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Joint ICTP/IAEA Workshop on Advanced Simulation and Modelling for Ion Beam Analysis

23 - 27 February 2009

IBA XVI Complementary Techniques
MEIS, LEIS, XRD, XRF, AES, TEM

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Complementary Techniques **I**

Joint ICTP/IAEA Workshop on Advanced Simulation and Modelling for Ion Beam Analysis

23 - 27 February 2009, Miramare - Trieste, Italy

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Friday February 27th 2009

Contents

- X-ray Fluorescence
- X-ray Diffraction
- Transmission Electron Microscopy
- Medium Energy Ion Scattering
- Low Energy Ion Scattering
- Auger Electron Spectroscopy

X-ray Fluorescence (XRF)

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- X-rays in, X-rays out
  - Atomic de-excitation as for PIXE
- *COMPETITOR TECHNIQUE!*
- Fluorescence cross-sections << particle ionisation
  - XRF absolute sensitivity ~ nanograms
  - *cp. μPIXE absolute sensitivity ~ femtograms*
- XRF flavours
  - TRXRF: total reflection XRF
  - Sy-XRF: synchrotron XRF
  - Polarisation
  - Confocal techniques with polycapillary lenses
- Apparatus simple compared to PIXE
- Less beam damage with XRF

XRF: when to use it?
use it when you can!

- **Incident X-ray beam more penetrating than protons**
  - **Advantage for XRF for thick homogeneous samples and coarse depth profiling of thick layered samples**
  - **Advantage for PIXE/EBS for thin layered samples**
- **XRF cross-section *decreases* towards lower energies**
  - **PIXE is opposite!**
  - **Sy-XRF can be used cleverly to distinguish close lines**
- **Quantification**
  - **Fundamental parameters: XRF (& PIXE) often hard**
  - **PIXE + backscattering is much easier**
- **Mapping clumsy for XRF**
  - **Real strength for μPIXE/EBS**

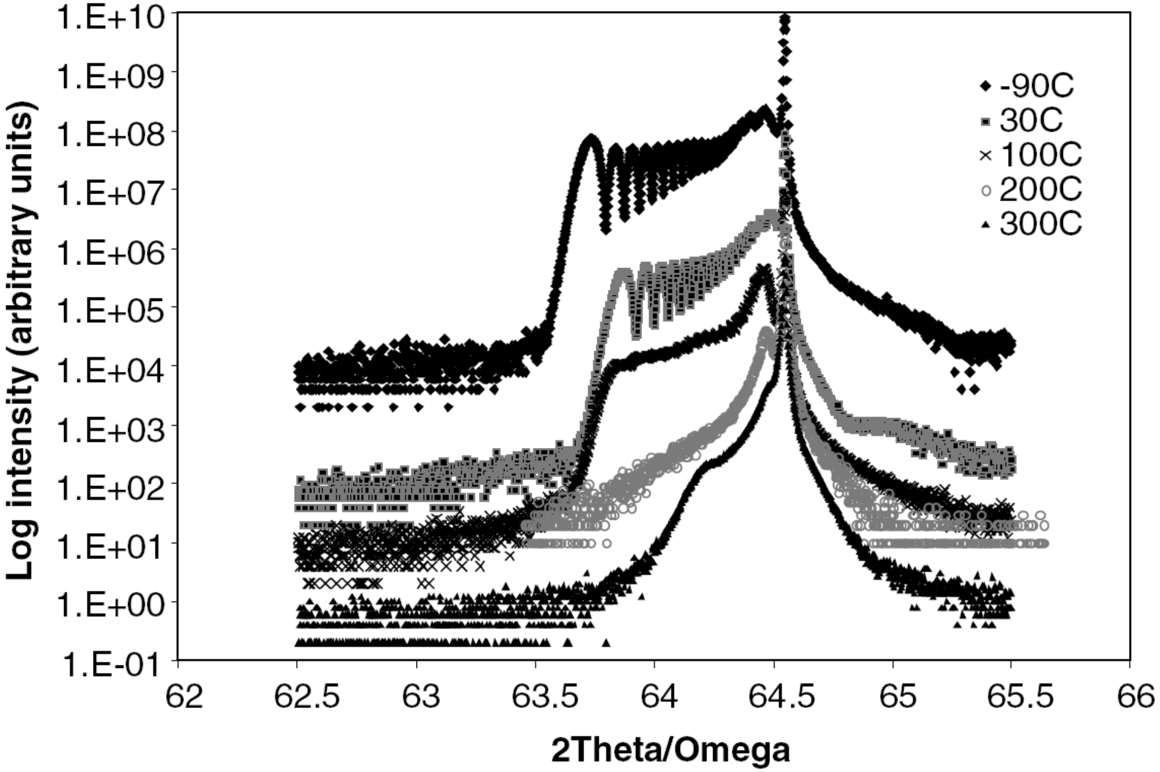
X-ray Diffraction (XRD)
also applies to electron diffraction

- Interference method: *essentially* in *reciprocal space*
  - no direct depth information
  - mathematically: Fourier transform of ensembles
  - selected area techniques give some 2D info
- Unit cell dimensions
  - Single crystals or polycrystalline samples
- Texture
  - preferred orientation
- Grain Size
  - Fourier transform of a constant is a delta function
  - limited grain size implies finite linewidth

XRD Methods

- **Powder diffraction**
- **Single crystal**
    - **back-reflection or transmission Laue method (white)**
    - **rotating crystal (monochromatic)**
    - **Lang topography**

Single Crystal XRD



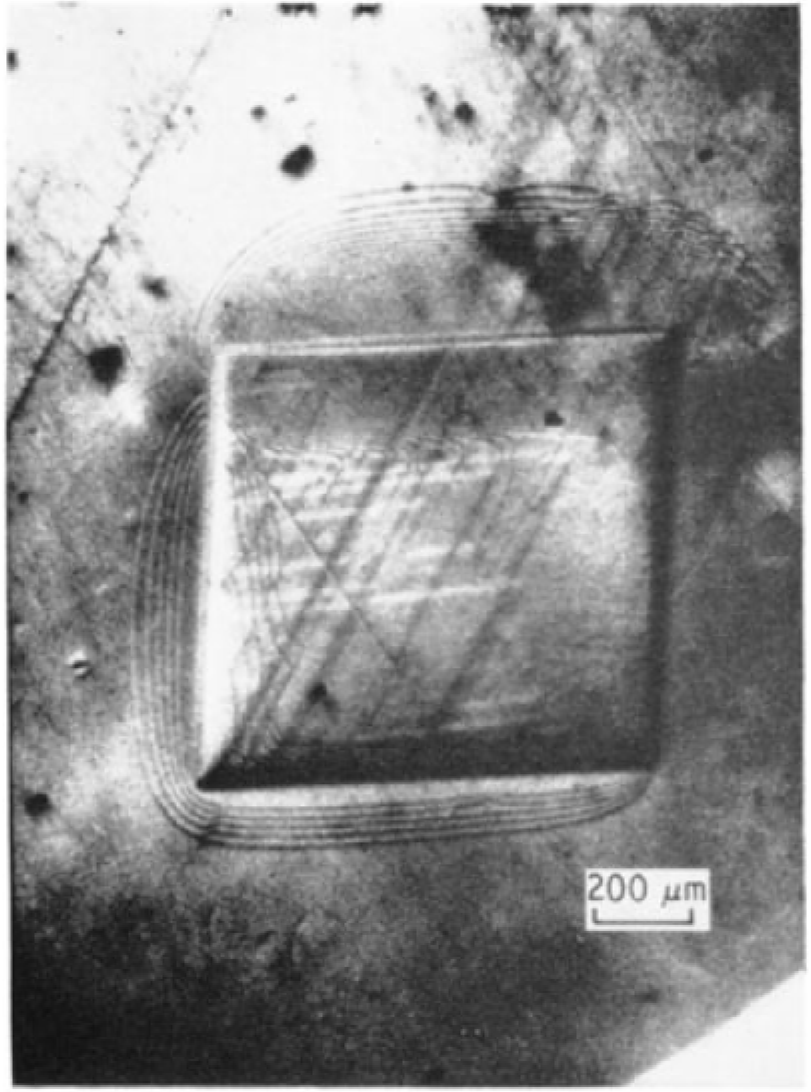
Double axis X-ray diffraction (004)

GaAs with 10^{17} H/cm^2

Different implantation temperatures shown

The influence of the ion implantation temperature and the flux on smart-cut© in GaAs, Webb M, Jeynes C, Gwilliam R, Too P, Kozanecki A, Domagala J, Royle A, Sealy B: *Nucl.Instrum.Methods B* 240, 2005, 142-145

Lang Topography



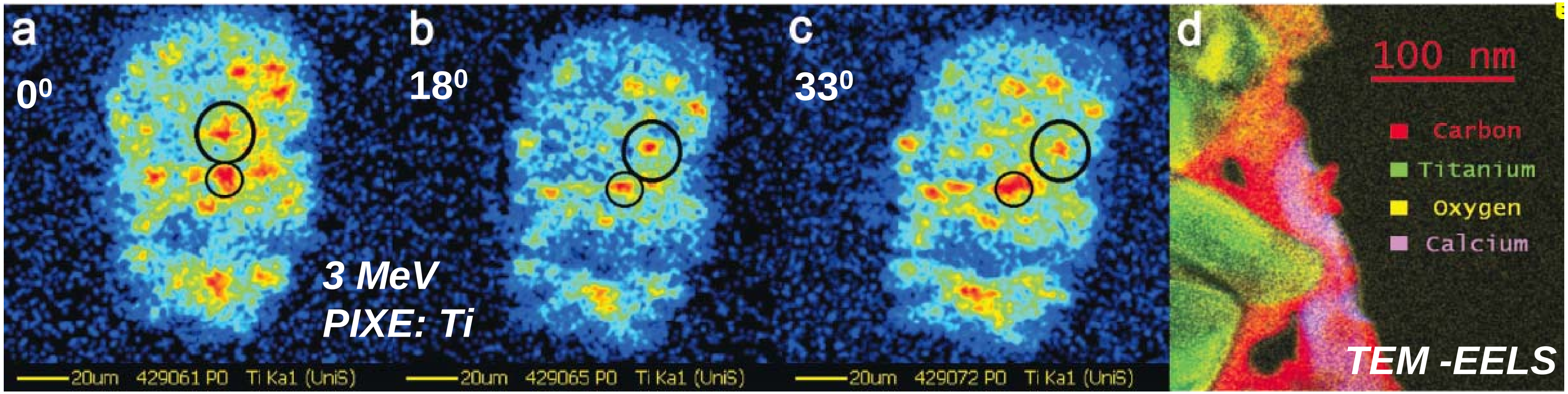
Lang Topograph

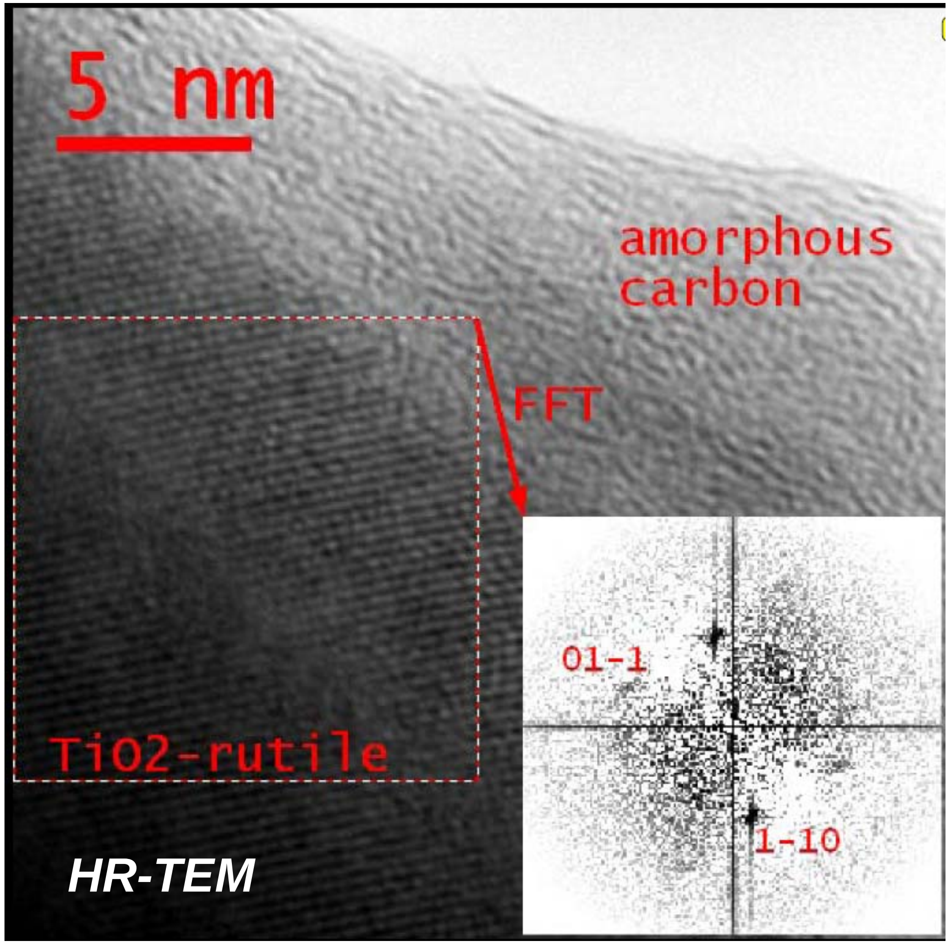
Divergent beam stationary topograph of B-doped Si: Cu Kβ radiation

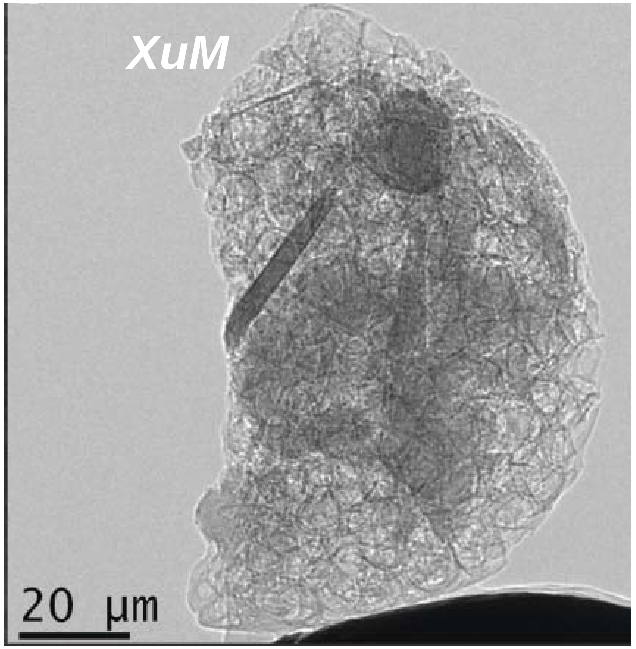
High resolution divergent beam X-ray topography, B.K.Tanner & C.J.Humphreys: J.Phys.D: 3, 1970, 1144-1146 (2 plates)

Transmission Electron Microscopy (TEM)

- **Extraordinarily powerful set of techniques**
  - imaging
  - high resolution (phase contrast)
  - ultra-high resolution (with aberration correction)
  - bright field / dark field (diffraction)
  - SAD (selected area diffraction)
  - EDX (quantitation hard)
  - EELS (electron energy loss spectroscopy): resonant absorption of electron energy at the atomic absorption edges give spacially resolved elemental information
  - confocal methods (STEM)
  - wonderful engineering







XuM: X-ray ultra-microscope

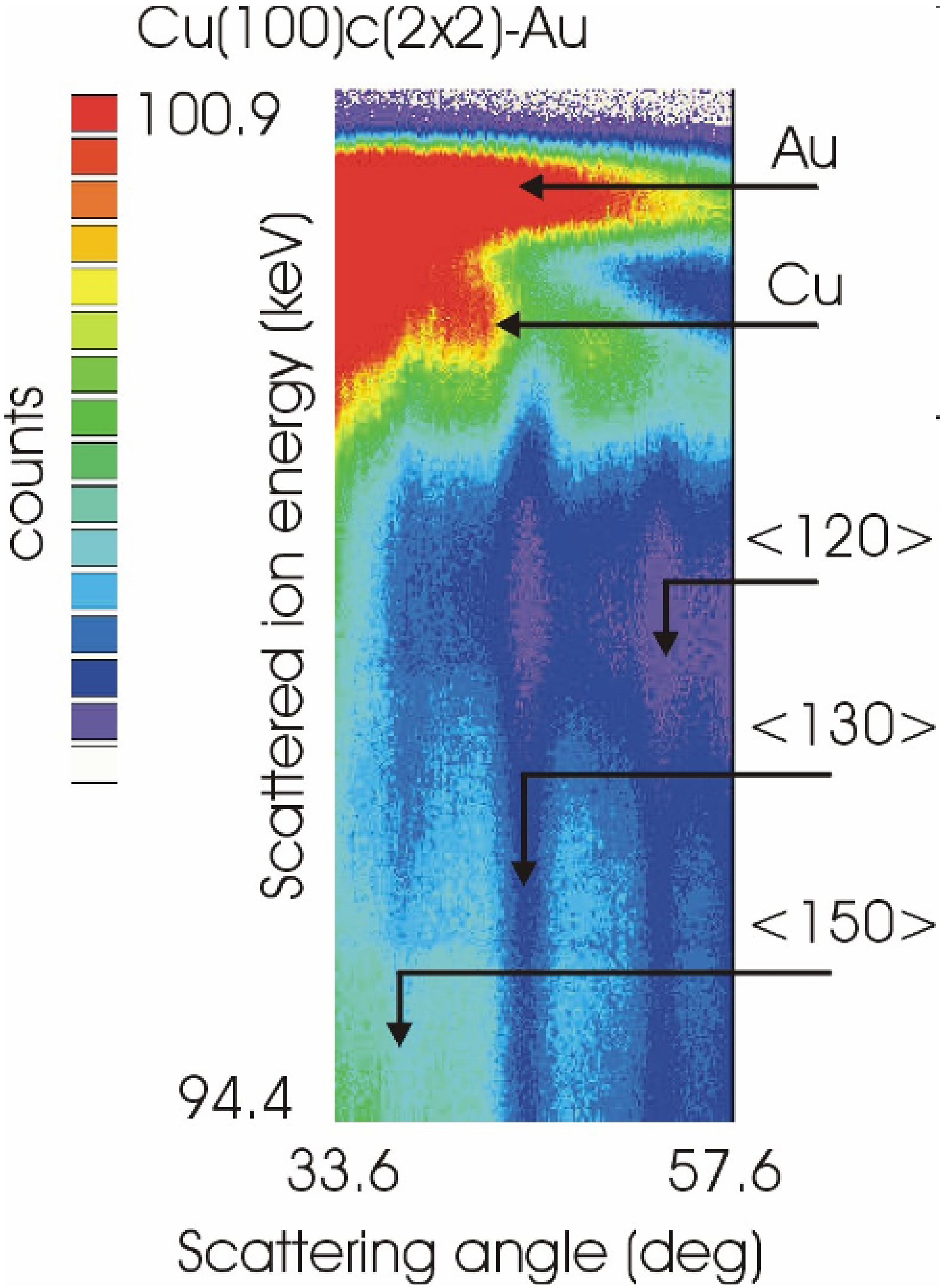
X-ray tomography with ultra-focussing for high spacial resolution

Inclusion in a Darwin impact glass: Ti micro-inclusions

The fate of organic carbon during meteorite impact: Kieren Howard, Melanie Bailey, Chris Jeynes, Vlad Stolojan *et al*, in preparation

Medium Energy Ion Scattering
MEIS

- RBS, but with eg. 100 keV H^+ beam
  - medium energy beam near maximum of stopping curve to maximise depth resolution
  - one atomic layer resolution in favourable cases
  - UHV required!
  - quantification hard: variable ionisation fraction
- Sophisticated toroidal (electrostatic) detector
  - energy and angle sensitive
  - simultaneous collection of all angles
- Double alignment geometry
  - surface structure determination



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Structure determination of the Cu(100)c(2x2)-Mn and Cu(100)c(2x2)-Au surface alloy phases by medium energy ion scattering, D.Brown, T.C.Q.Noakes, D.P.Woodruff, P.Bailey and Y.Le Goaziou, J.Phys.: Condens.Matter 11 (1999) 1889-1901

http://physweb.spec.warwick.ac.uk/~sppw/meis.html

Low Energy Ion Scattering
LEIS

- **RBS, but with eg. 5 keV He^+**
  - **Highly sensitive to *first atomic layer***
  - **Electrostatic toroidal detector similar to MEIS**
  - **Shadow cones too large for high angular sensitivity**
  - **Depth profiling (to 10nm!) with ion sputtering**
- **Applications**
  - **Extraordinarily valuable where the surface configuration is critical**
  - **Catalysts**
  - **Adhesion**
  - **Wetting**

High Sensitivity LEIS

“Calipso” company (Hidde Brongersma)

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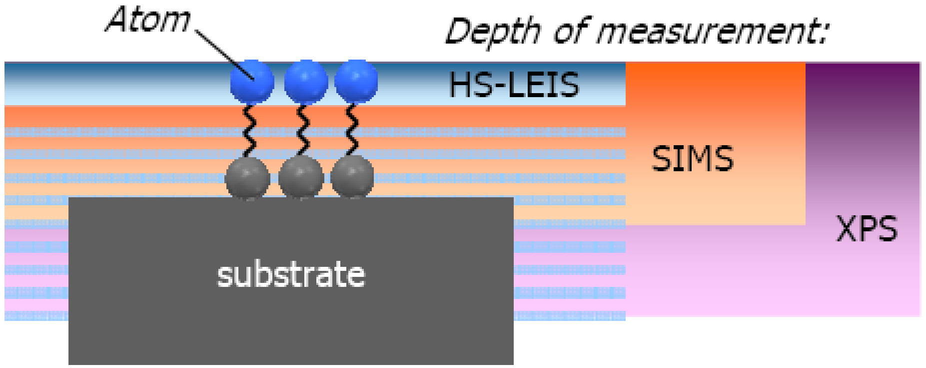
HS-LEIS compared to SIMS and XPS:



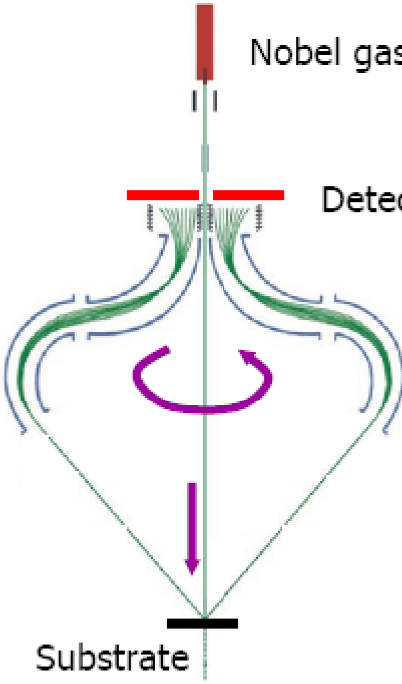
schematic representation of cross section of surface

HS-LEIS - quantitative 1st atomic layer
- in-depth profile 0-10 nm (shaded area)

SIMS - not quantitative (for 1st atomic layer)
- chemical information

XPS - information depth of 3 – 10 nm

Unique HS-LEIS analyzer:



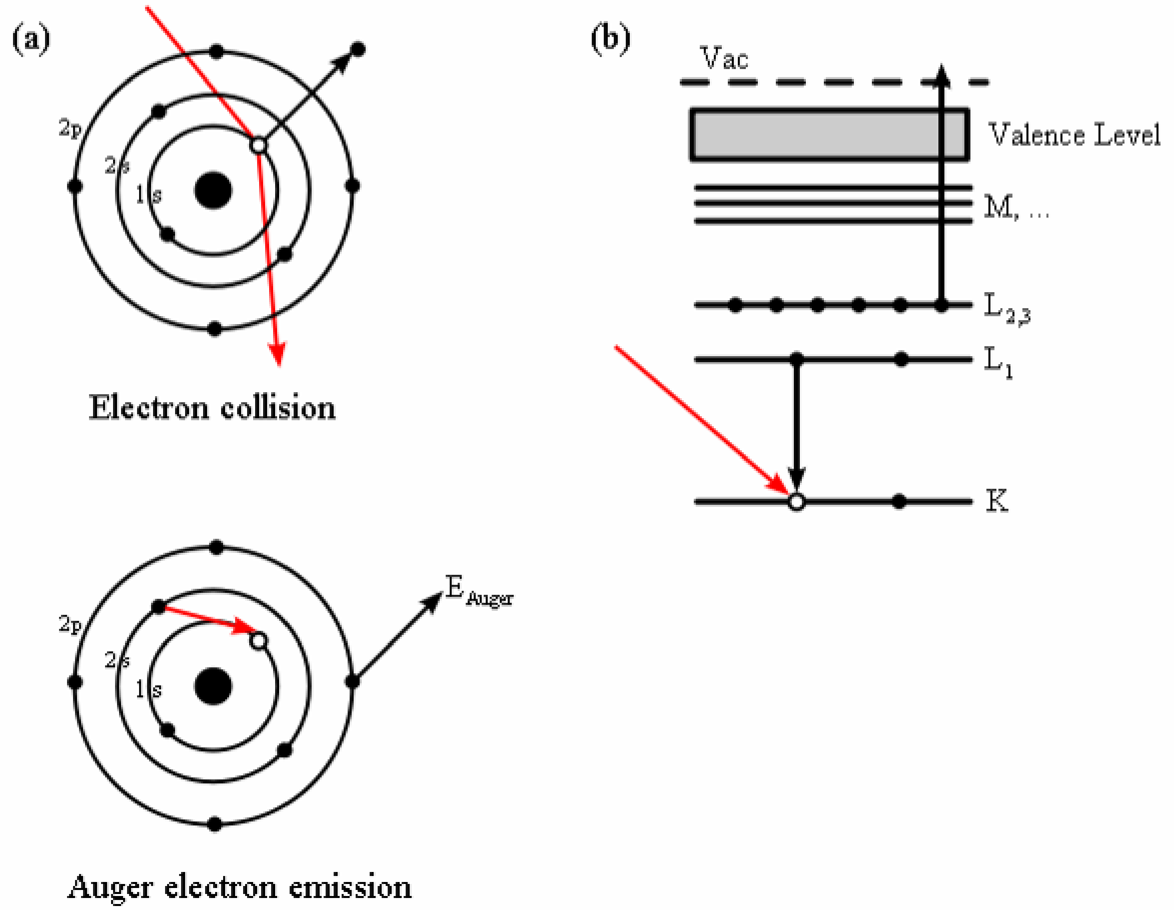
Picture of analyzer

http://www.calipso.nl/handout%202007.pdf

Auger Electron Spectroscopy

- **Surface Science technique (UHV)**
- **Electrons ionise target, Auger electrons detected**
  - **scanning electron microscope (SEM) technique**
  - **information depth from the *inelastic mean free path* hence a surface method**
- **Auger electron energy spectrum: characteristic lines**
  - **good elemental sensitivity**
  - **chemical information (valence electrons) present only obscurely in Auger process. The primary photoelectron process (XPS) is clearer**
  - **spacial resolution almost that of the electron beam**

Auger Mechanism



Taken from the Wikipedia article on Auger Electron Spectroscopy 18th February 2009
Auger_Process.svg from Wikipedia Commons.

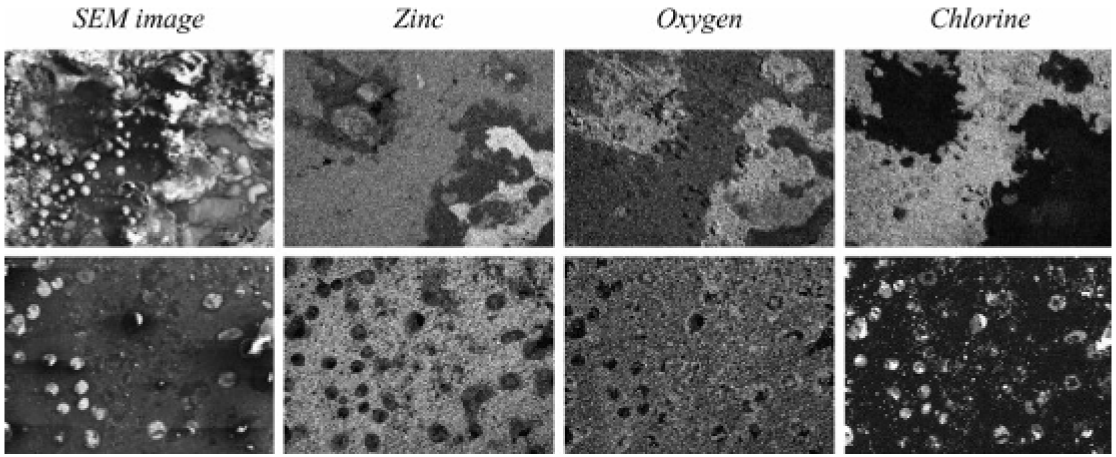


Fig. 9. SEM image and elemental composition analyzed by EDX for Zn (top) and ZnMg2 (bottom) exposed with NaCl deposits (magnification ×30).

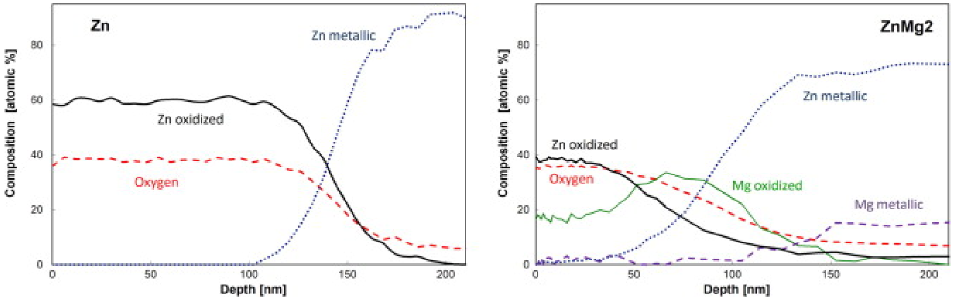


Fig. 10. AES depth profiles of untreated Zn and ZnMg2 exposed for 28 days at 20 °C and 80% RH.

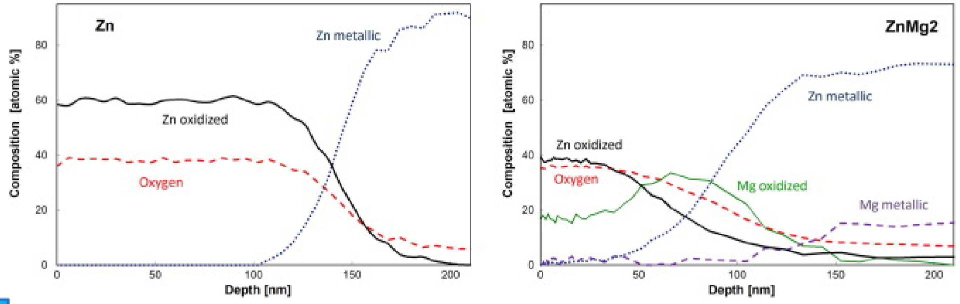


Fig. 11. AES depth profiles of Zn and ZnMg2 with deposited 1.40 g/m2 chloride and exposed for 28 days at 20 °C and 80% RH.

***Corrosion mechanism of model zinc–magnesium alloys in atmospheric conditions*, T. Prosek, A. Nazarov, U. Bexell, D. Thierry and J. Serak, Corrosion Science 50, 2008, 2216-2231**

Scanning Auger Microscopy

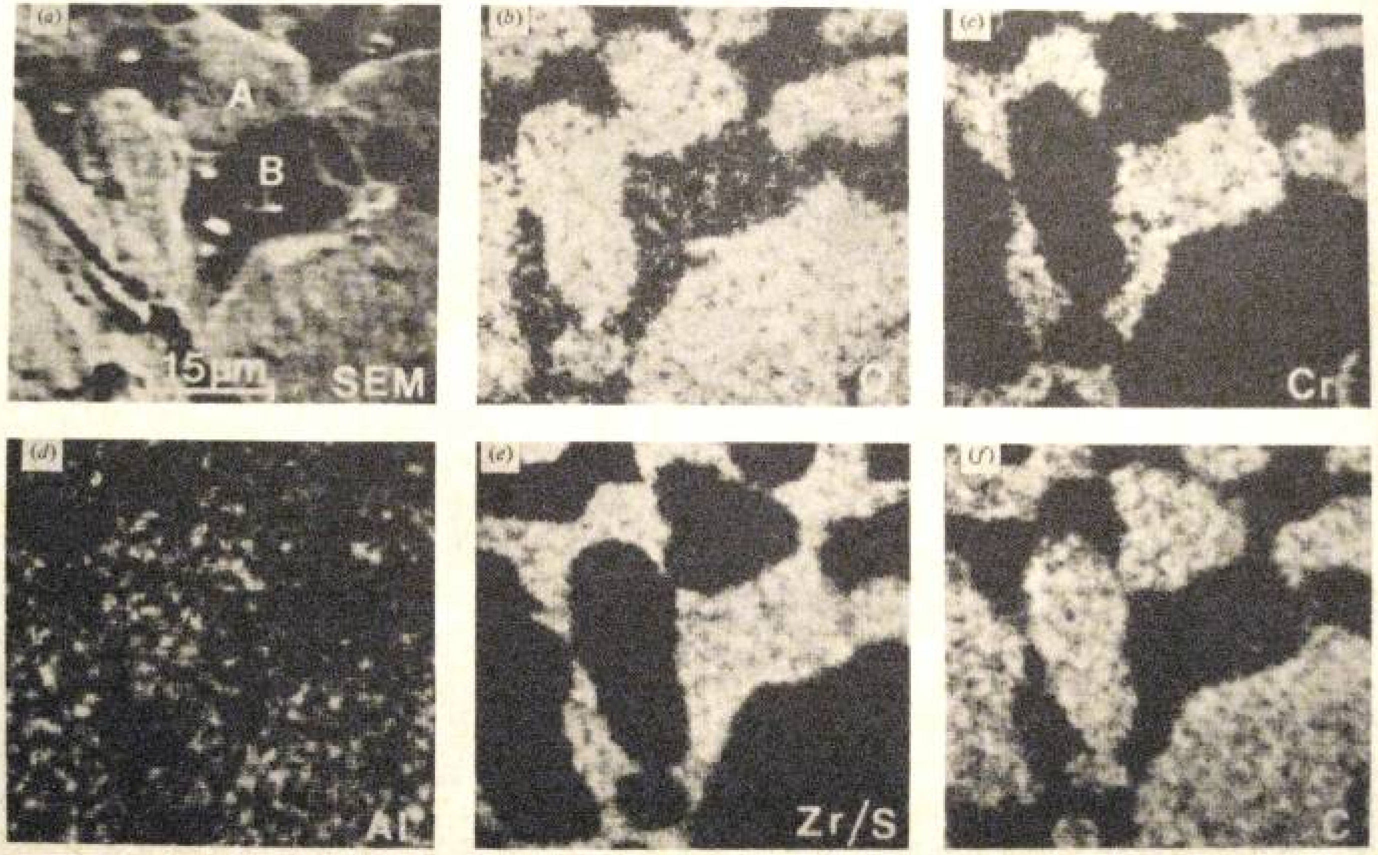


Fig. 4.26. Auger maps from superalloy, heated in vacuum, (a) SEM image, (b) O, (c), Cr, (d) Al, (e) Zr/S, (f) C.

Phase segregation of superalloy, ion cleaned and heated to 350^0C.

The A phase is rich in Cr & Zr, the B phase has high C & O

M.M.El Gomati, C.G.H.Walker, D.C.Peacock, M.Prutton, H.E.Bishop, R.M.H.Hawes, J.Smialek, Surface Science, 152/153, 1985, 917; reprinted in *Methods of Surface Analysis*, J.M.Walls (ed.) Chapter 5, *Auger Electron Spectroscopy*, H.E.Bishop

General Remarks

Not many critical comparative studies
Here is a recent example

SURFACE AND INTERFACE ANALYSIS
Surf. Interface Anal. 2004; **36**: 1269–1303
Published online 1 September 2004 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/sia.1909

SIA

Critical review of the current status of thickness measurements for ultrathin SiO_2 on Si
Part V: Results of a CCQM pilot study

M. P. Seah,[1]* S. J. Spencer,[1] F. Bensebaa,[2] I. Vickridge,[3] H. Danzebrink,[4] M. Krumrey,[5] T. Gross,[6] W. Oesterle,[7] E. Wendler,[8] B. Rheinländer,[9] Y. Azuma,[10] I. Kojima,[10] N. Suzuki,[11] M. Suzuki,[12] S. Tanuma,[13] D. W. Moon,[14] H. J. Lee,[15] Hyun Mo Cho,[16] H. Y. Chen,[17] A. T. S. Wee,[18] T. Osipowicz,[19] J. S. Pan,[20] W. A. Jordaan,[21] R. Hauert,[22] U. Klotz,[22] C. van der Marel,[23] M. Verheijen,[23] Y. Tamminga,[24] C. Jeynes,[25] P. Bailey,[26] S. Biswas,[27] U. Falke,[28] N. V. Nguyen,[29] D. Chandler-Horowitz,[29] J. R. Ehrstein,[29] D. Muller[30] and J. A. Dura[31]

(see Appendix for addresses)

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Complementary Techniques: XPS, SIMS, TEM, ellipsometry, GIXRR (grazing incidence Sy-X-ray reflectometry at BESSY), neutron reflectometry (NIST), MEIS, NRA, EBS, RBS

HR-TEM and MEIS much more equivocal than expected

NRA anomalous (7%)

Neutron reflectometry very low uncertainties (<1%): absolute interference method

RBS/EBS absolute uncertainty 6%

With new value of IMFP determined by this work, XPS acheived uncertainties of 2% (k=1)

Summary

- **PIXE, XRF, AES (and XPS), EELS are all variants of the same atomic excitation process**
- **The same diffraction techniques are seen with X-rays and electrons**
- **The same scattering process is seen in RBS (etc), MEIS, LEIS**
- **Similar types of mapping capabilities are seen with μbeam IBA, AES (SAM), TEM**
- **Some *textbook* examples can be *better* done with IBA**
- **IBA *inferior* in other cases**
- **Many cases where IBA and other methods strictly *complementary***