Initial Growth of Platinum on Clean and Oxidised Ni(110) Surfaces

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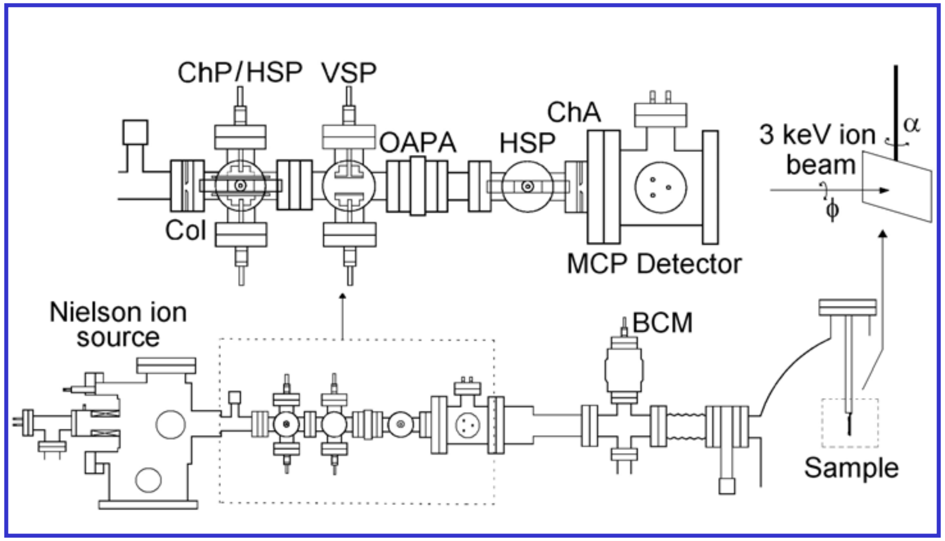
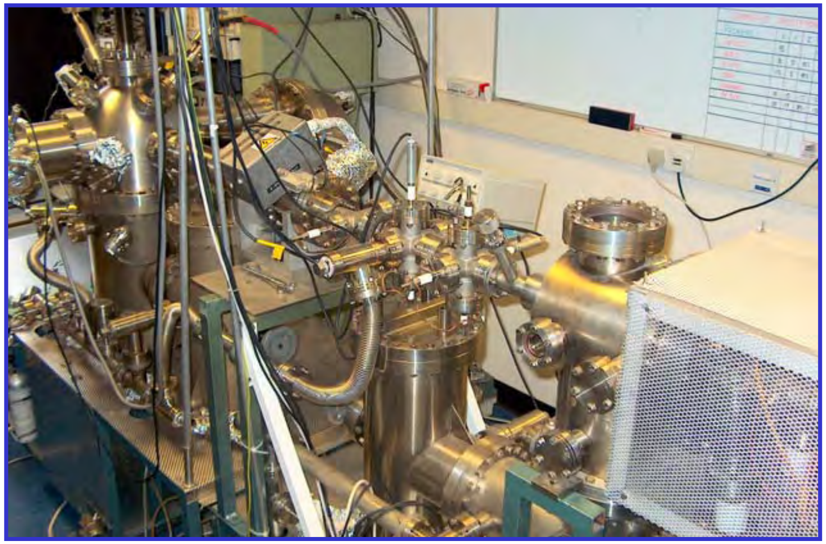
Presentation Outline

- *Introduction to experiment*
- *The structure of clean Ni(110) surface.*
- *Deposition of Pt on the clean Ni(110) surface.*
- *Oxidation of the Ni(110) surface.*
- *Deposition of Pt on to the oxidised surface.*
- *Conclusions.*

Co-axial impact collision ion scattering spectroscopy (CAICISS)

- *Use 1-5 keV He^+ or Ne^+, generated in a Nielson ion source.*
- *Short pulses of ions pass through the detector and strike sample.*
- *Detect ions & neutral particles in time-of-flight mode.*
- *Time-of-flight ⇨ kinetic energy ⇨ mass of scattering atom.*





Shadow cones

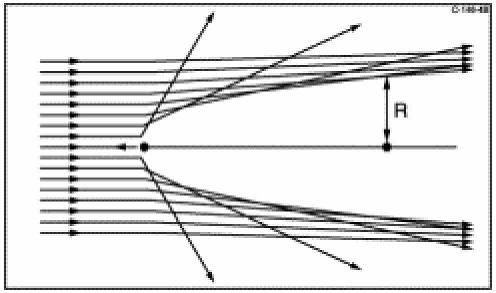
- *Scattering process at low incident ion energies can be described by a screened Coulomb interaction potential.*

- *Ion-atom interaction ⇨ region in to which ions cannot penetrate.*

    - *Shadow cones*

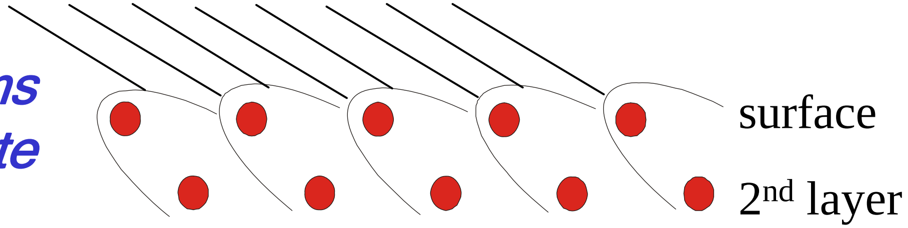
⇨ increased flux at shadow cone edge

⇨ increased backscattered yield when edge of cone is incident on another atom.

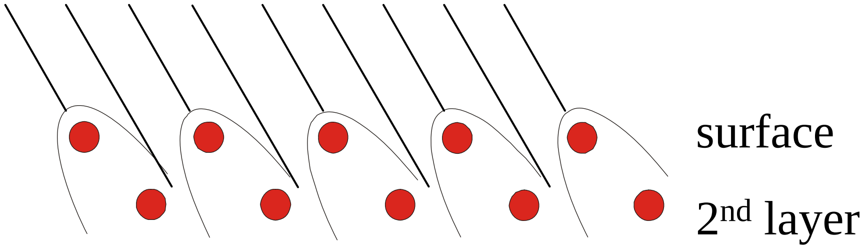


Structure determination

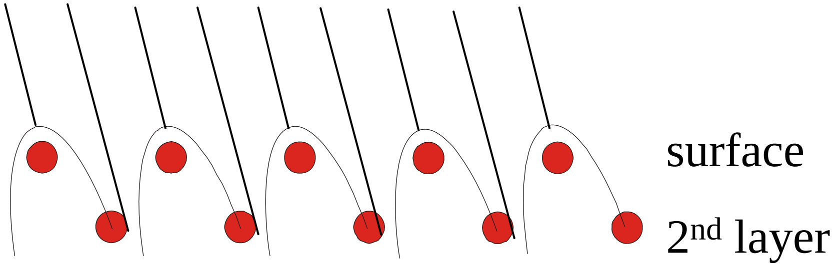
- *Critical angle - All sub-surface atoms are shadowed. Used to calculate surface layer inter-atomic spacing.*



- *Increase polar angle. Cone edges no longer incident on a neighbouring atom ⇨ drop in backscattered yield.*

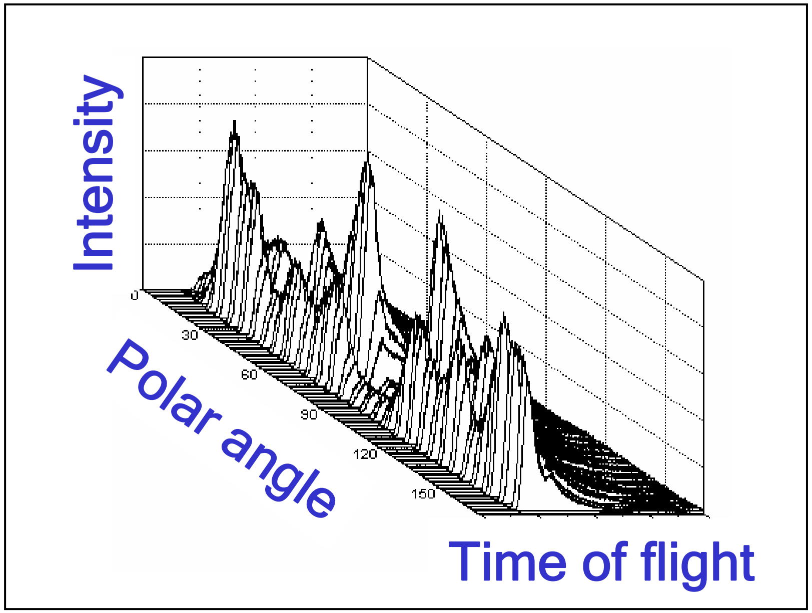


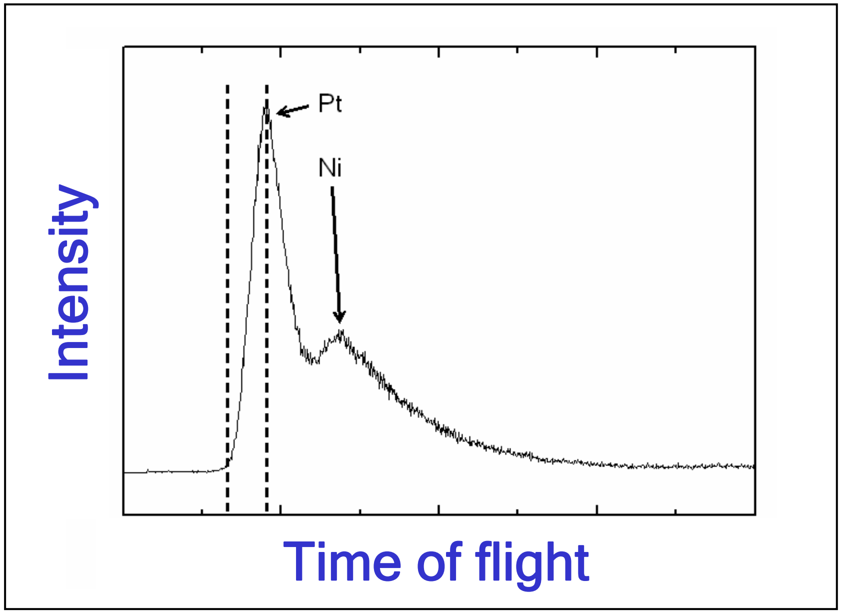
- *Further increase brings cone edge on to a second layer atom, increasing the backscattered yield. Used to calculate sub-surface structure and composition.*



Extracting information from CAICISS

- *Sample rotated from 0° to 180° during experiment.*
  Measure intensity vs. time-of-flight at each step.
- *Generate a 3D plot of intensity vs. time-of-flight and polar angle.*
- *Determine TOF corresponding to each element in the sample.*

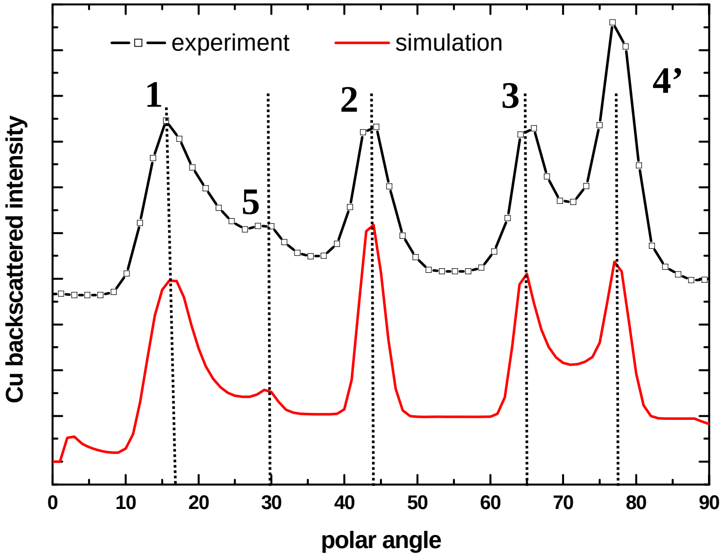


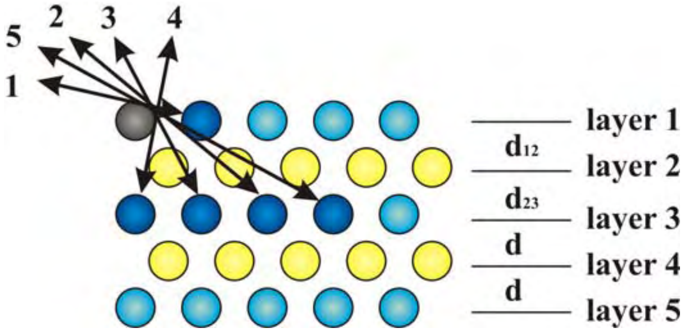


Extracting information from CAICISS

- *Generate intensity vs. polar angle plot for each element.*
- *Use FAN simulation package [1] to test trial structures.*
- *adjustable parameters include:*
    - *Incident beam properties*
    - *Scattering angle*
    - *Interaction potential*
    - *Debye temperatures*
    - *Crystal structure*
    - *Crystal composition*

clean Cu(100): <110>





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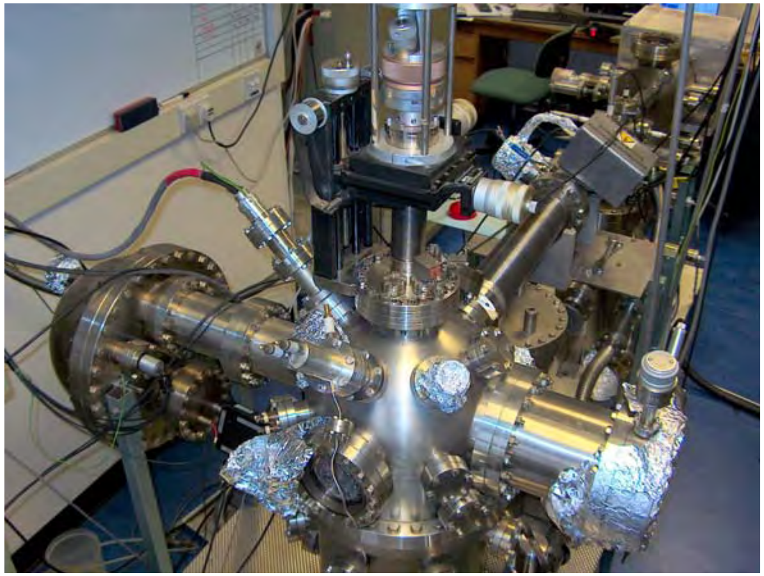
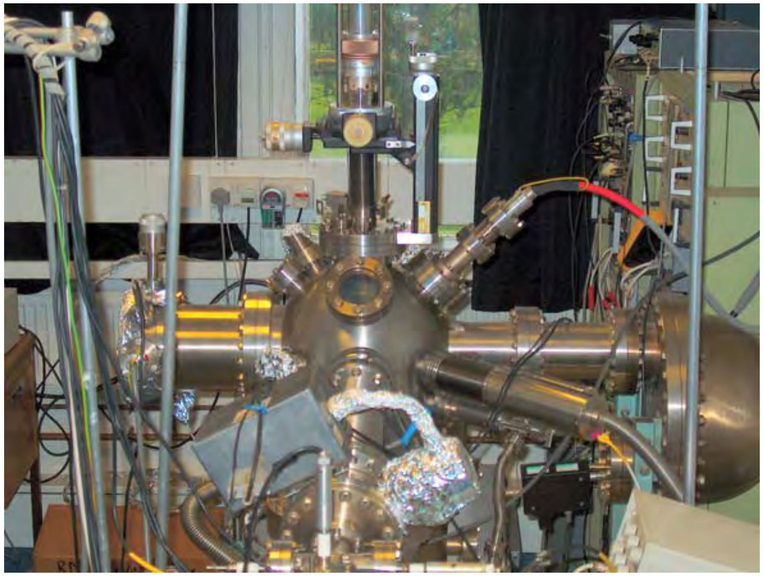
[1] H. Niehus and R. Spitzl, Surf. Interf. Anal. 17 (1991) 287.
(Available from http://asp2.physik.hu-berlin.de/)

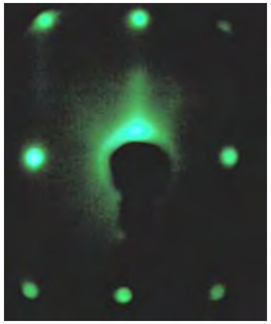
Experimental setup (→ Poster P-OGD2)

- *LEED - Surface periodicity information.*
- *XPS - Chemical information.*
- *Thermal gas cracker - atomic oxygen.*
- *Sample heating.*
- *Sputter gun.*
- *Evaporation sources.*

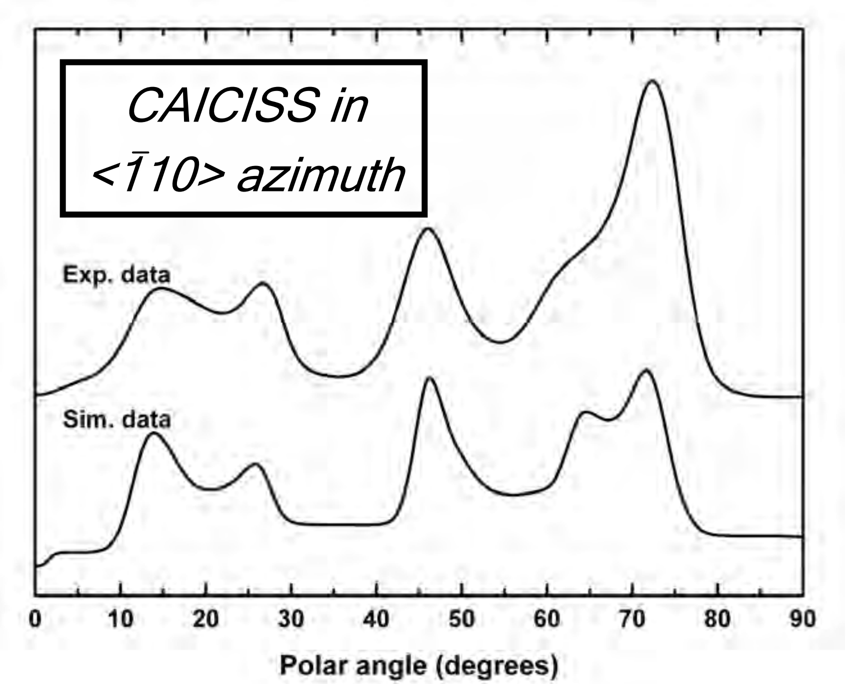




Clean Ni(110) surface structure



- *Cleaned using ion bombardment and annealing cycles.*
- *(1x1) LEED pattern at 78 eV. No contaminants in XPS.*
- *First interlayer spacing, Δ_{12}, was contracted by 4% relative to bulk value of 1.246 Å.*
- *9% expansion in Δ_{23}.*
- *4.4% contraction in Δ_{34}.*
- *Bulk structure from 4th layer and regions deeper in to the crystal.*

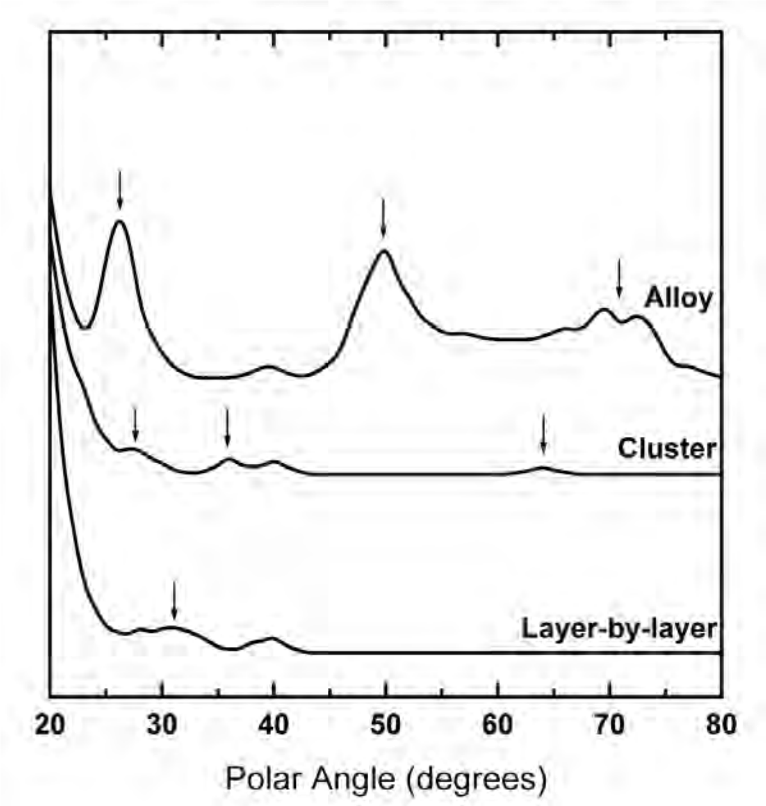


Pt deposition on clean Ni(110)

- *Simulations carried out prior to Pt deposition to identify features associated with certain models.*

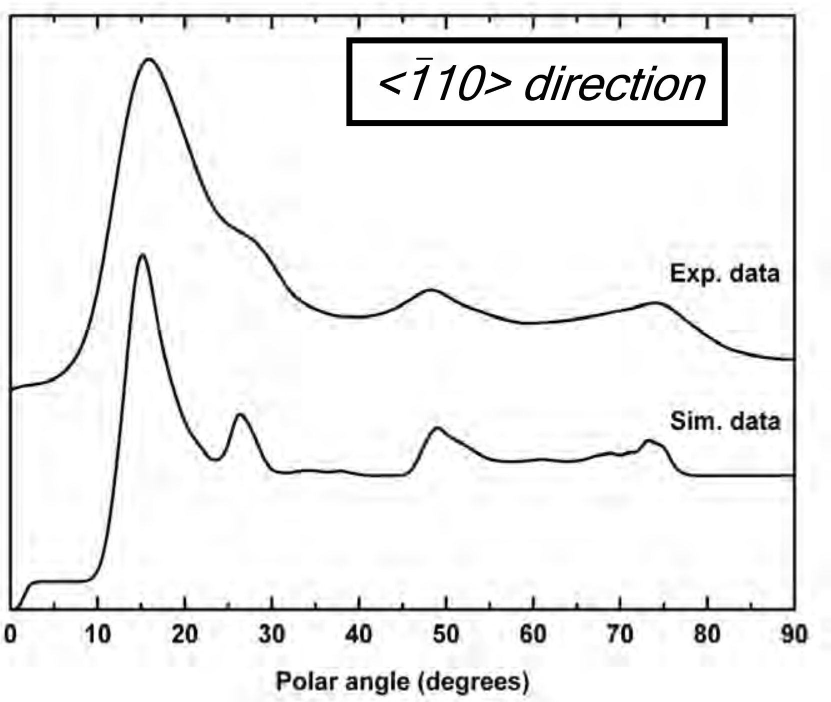
- *Models simulated include:*
  - *Layer-by-layer Pt film growth.*
  - *Ni-Pt alloy in top three layers.*
  - *3D Pt clusters formed on the surface.*

- *Each model has unique features. Use these results to identify the result of Pt deposition.*



Pt deposition on clean Ni(110)

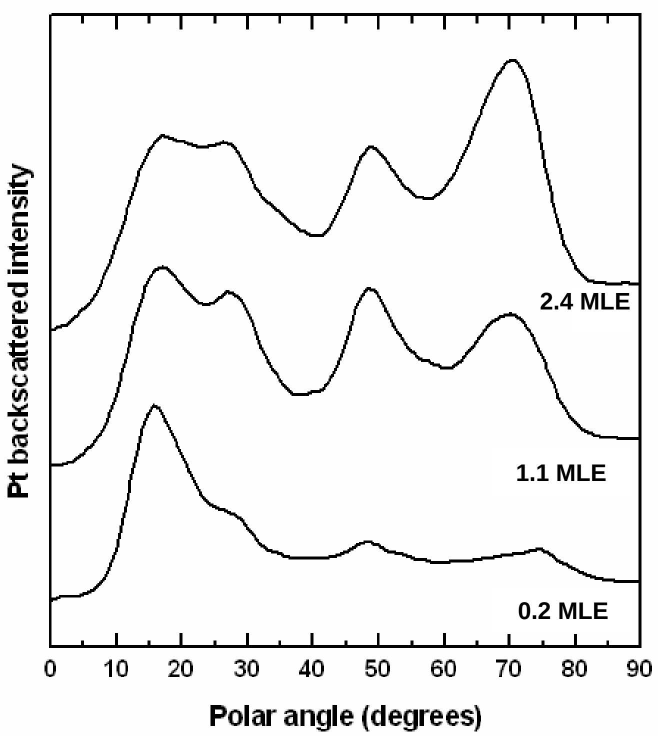
- *0.22 MLE of Pt deposited on to the clean Ni(110) surface at 300 K.*
- *No LEED pattern observed ⇨ Disordered surface.*
- *Pt spectrum correlates well with the three-layer Ni-Pt alloy model.*
- *Deposited Pt atoms found in Ni lattice sites in the top three layers of the structure.*
- *Expanded interlayer spacings due to Pt incorporation in to the Ni(110) structure.*
- *No Pt atoms or changes to the structure observed in the fourth layer or below.*



Pt deposition on clean Ni(110)

- *Continued deposition up to coverage of 2.4 MLE (from XPS).*
- *No LEED patterns observed ➢ disorder at the surface.*

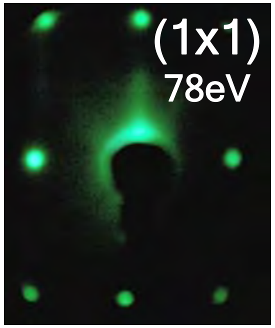
Pt Coverage	0.2 MLE	1.1 MLE	2.4 MLE
Layer 1 Pt	15%	12%	32%
Layer 2 Pt	5%	35%	85%
Layer 3 Pt	2%	22%	48%
Layer 4 Pt	0%	15%	15%
Layer 5 Pt	0%	13%	18%
Layer 6 Pt	0%	0%	18%

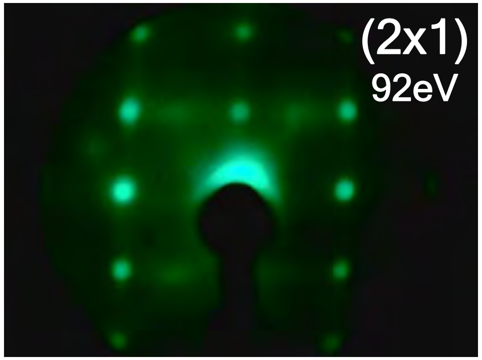


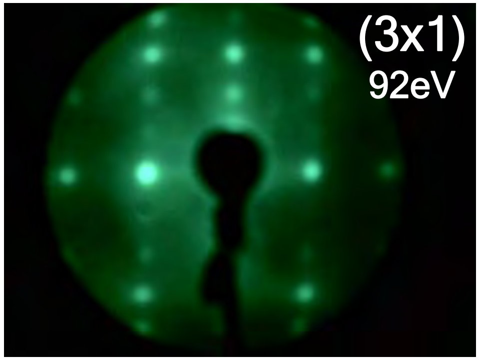
➢ *Room temperature Pt deposition yields a disordered extended Ni-Pt alloy.*

Oxidation of Ni(110) - LEED

- *(1x1) LEED pattern after preparation.*
- *1.5 L O* exposure at 300 K to reach O overlayer with a (2x1) structure (0.5 MLE coverage [2,3]).*
- *3.0 L exposure to reach O overlayer with a (3x1) structure (0.66 MLE coverage [2,3]).*
- *Possible (9x5) phase seen after 5.0 L exposure (approx. 1.0 MLE [2,3]).*
- *Further exposure to O* (above 10 L) led to loss of LEED pattern.*







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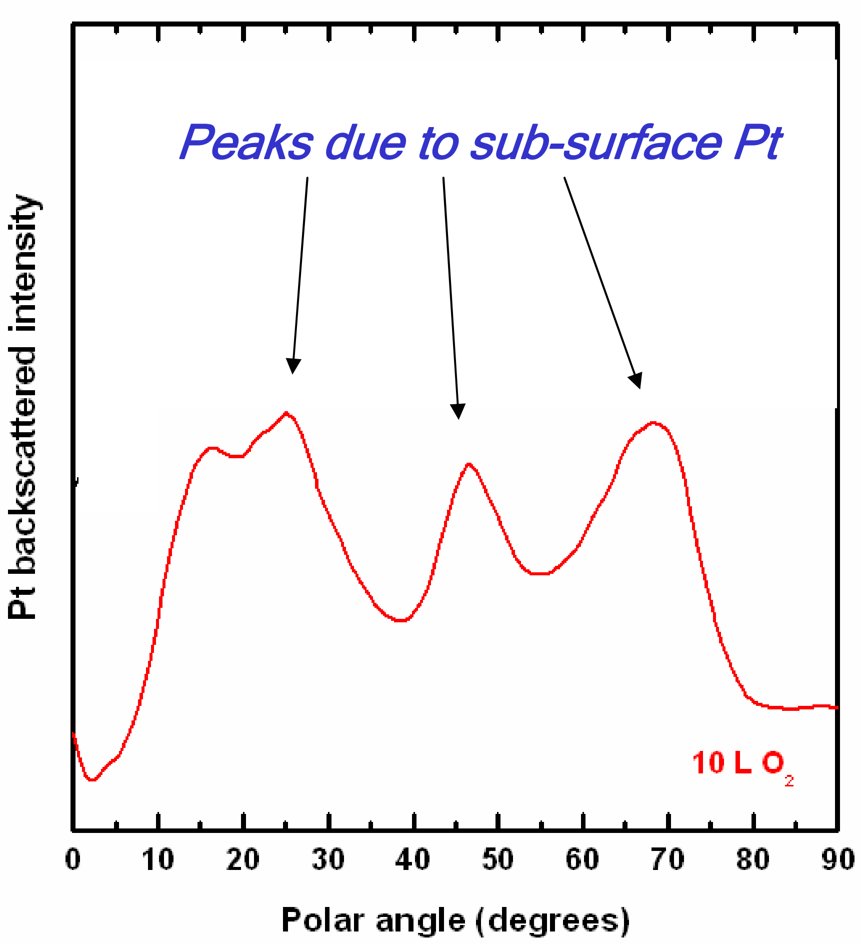
[2] K. Yagi-Watanabe et al., Surf. Sci. 482-485 (2001) 128.
[3] P.R. Norton et al., Surf. Sci. 175 (1986) 313.

Pt deposition on the Ni(110)-(3x1)-O surface

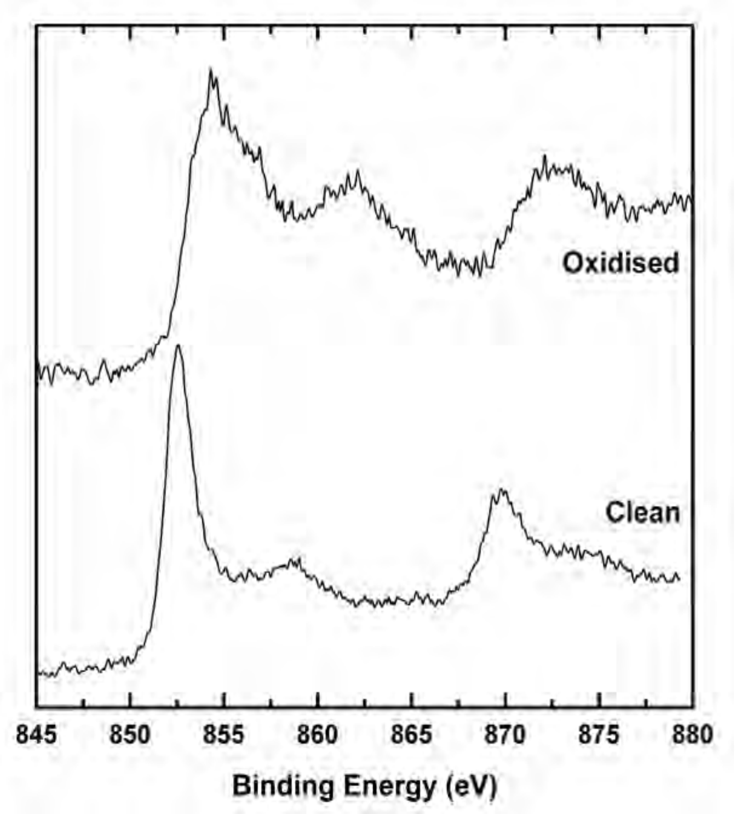
- *~0.5 MLE of Pt on to the Ni(110)-(3x1)-O surface.*
- *Features in the central region of the spectrum remain.*
- *Low O_2 exposures do not inhibit alloy formation.*
- *Use higher doses of atomic oxygen to form a thick NiO film prior to Pt deposition.*



Oxidation of Ni(110) - XPS

- *XPS taken from surface before and after exposure of clean surface to O* (1800 L total exposure).*

Peak	Clean Ni(110)	Oxidised Ni(110)	Shift
$2p_{1/2}$	869.8 eV	872.2 eV	2.4 eV
$2p_{3/2}$	852.5 eV	854.3 eV	1.8 eV
$2p_{3/2}$ (satellite)	858.7 eV	861.9 eV	3.2 eV

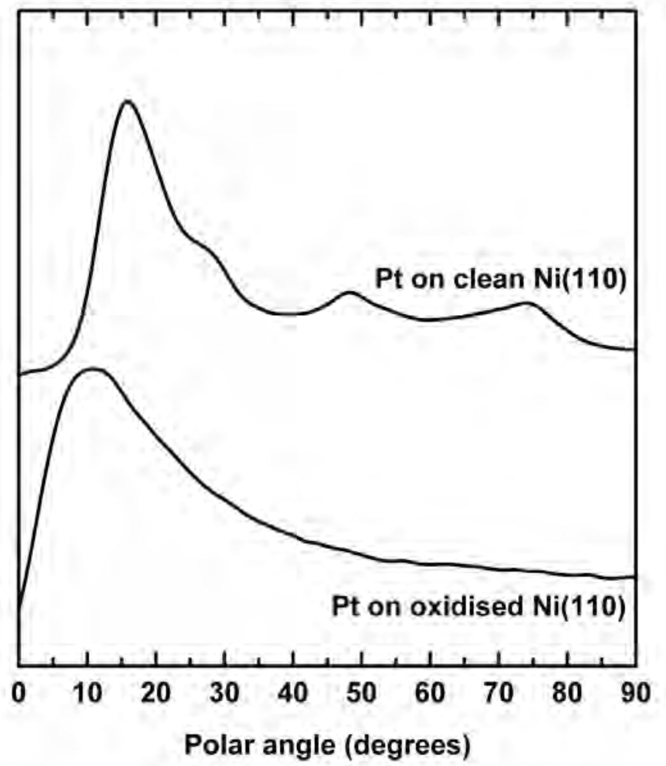


- *No evidence of metallic Ni signal in XPS measurements.*

Pt deposition on oxidised Ni(110)

- *0.3 MLE of Pt deposited on to the NiO surface at 300 K.*
- *Compared Pt profile to Pt deposited on clean Ni(110).*
- *No peaks due to sub-surface Pt.*
- *Increase in the inter-atomic spacing in the layer containing Pt atoms (surface peak shifted by 6°).*
- *Broadness of peak indicates a range of spacings between Pt atoms (random Pt arrangement).*

> ➢ *Pt appears to be solely on top of the NiO film.*



Pt on oxidised Ni(110) - XPS

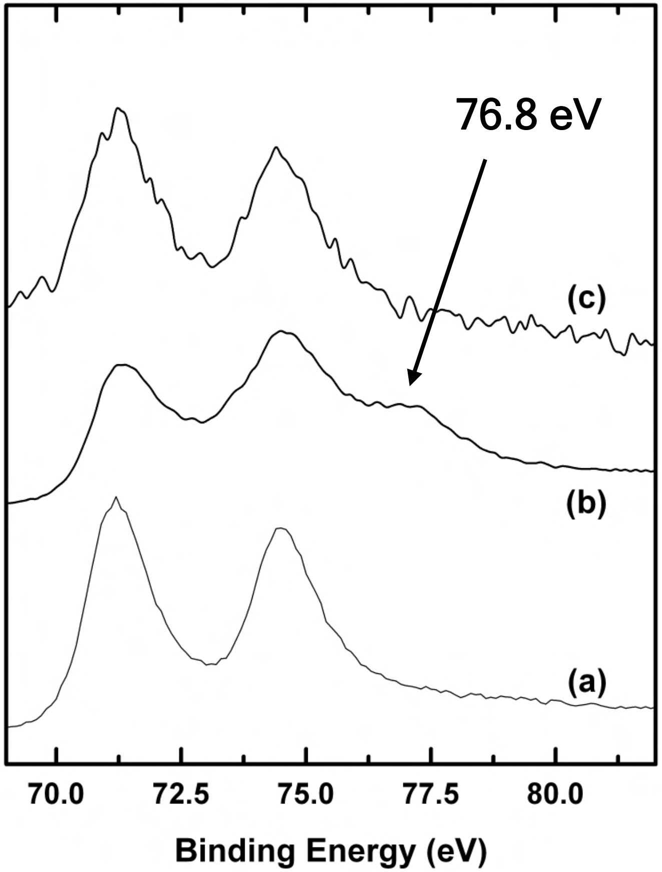
- *Compare Pt 4f peaks to previous work [4].*

- *(a) - clean Pt(111) [4].*
- *(b) - oxidised Pt(111) [4].*
- *(c) - Pt on NiO(110).*

- *Only see the peak at 76.8 eV in the oxidised Pt(111) data.*

- *76.8 eV feature not seen in the Pt on NiO(110) case. Therefore no Pt oxide.*

- *Another indication of Pt overlayer and possible onset of layer-by-layer growth.*



[4] C.R. Parkinson et al., Surf. Sci. 545 (2003) 19.

Conclusions

- *Clean Ni(110) showed significant relaxations in the surface region.*
- *Extended Ni-Pt alloy formed if deposit on clean surface at 300 K.*
- *Observed (2x1), (3x1) and (9x5) reconstructions of O on the Ni(110) surface at low O* exposures.*
- *Deposition of Pt on to Ni(110)-(3x1)-O surface yields a Ni-Pt alloy.*
- *Thick NiO film formed after exposure to 1800 L of O*.*
- *Pt appears to grow layer-by-layer on heavily oxidised surface, in contrast to the alloy formation observed on the clean surface.*

Acknowledgements

- *Marc Walker, Chris McConville, Charles Parkinson and Rob Johnston (technician).*

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EPSRC Engineering and Physical Sciences
Research Council

- *Austrian Science Fund (FWF), Erwin Schrödinger Fellowship (Project Number J2417-N08) [MD].*

FWF Der Wissenschaftsfonds.

Applications of Ni oxides and Pt films

- *Nickel oxides used in many industries, for example:*
    - *Heterogeneous catalysis*
    - *Electrical ceramics (thermistors, varistors)*
    - *Pigments for ceramics and glasses*

- *Thin Pt films used in:*
    - *Vehicle exhaust systems*
    - *Nitric acid production*
    - *Manufacturing of specialist silicones*

- *Aim to improve understanding of both oxide and Pt film formation to save costs and improve efficiency in such industries.*

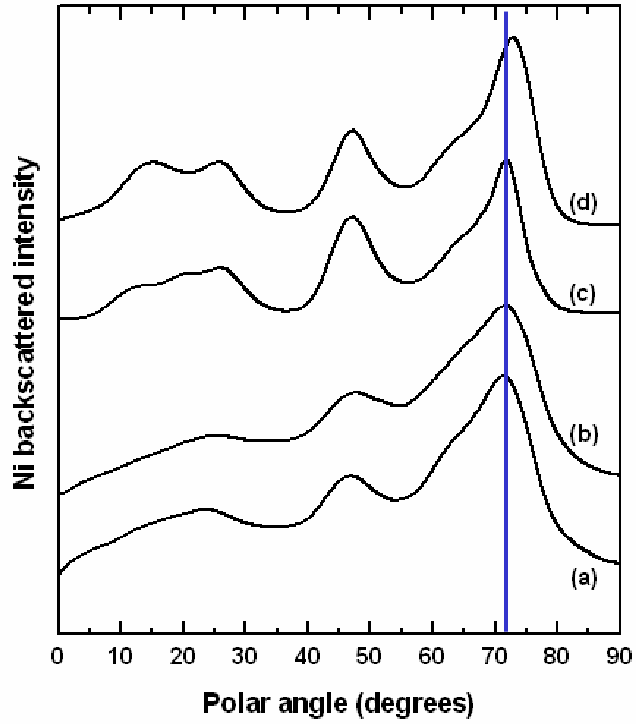
CAICISS……

- *…… offers the chance to probe the structure and composition of surfaces with a high degree of surface specificity.*
- *Time-of-flight ⇨ composition information.*
- *Shadow cones ⇨ structural information.*
- *Use FAN code to determine structure and composition.*
- *Other techniques to complete the characterization*

Pt on oxidised Ni(110) - CAICISS

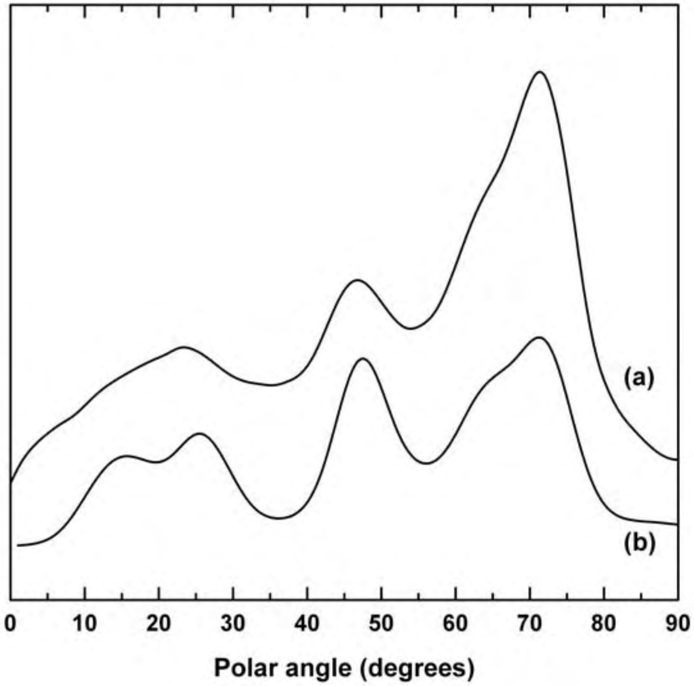
- *Inclusion of Pt in to the NiO film would change interlayer spacings.*
- *Look for changes in the Ni signal before and after Pt deposition.*
  - *(a) - NiO surface.*
  - *(b) - Pt-covered NiO surface.*
  - *(c) - Simulation of (b).*
  - *(d) - Pt on clean Ni(110).*
- *Little change as a result of Pt deposition.*
- *No expansion in Δ_{12}, as with the clean Ni surface (b & d, 72° peak).*
- *Data accurately described by Pt atoms on top of NiO film (b & c).*

> ➢ *Layer-by-layer Pt film growth.*



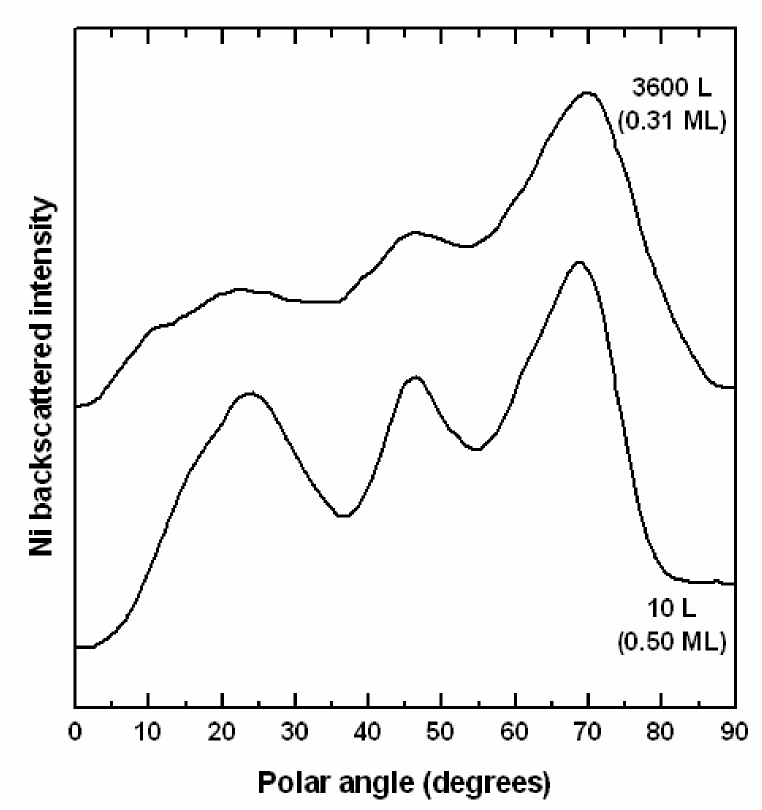
Oxidation of Ni(110) - CAICISS

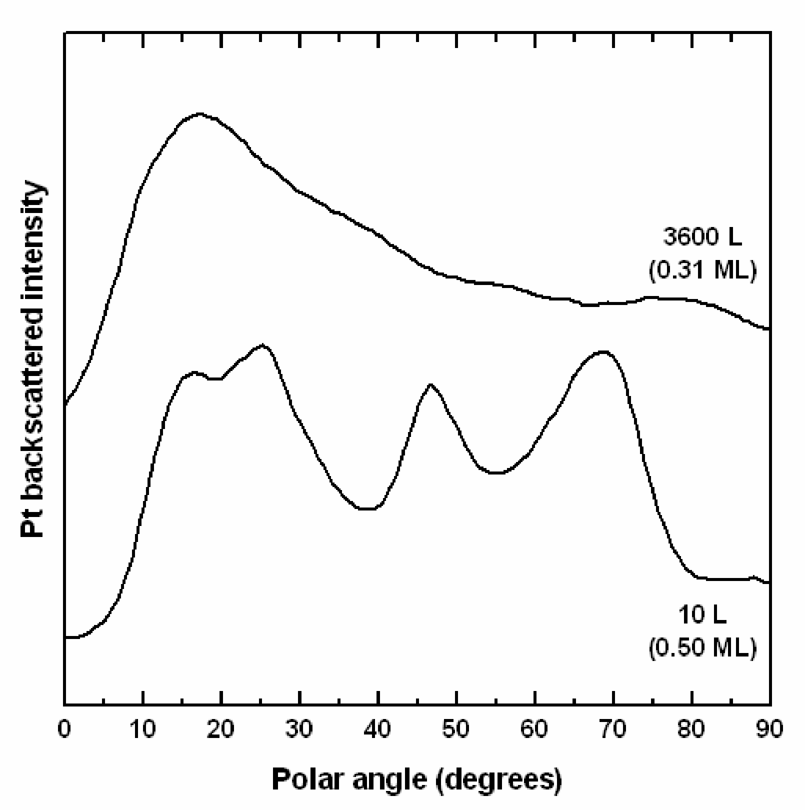
- *XPS indicated no degradation of O content during CAICISS experiment.*
- *Broad features in the data (a) ➢ disordered surface.*
- *Substitutional NiO(110) film, with an O adlayer predicted by FAN (b).*
- *NiO film thickness greater than CAICISS probing depth (~ 10 Å).*
- *Δ_{12} expanded by 12% relative to bulk Ni. All deeper layers separated by bulk Ni(110) spacing.*



Pt deposition on oxidised Ni(110)

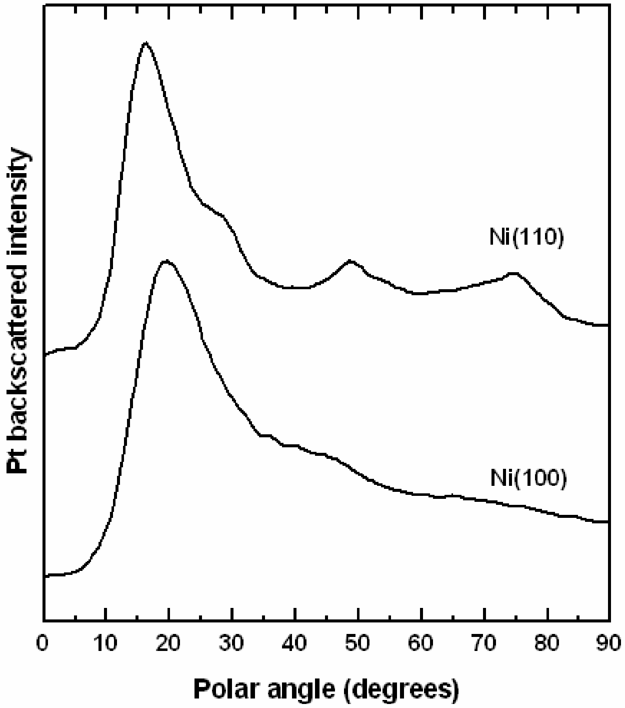
- *Compare yield from Pt on Ni(110) exposed to O_2 doses of 10 L & 3600 L.*





Pt deposition on clean Ni(100)

- *Compare growth on clean Ni(110) to growth on clean Ni(100).*
- *See features at ~ 30°, 50° and 75° from Ni(110) sample which correspond to sub-surface Pt.*
- *No distinctive features at higher angles observed in signal from Pt-covered Ni(100).*
- ➢ *Suggests layer-by-layer growth.*
- ➢ *Difference in initial growth modes of Pt on the Ni(100) and Ni(110) surfaces.*
- *Experiments looking at higher Pt coverages on Ni(100) in progress.*

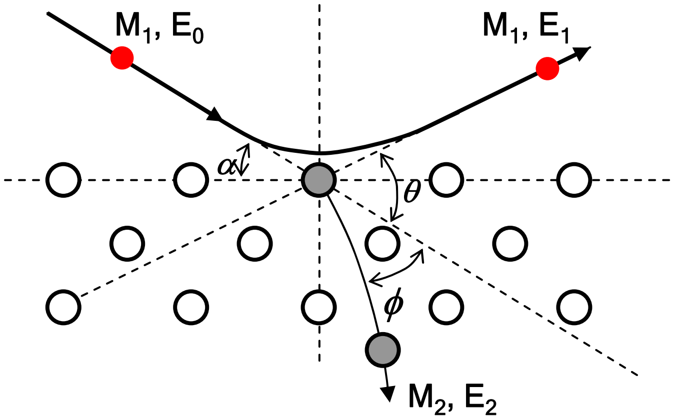


The scattering process

- *Model scattering using a binary collision in the most simple case.*
- *Ion incident at angle α with respect to the surface, and is scattered through angle θ.*
- *Energies E_0 (primary) and E_1 (final) are related by:*

$$\frac{E_1}{E_0} = \frac{1}{(1+A)^2}\left(\cos\theta \pm \sqrt{A^2 - \sin^2\theta}\right)^2$$

(where $A = M_2 / M_1$)



- *At θ = 180°, this simplifies to:*

$$\frac{E_1}{E_0} = \frac{(A-1)^2}{(A+1)^2}$$

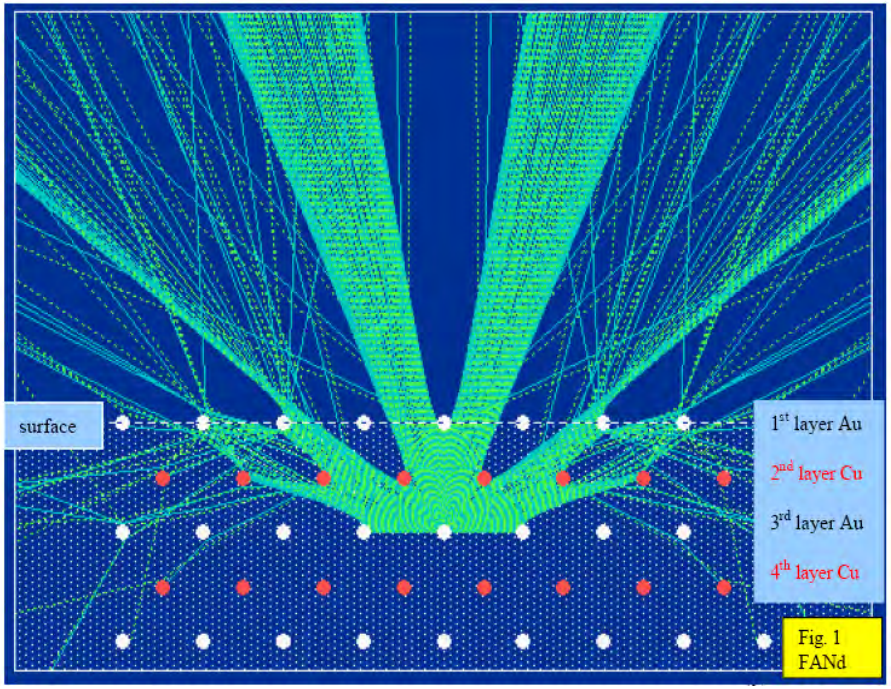
➢ *Measuring E_1 leads to determination of M_2.*

The FAN simulation program

- *Enables fast simulations of particle trajectories (ions & neutrals).*
- *Designed specifically for backscattering techniques (unlike Monte Carlo simulations).*
- *Capable of simulating both polar and azimuthal crystal rotations.*
- *Trial structures can incorporate three different atomic species.*
- *Enables choice of interaction potential (Moliére or ZBL) and screening factor.*
- *Includes temperature and neutralisation effects, as well as off-axis scattering.*
- *Limitations include a limit on lattice points (1500), so not ideal for simulating complex structures (eg. Quasicrystals).*
- *Also does not include inelastic energy losses along the trajectory.*

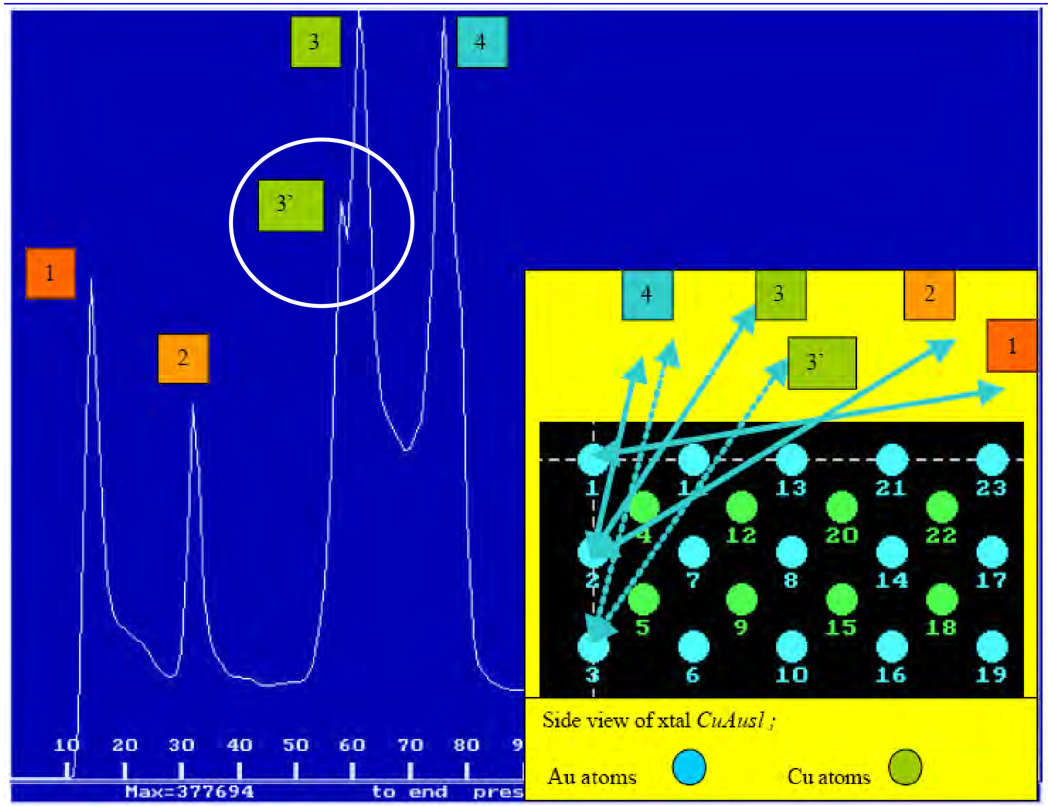
Trajectory calculation

- *Simulated trajectories start at the chosen lattice point.*
- *A 180° "fan" of trajectories are created around this point.*
- *Utilises blocking cones to calculate the angular distribution of scattered particles.*
- *Integrates over all lattice points to derive an intensity vs polar or azimuthal angle plot for each atomic species.*
- *Compare the results to the experimental data.*



Understanding the results

- *Use FAN output to examine the trial structure by comparing the profile for each element with the experimental data.*
- *Each peak corresponds to a unique scattering geometry.*
- *See features due to surface relaxations (e.g. 3’).*
- *Peak intensities can be changed by altering the layer-by-layer composition of the trial structure.*

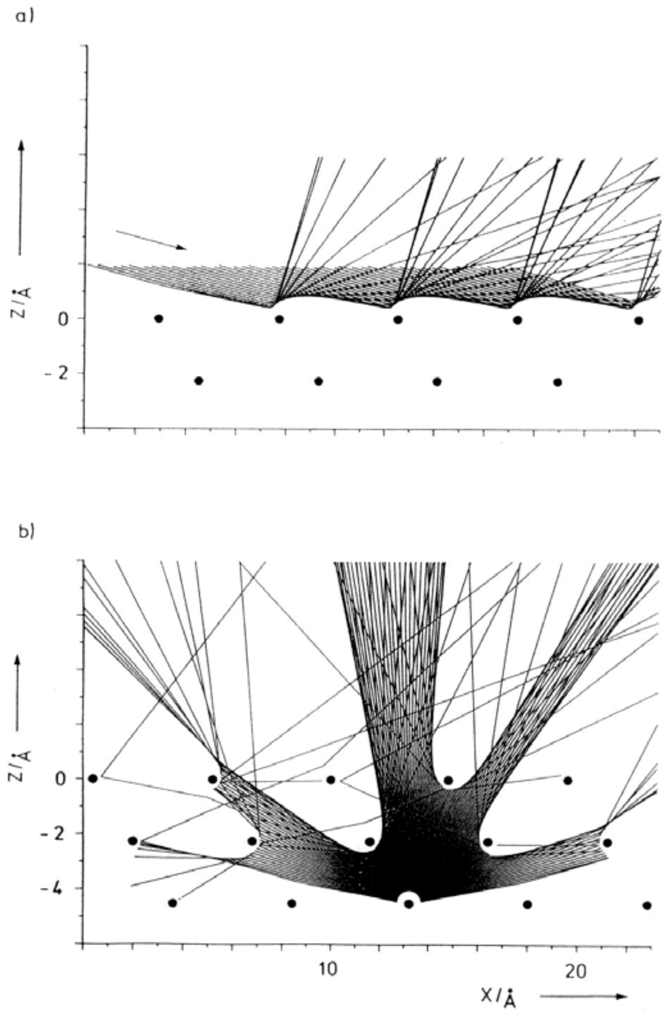


Structure determination

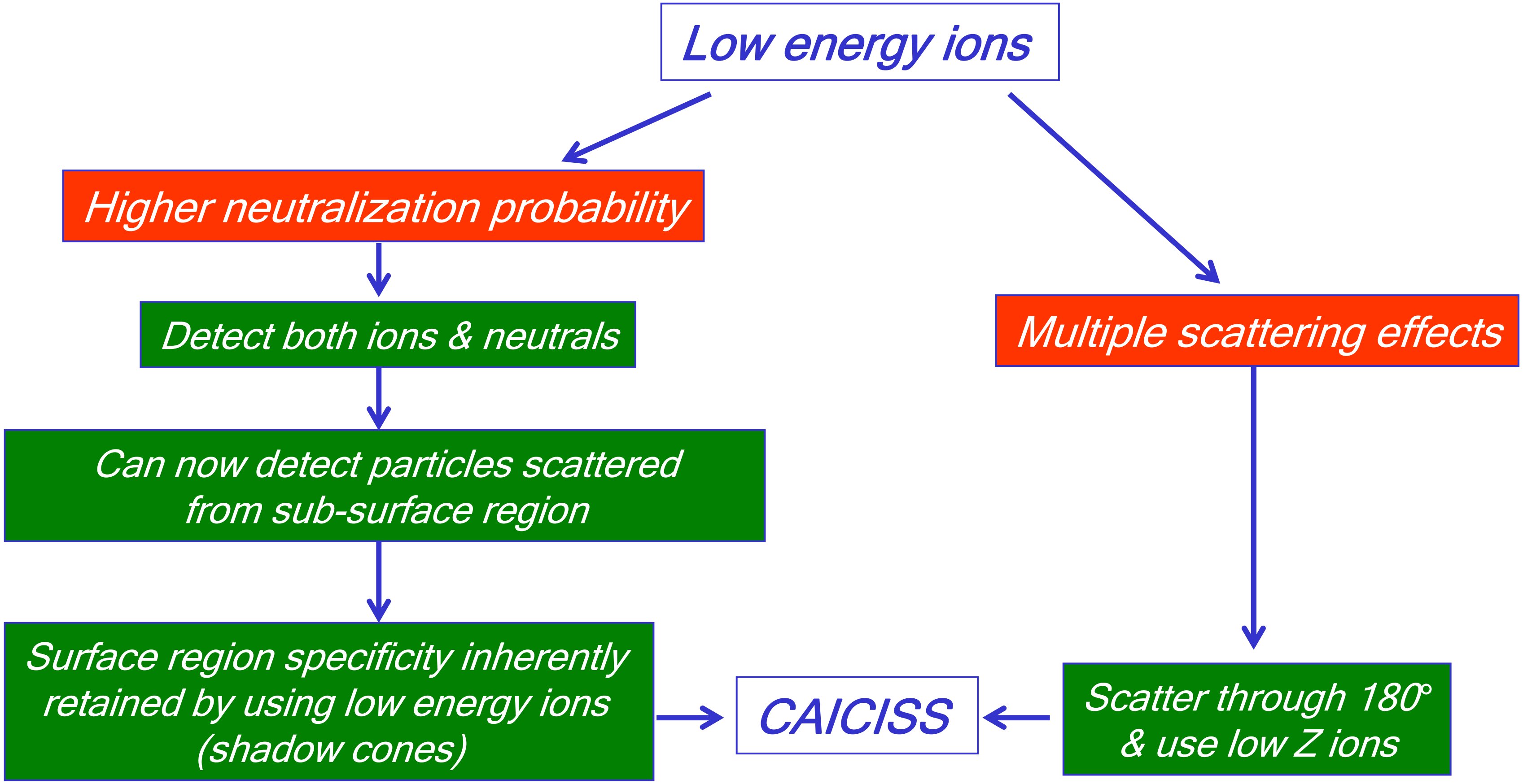
- *Critical angle – All sub-surface atoms are shadowed. Used to calculate surface layer inter-atomic spacing.*

- *Increase polar angle. Cone edges no longer incident on a neighbouring atom ⇨ drop in backscattered yield.*

- *Further increase brings cone edge on to a second layer atom, increasing the backscattered yield. Used to calculate sub-surface structure and composition.*



Low energy ion scattering



Low energy ions

Higher neutralization probability

Detect both ions & neutrals

Can now detect particles scattered from sub-surface region

Surface region specificity inherently retained by using low energy ions (shadow cones)

Multiple scattering effects

Scatter through 180° & use low Z ions

CAICISS