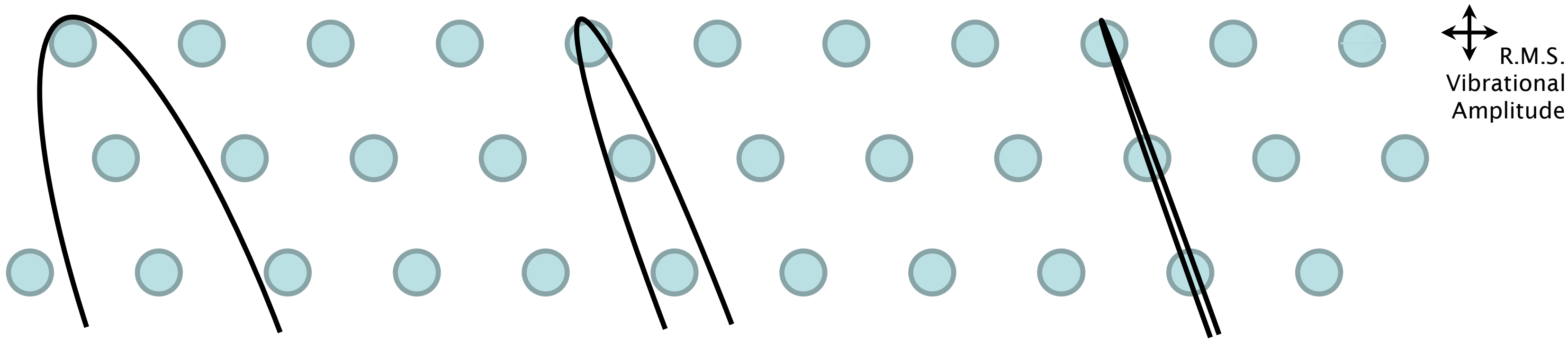
Angular Intensity Variation

- Shadowing effects used to select number of layers illuminated
- Blocking effects reveal relative positions of the atoms(i.e. the structure!)
- Shifts in blocking dips related to layer spacings (surface relaxations, strain)
- Amplitudes of dips indicate additional illumination (thermal vibrations, disorder)



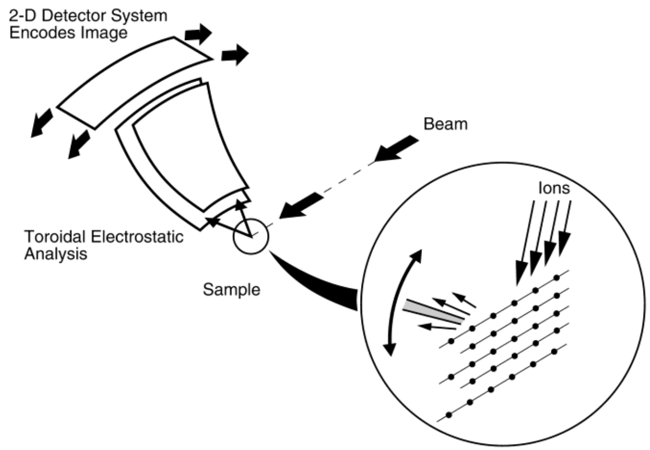
LEIS, MEIS and RBS

LEIS (1-5keV)	MEIS (50-400keV)	RBS (0.5-4MeV)

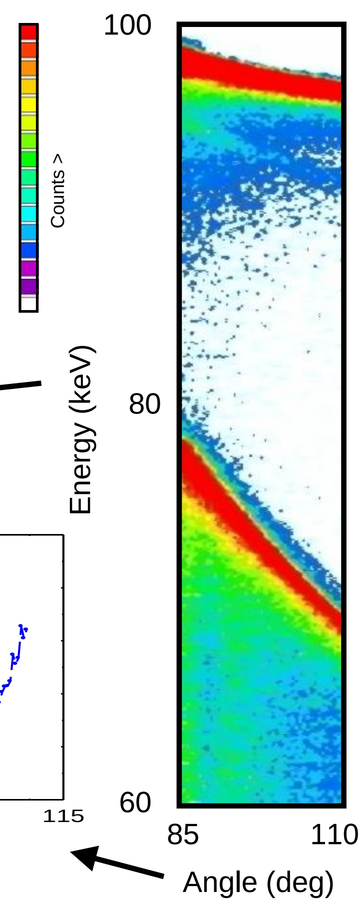


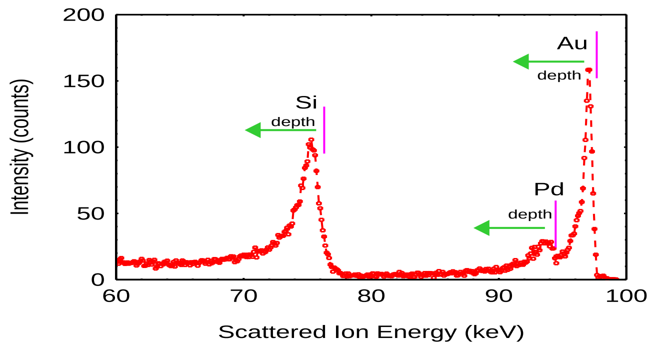
Shadow cone > vibrational amplitude	Shadow cone ≈ vibrational amplitude	Shadow cone « vibrational amplitude
Intrinsic surface specificity (1-3 atomic layers)	Tunable surface specificity (1-100 atomic layers)	Low surface specificity (20-thousands atomic layers!

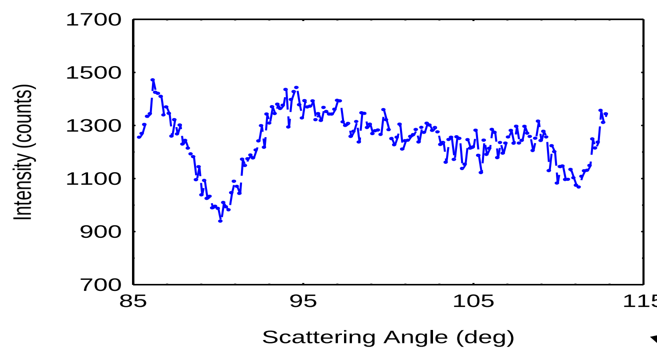
Medium Energy Ion Scattering



2D image







Elastic scattering gives compositional information

Inelastic scattering provides depth information (and morphology!)

Angular variation in the scattering intensity gives structure

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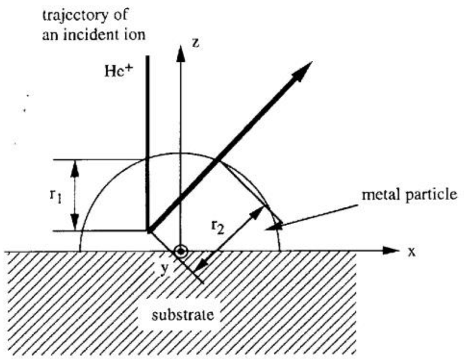
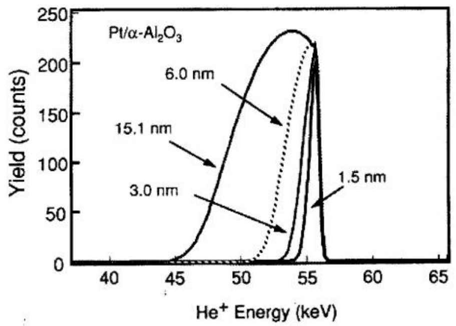
Capabilities of MEIS

- Depth selectivity, excellent structural sensitivity
  - **Surface structure (~2 pm resolution)**
- Compositional sensitivity over the near surface
  - **High resolution depth profiling (2 - 5 Å resolution)**
- Ability to simultaneously determine composition and structure
  - **Full characterisation of thin film materials**
- Path length sensitivity
  - **Composition, structure and morphology of nanoparticles**





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Surface Structure

Metals and metal alloys

- Adsorbate induced reconstruction
- Model catalysts
- Complex metal alloys (e.g. quasicrystals)

Semiconductor materials

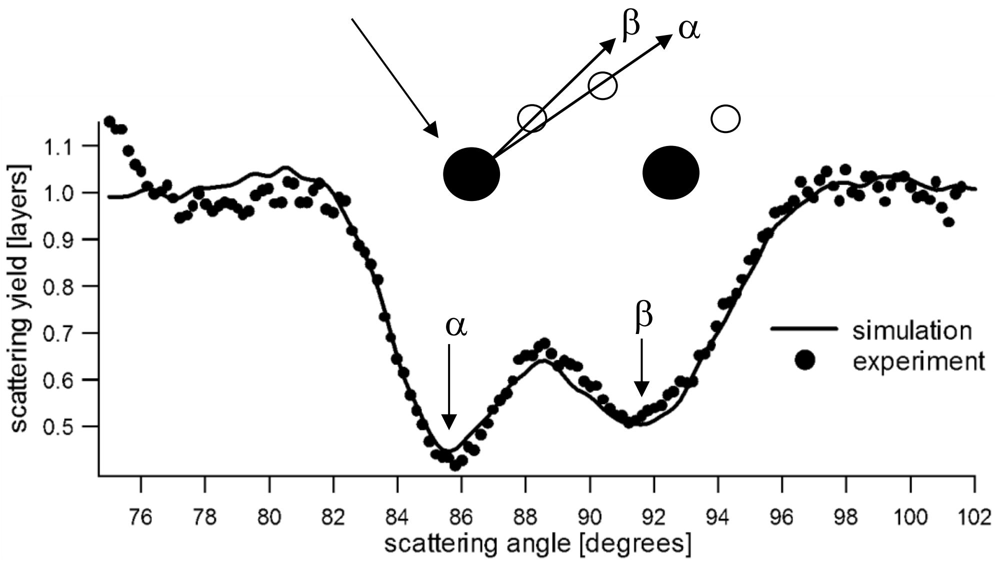
- 'Ideal' Schottky Barriers
- III-V growth surfaces

Oxides

- Catalyst supports (e.g. TiO_2)

Rare Earths and Semiconductors

- Rare earth silicides have low Shottky barrier heights – useful for metal/ semiconductor junctions
- 1 monolayer of rare earth on Si or Ge can form a 2-dimensional compound
  - Er on Si(111), Ho on Si(111), Dy on Si(111), Gd on Si(111), Y on Si(111), Tm on Si(111), Dy on Ge(111)
- Example is dysprosium germanide on Ge(111) – angle spectrum contains surface structural information



- Dy is covered by a single bi-layer of Ge
- Orientation of the bi-layer is reversed with respect to the bulk atoms

Dy on Ge(1x1) - Hydrogen Termination

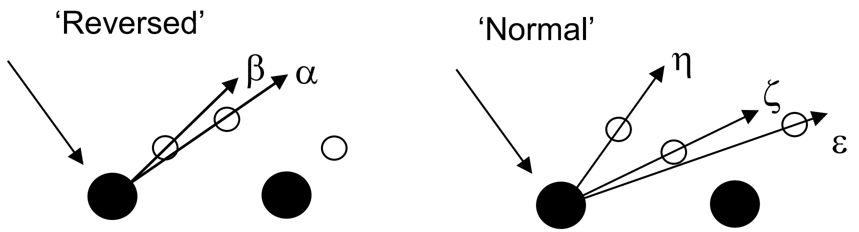
Ge(111) – (1x1) – Dy surface dosed with 0.7 ML atomic H

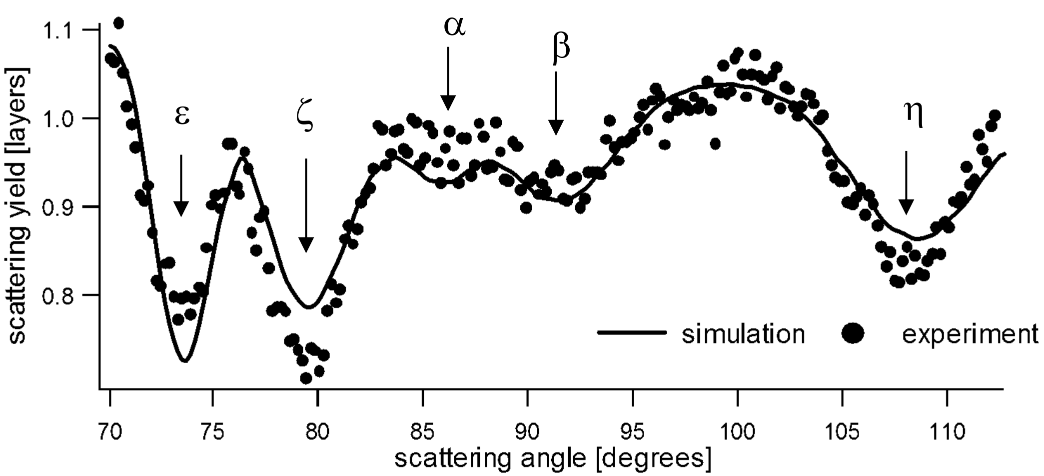
Induces dramatic reconstruction of the surface

Large increase in the Dy-Ge bond length possibly indicating inclusion of H into the layer

Ultimate goal to grow 'normally' oriented Si above 2D silicide

- 'Ideal' delta doped layer
- Searchlight technique for other structures on Si





Spence et al, Phys. Rev. B 62 (2000) 5016

High Resolution Depth Profiling

Semiconductor device fabrication

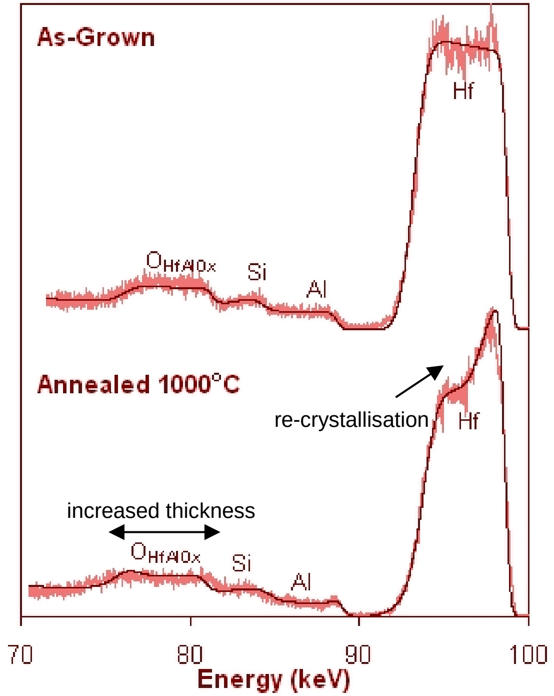
- Ion implants for semiconductor devices
- High-κ gate dielectric materials

Structural materials

- Oxide layers for Corrosion protection of light metal alloys
    - Construction materials
    - Automotive, aerospace, rail and marine transport applications
- Biocompatible coatings for medical implants

MEIS of ALD grown high-K films

- Moore's Law (ITRS) requires high dielectric constant gate oxides to reduce leakage currents
- Amorphous Hafnium oxide has high permittivity but high temperature processing can cause sub-surface SiO_2 growth and film re-crystallisation



- MEIS energy spectra sensitive to both sub-surface SiO_x growth and re-crystallisation
- Quantitative information on sub-surface oxide thickness obtained by fitting data with simulated spectra

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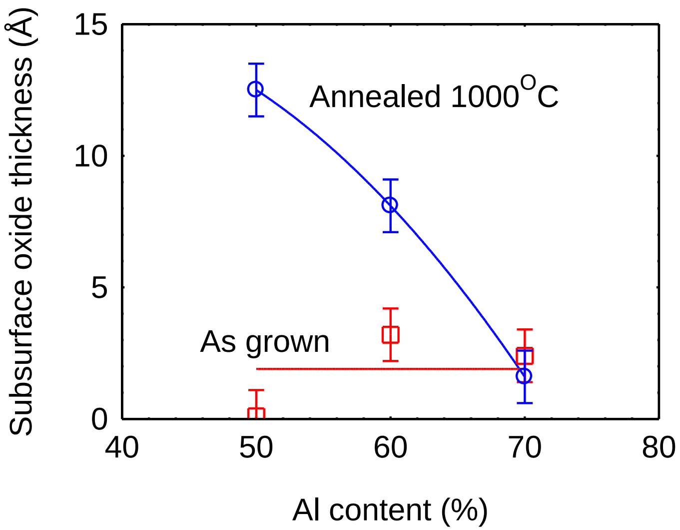
MEIS of ALD grown high-K films

Anneal Temp (°C)	Al:Hf ratio (%)	$HfAlO_x$ (nm)	SiO_x (nm)	Interface (nm)
As grown	61	12.2	3.2	0.84
800	59	11.8	2.8	0.85
900	58	11.3	3.9	1.04
1000	58	11.1	8.1	1.01
As grown	47	13.1	0.1	1.05
1000	48	11.5	12.5	1.14
As grown	73	14.5	2.4	0.90
1000	73	14.3	1.6	1.89



- 70% Al content shows no difference between as-grown and annealed samples
- Binary alloys such as $HfAlO_x$ and $HfSi0_x$ can suppress sub-surface SiO_2 growth
- From 45 nm node $HfSiO_xN_y$ used

Potter et al, App. Phys. Lett. 205 (2003) 121

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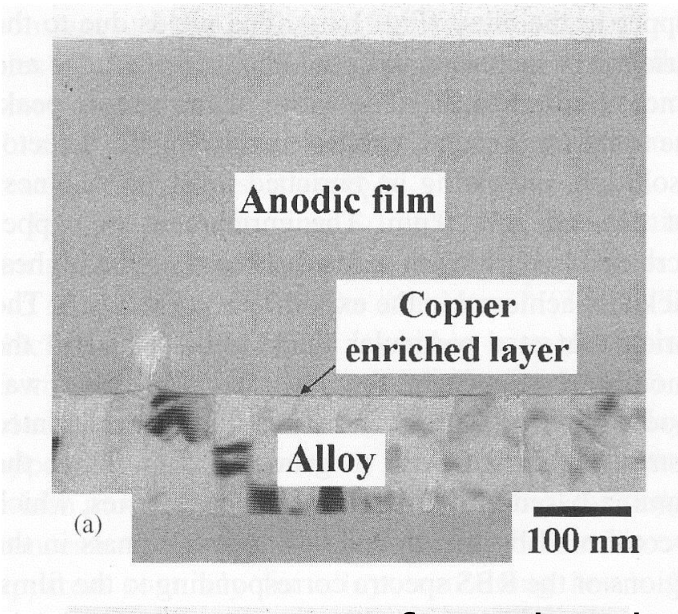
Corrosion Protection of Light Alloys

Typically dilute alloys of Aluminium used for improved corrosion resistance

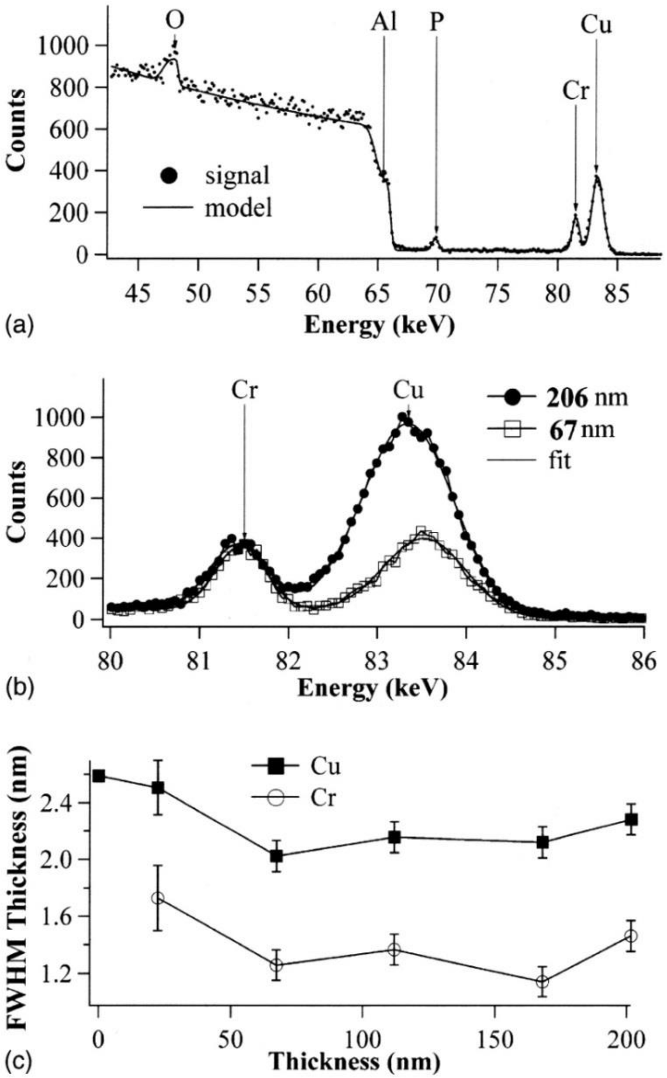
- Al-0.3at%Zn
- Al-0.7at%W
- Al-0.2at%Mn
- Al-0.4at%Cu



X-TEM image of anodized Al-0.4at%Cu sample

What happens to minor alloying element during oxide film growth?

Enrichment in Al-0.4at%Cu Alloy



- Anodic oxidation leads to Cu enriched layer below the grown film
- Film is stripped using chromic/phosphoric acid before analysis
- Data reveals constant thickness of enriched layer with anodization time
- Increase in Cu content attributed to increased cluster generation

Garcia-Vergara et al, App. Surf. Sci. 205 (2003) 121

Thin Film Characterisation

Systems which benefit from the simultaneous elucidation of composition and structure

- Metal-on-metal growth (giant magneto-resistance films)
- Quantum well systems (III-V materials, metals)
- Spintronic materials (metal/semiconductor hybrids)

Fe on *i*-AlPdMn

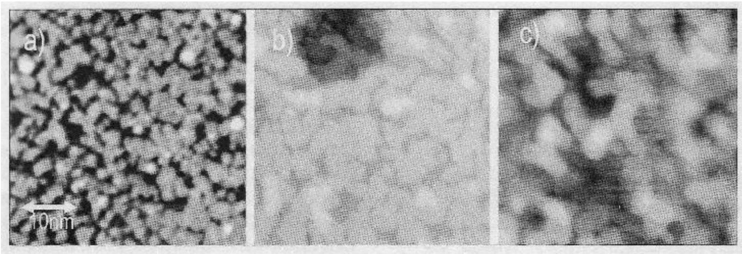
Growth of magnetic films on five-fold surface of *i*-AlPdMn quasicrsytal – unusual properties?

Weisskopf et al [Surf. Sci. 578 (2005) 35] LEED, SEI and MOKE

- < 4 ML Fe diffuses, surface disordered
- 4–8 ML Fe_3Al film formed, five domain cubic(110) showing magnetic ordering
- 8 ML bcc(110) planes tilt by 0.5˚
- Sputtering films leaves Al depleted surface

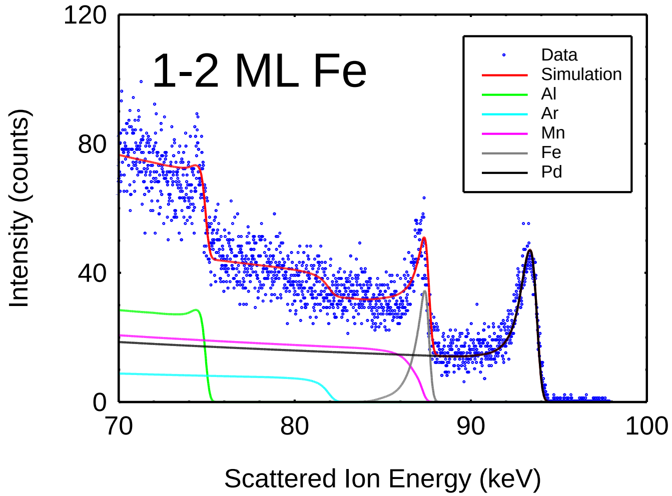
Wearing et al [Surf. Sci. 601 (2007) 3450] STM and AES

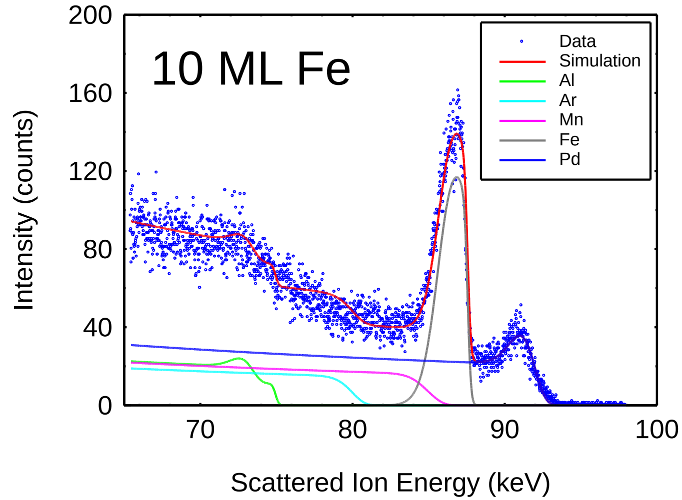
- Layer-by-layer growth of disordered pure Fe below 3 ML
- Five domains of bcc(110) oriented Fe above 3 ML

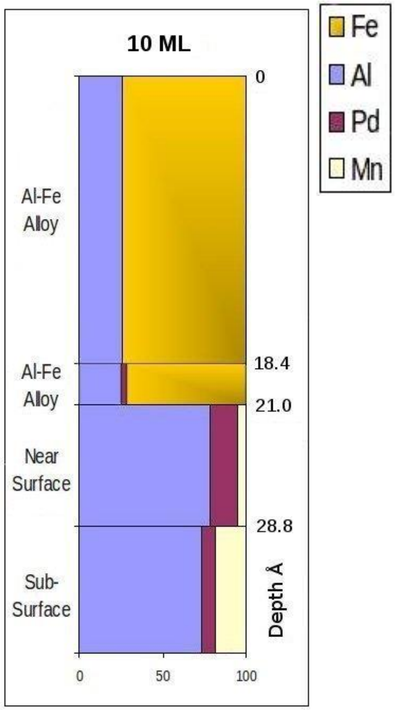


1.3 MLE 2.6 MLE 4.5 MLE

Composition Data







Thin (1-2 ML Fe)

Alloy formation indicated

Thick (~10 ML Fe)

Fe_3Al film formed at surface

Sub-surface layer of mixed Fe and Al with some Pd (possibly Mn as well)

No Al depleted layer

- sputtering artefact!

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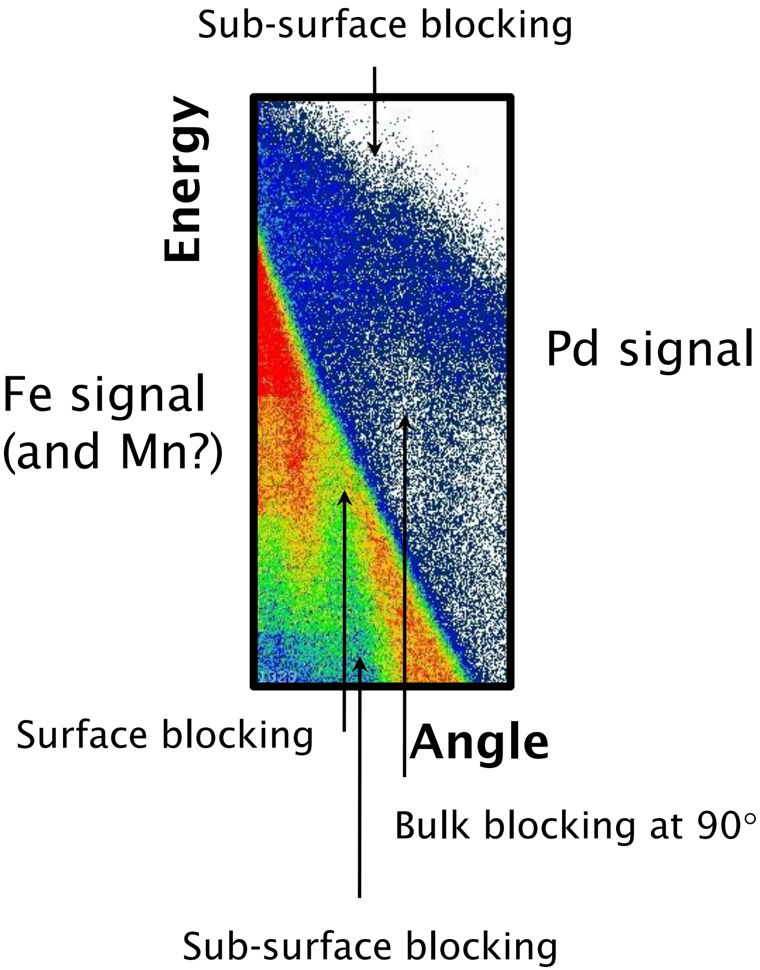
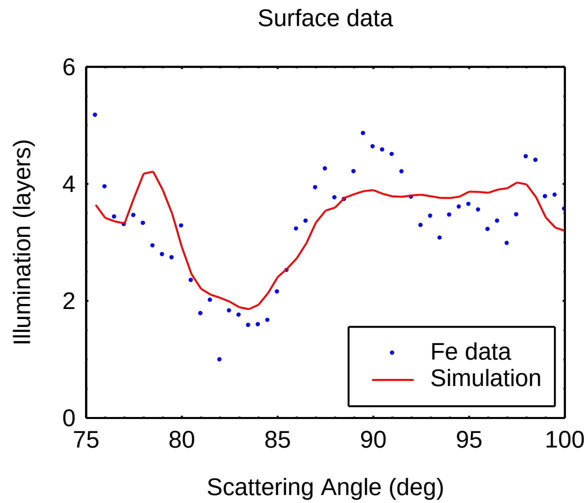
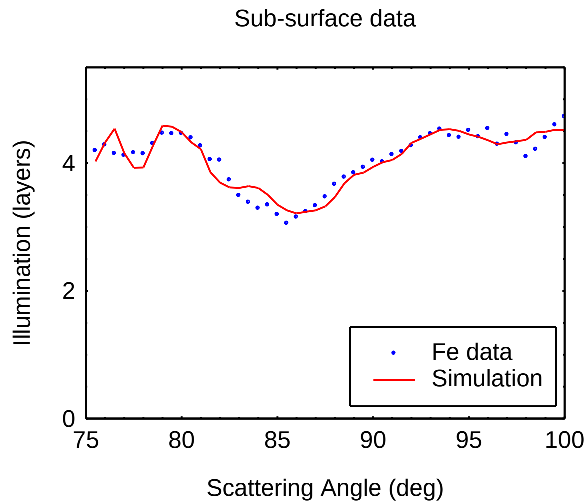
Thick Fe Film structure





- bcc-like
- (110) orientation
- well ordered
- compressed 5.5% (lattice parameter 2.98Å)

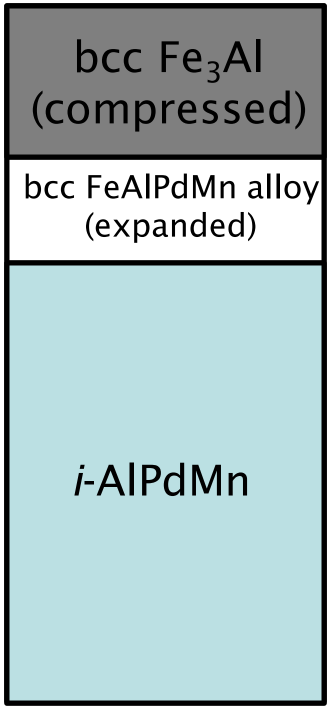


- bcc-like
- (110) orientation
- 40% disorder
- expanded 2.0% (lattice parameter 3.05Å)

Fe data extracted by curve fitting routine
Fitted using VEGAS simulation code

Fe on *i*-AlPdMn

- If Fe content drops significantly below 75% film becomes non-magnetic and lattice parameter changes
- However, lattice parameter change is in the wrong direction!
- Change likely to be caused by high degree of disorder as seen in previous studies of cold-worked FeAl alloys
- Film probably in the magnetic phase throughout
- Results more consistent with previous LEED/SEI/MOKE studies



Noakes et al, Surf. Sci. 620 (2014) 59

Nanoparticle Characterisation

Topographical information

- Single element clusters

Compositional information

- Bimetallic alloys (model catalysts)
- III-V quantum dots

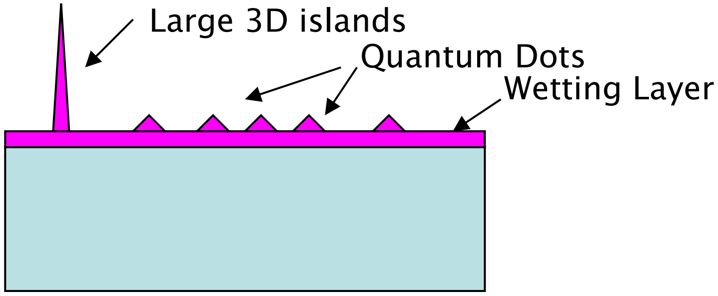
Structural Information

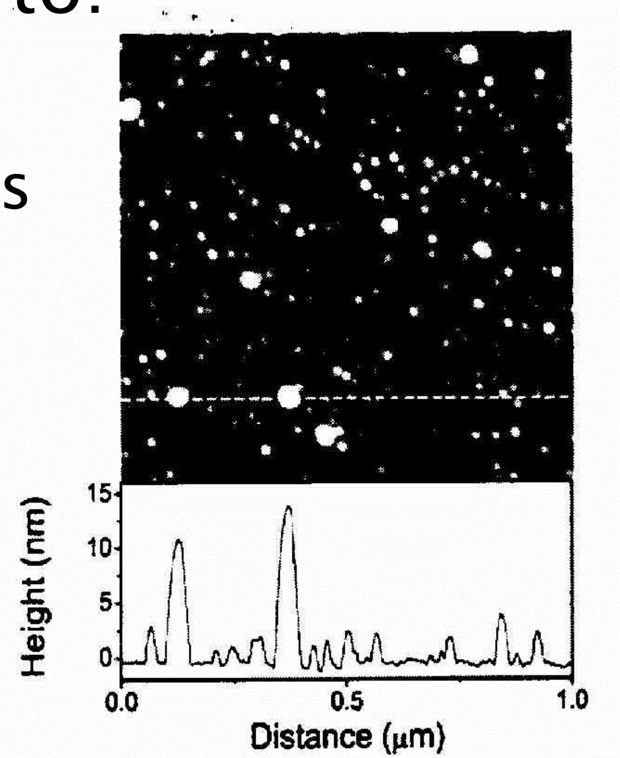
- All the above!

Self-assembled InAs Quantum Dots on GaAs

InAs deposition on GaAs leads to:

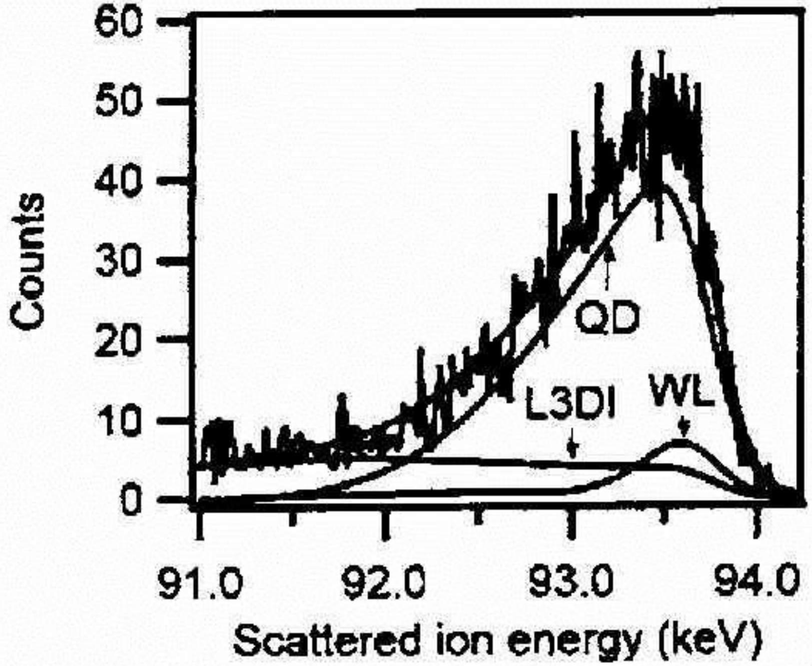
- InGaAs wetting layer
- Regular well-defined quantum dots
- Larger 3D islands





Dot size and shape determined from AFM

Quantum Dots Results



Wetting layer and large 3D islands included as well as quantum dots

In intensity fitted using linear profile from 20% to 100% at the top of the QD

First independent measurement of the composition profile of materials of this type!

P.Q. Quinn et al, App. Phys. Lett. 87 (2005) 153110

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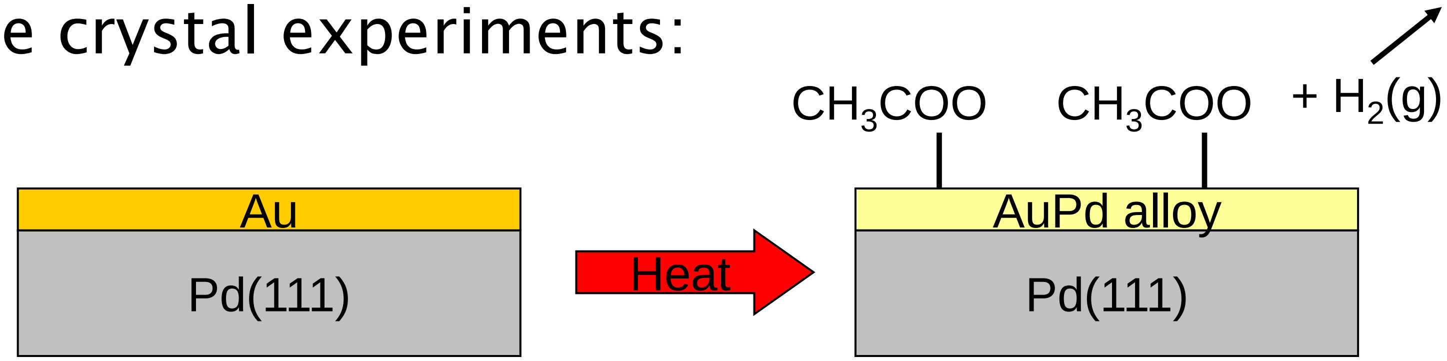
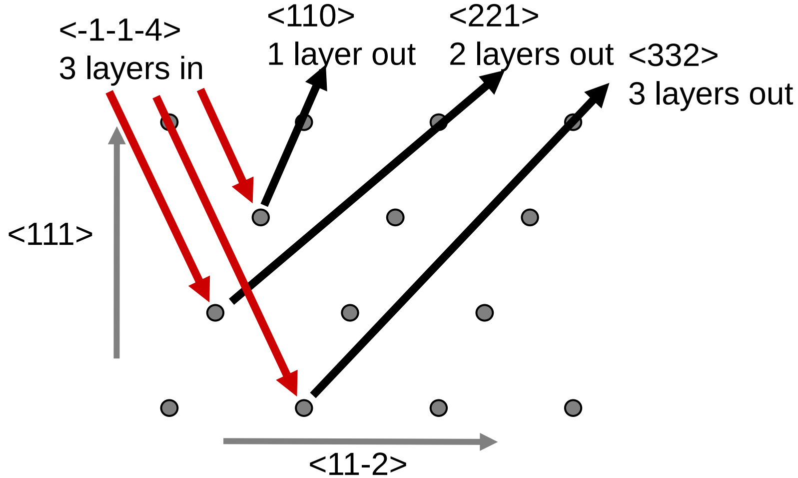
Au-Pd Catalysts for Vinyl Acetate Monomer Synthesis

$$C_2H_4(g) + CH_3COOH(g) + \frac{1}{2}O_2(g) \rightarrow CH_3COOC_2H_3(g) + H_2O(g)$$

Single crystal experiments:

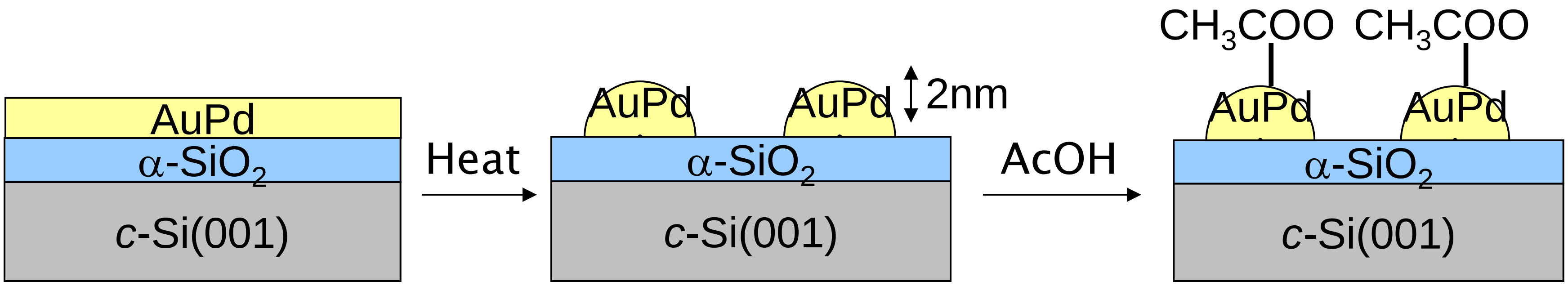


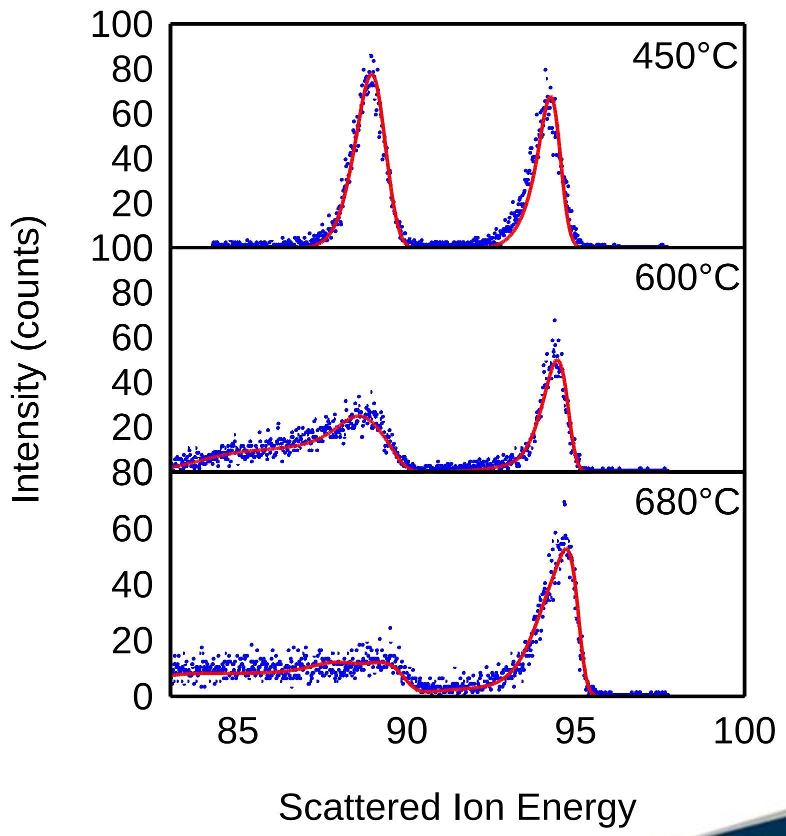


MEIS experiments can easily reveal the layer-by-layer composition using selective illumination geometries

How relevant is this to real catalysts?

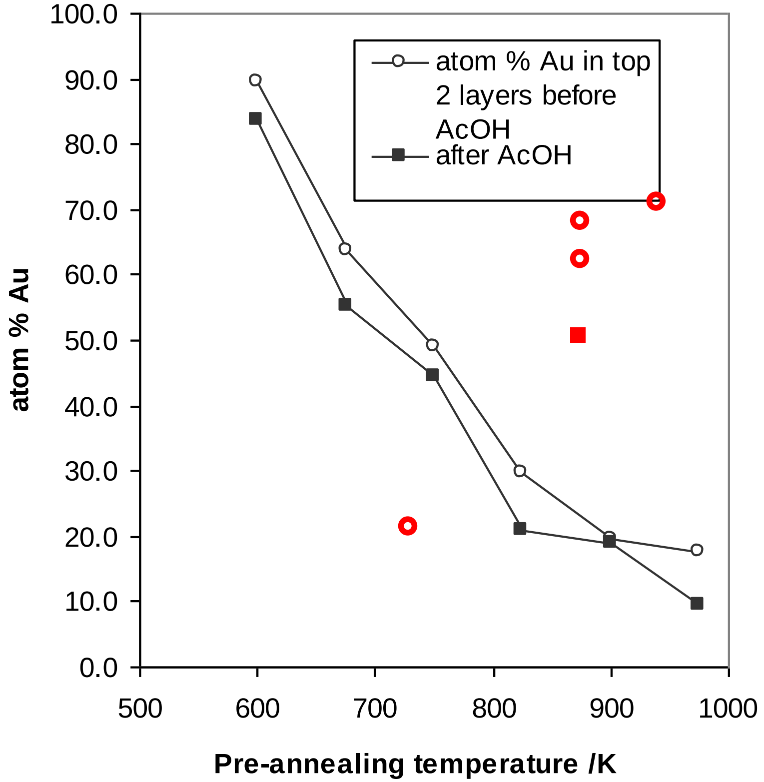
Au-Pd Clusters on SiO_2/Si(100)





Detailed fitting of the MEIS energy spectra including information on cluster size and coverage

Comparison with Single Crystal Work



Temperature dependence opposite of single crystal studies

Adsorbate induced surface segregation still seen

More realistic models improve the catalytic relevance of the results!

Haire et al, Surf. Sci. 605 (2011) 214

Future Research Using MEIS

Semiconductor device fabrication

- Dielectric layers
- Ion implantation
- Metalisation

Catalysts

- Oxide support materials
- Bimetallic nanoparticles
- Adsorbate induced segregation studies

Structural materials (light metal alloys)

- Rail, automotive, marine and aerospace applications

Future Research Using MEIS

Biomedical applications

- Joint replacements, dental implants

Photovoltaic materials

- Multi-junction solar cells
- II-VI quantum dot based solar cells
- III-V quantum well LED's

Magnetic materials

- Magnetic tunnel junctions
- Novel memory materials (MRAM, race track, etc)
- Spintronic materials (metal-semiconductor hybrids)

Future Research Using MEIS

The ‘Hydrogen economy’

- Photo-catalysts
- Hydrogen storage materials
- Fuel cells

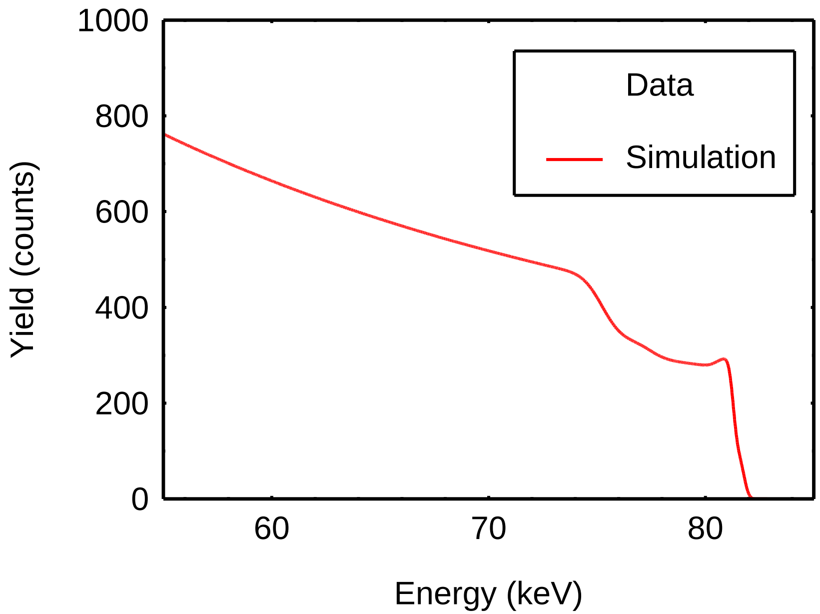
Nanometrology

- SIMS Calibration
- Elipsometry and other optical techniques

Others???

Photocathode R&D

Cu photocathode for VELA accelerator cleaned using O plasma treatment – surface chemistry?



MEIS can elucidate the thickness and stoichiometry of the oxide layers and the effect of heat treatment

Summary

MEIS is a fantastic technique for investigating the surface and near-surface region of materials

Simultaneous measurement of composition and structure

High sensitivity to structural parameters (~2 pm)

Virtually monolayer depth resolution

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Acknowledgements

Daresbury – Paul Bailey, Kevin Connell, Steve Bennett, Graham Bushnell-Wye, Brian Blackwell, Mark Pendleton, Paul Whitfield, Steve Davis, Simon Letts, Vic Pucknell

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