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

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# Presentation Outline

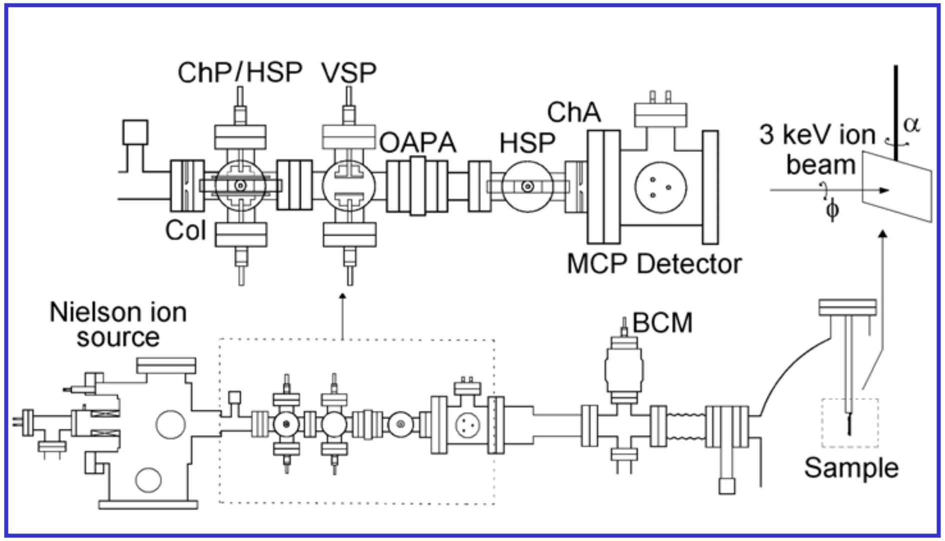
- *Potential material applications.*
- *Introduction to the Warwick CAICISS system.*
- *The structure of the clean Ni(110) surface.*
- *Deposition of Pt on the clean surface.*
- *Oxidation of the Ni(110) surface.*
- *Deposition of Pt on to the oxidised surface.*
- *Conclusions.*

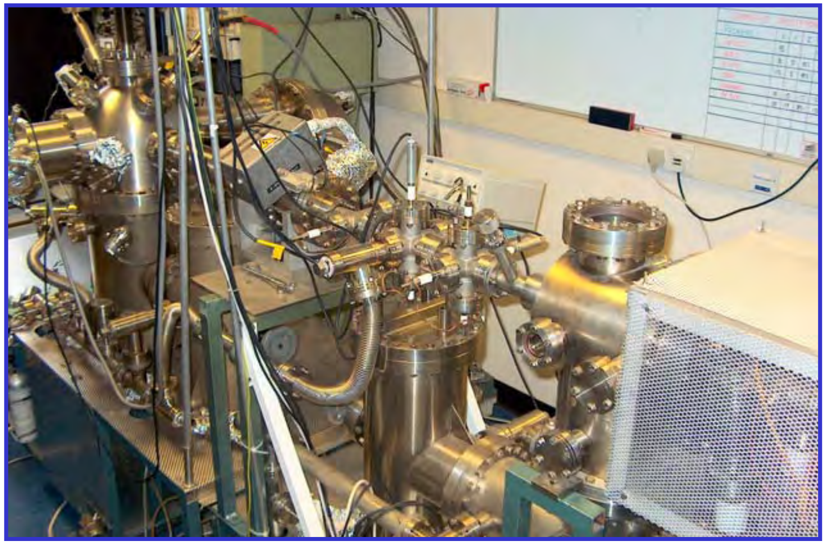
# Applications of Ni oxides and Pt films

- *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.*

# Co-axial impact collision ion scattering spectroscopy (CAICISS)

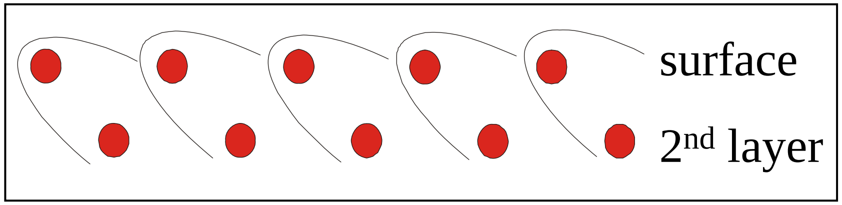
- *Use 1-5 keV He$^+$ or Ne$^+$, generated in a Nielson ion source.*
- *Short pulses of ions pass through the detector and strike sample.*
- *Detect ions & neutral particles in time-of-flight mode.*
- *Time-of-flight ⇨ kinetic energy ⇨ mass of scattering atom.*



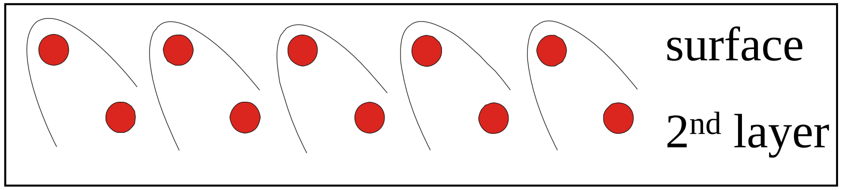


# Structure determination

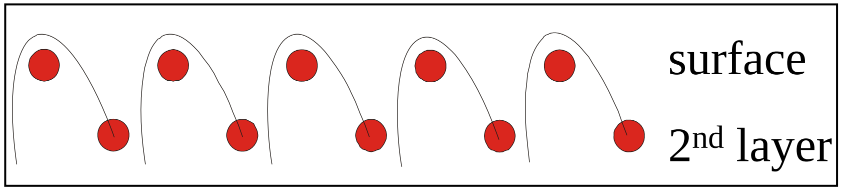
- *Critical angle - All sub-surface atoms are shadowed. Used to calculate surface layer inter-atomic spacing.*



- *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.*



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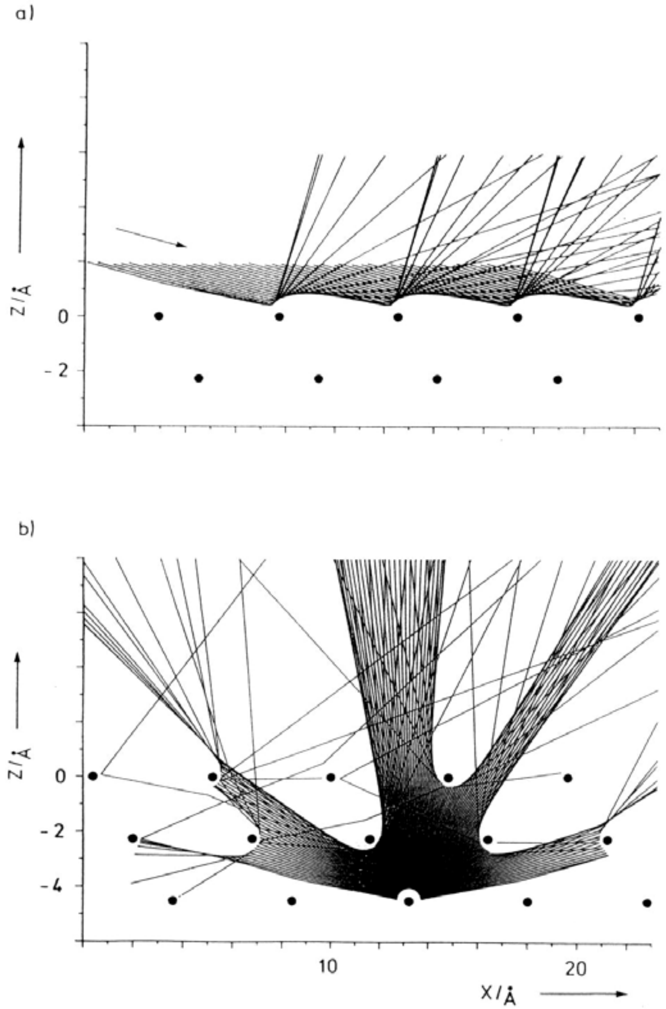
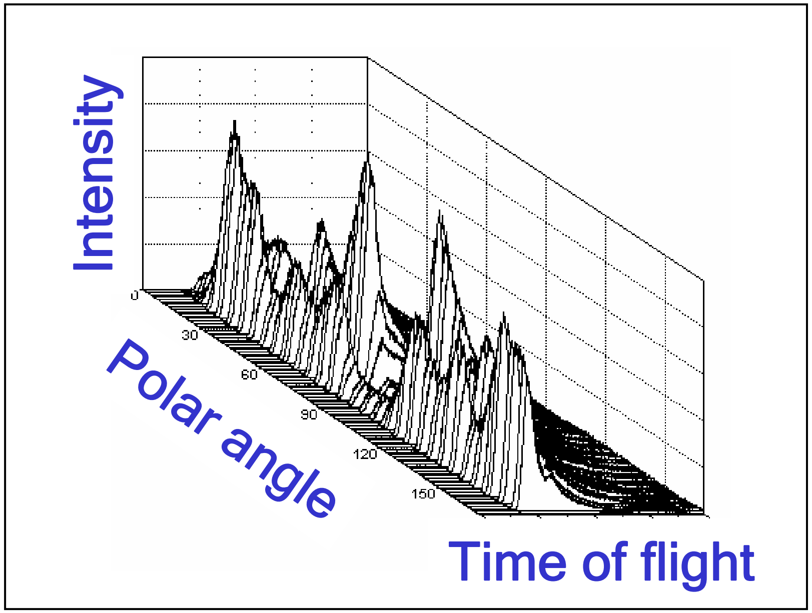
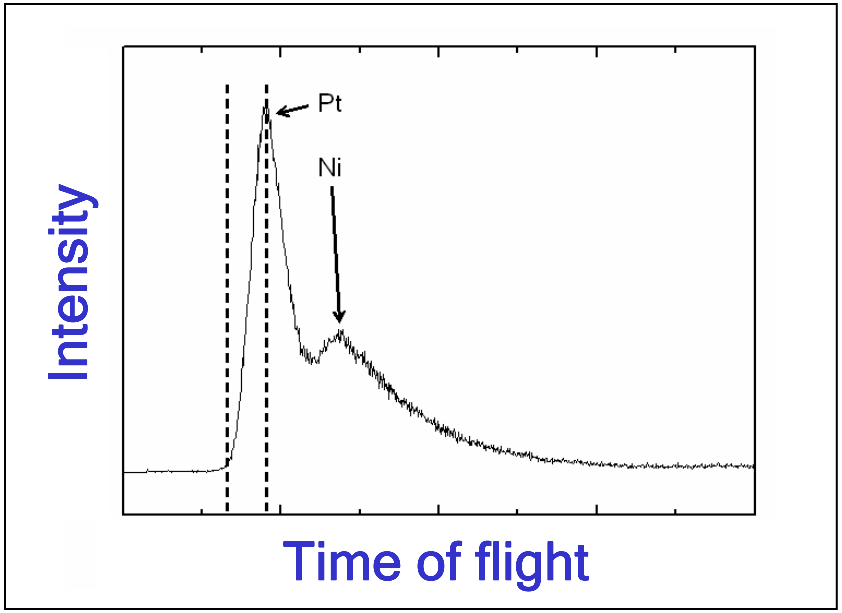


# Extracting information from CAICISS

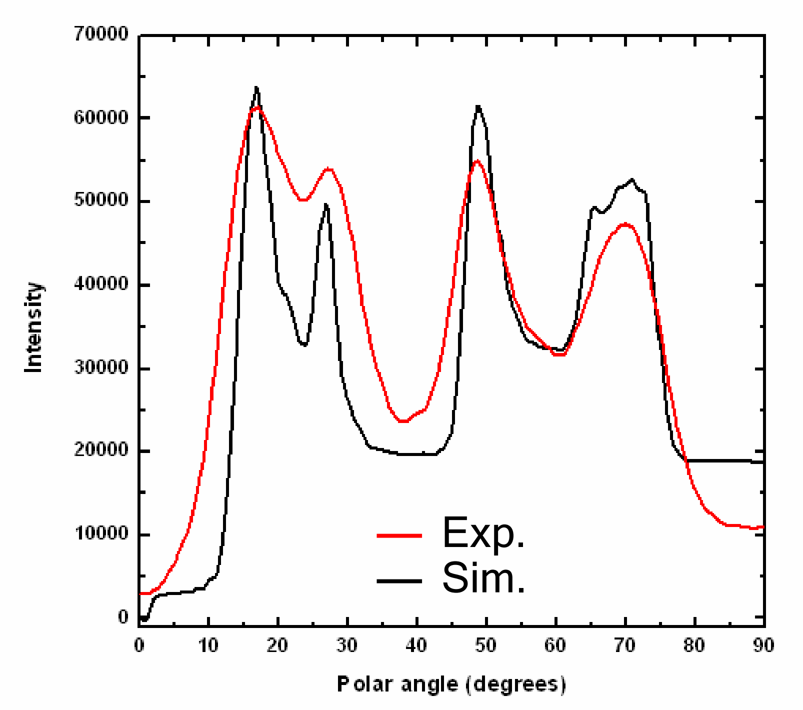
- *Sample rotated from 0° to 180° in 1.8° steps during experiment. Measure intensity vs time-of-flight at each step.*
- *Generate a 3D plot of intensity vs time-of-flight and polar angle.*
- *Determine TOF corresponding to each element in the sample.*





# Extracting information from CAICISS

- *Generate intensity vs polar angle plot for each element.*
- *Use FAN simulation package [1] to test trial structures.*
- *Several features of FAN are adjustable to enable the accurate simulation of the experimental conditions.*



  - *Crystal structure*
  - *Crystal composition*
  - *Interaction potentials*
  - *Incident beam properties*
  - *Debye temperatures*
  - *Scattering angle*

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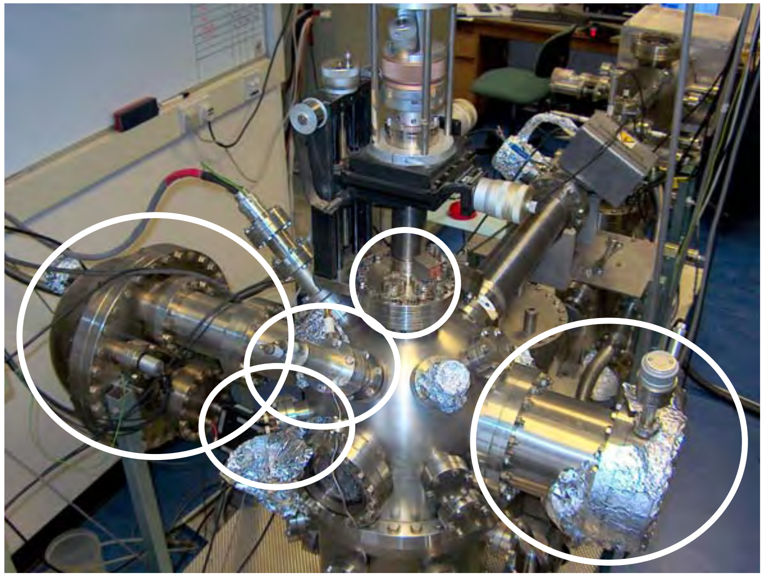
*[1] H. Niehus and R. Spitzl, Surf. Interf. Anal. 17 (1991) 287.*
*(Available from http://asp2.physik.hu-berlin.de/ )*

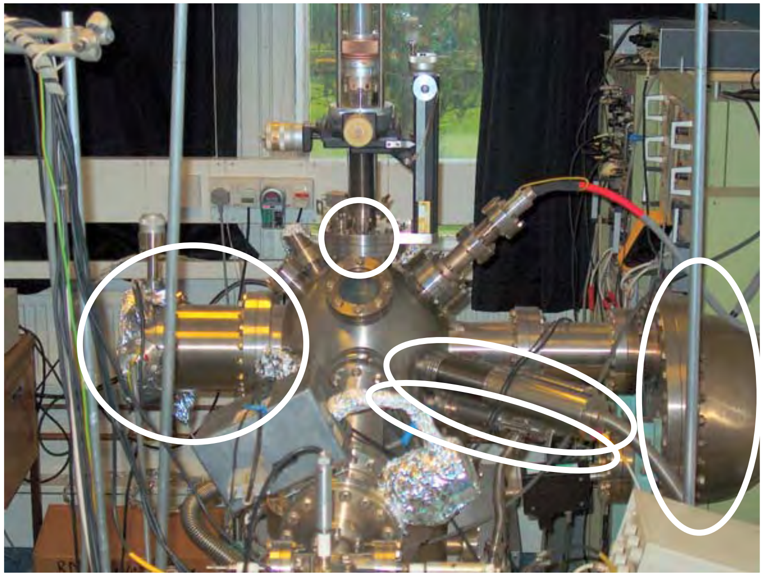
# In summary……

- *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.*
- *Need other techniques to complete the characterization (LEED, XPS, etc) .*

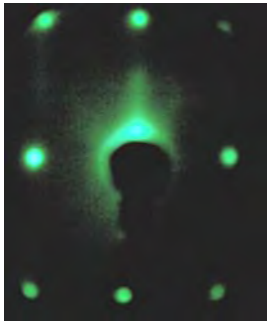
# Other techniques & equipment

- *LEED - Surface periodicity information.*
- *XPS - Chemical information.*
- *Thermal gas cracker - atomic oxygen.*
- *Filament for annealing.*
- *Low energy ion gun.*
- *Pt evaporation source.*

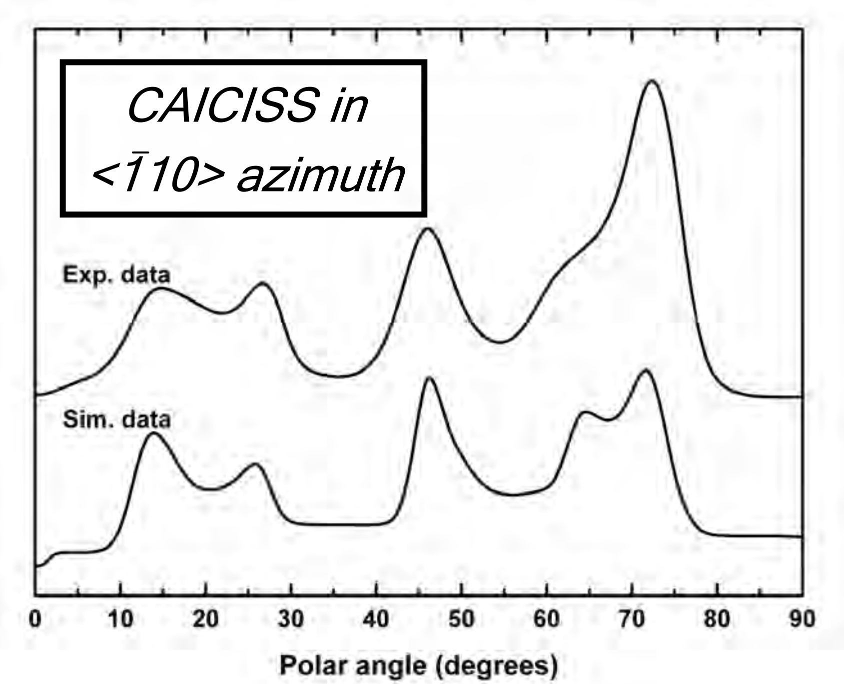




# Clean Ni(110) surface structure



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



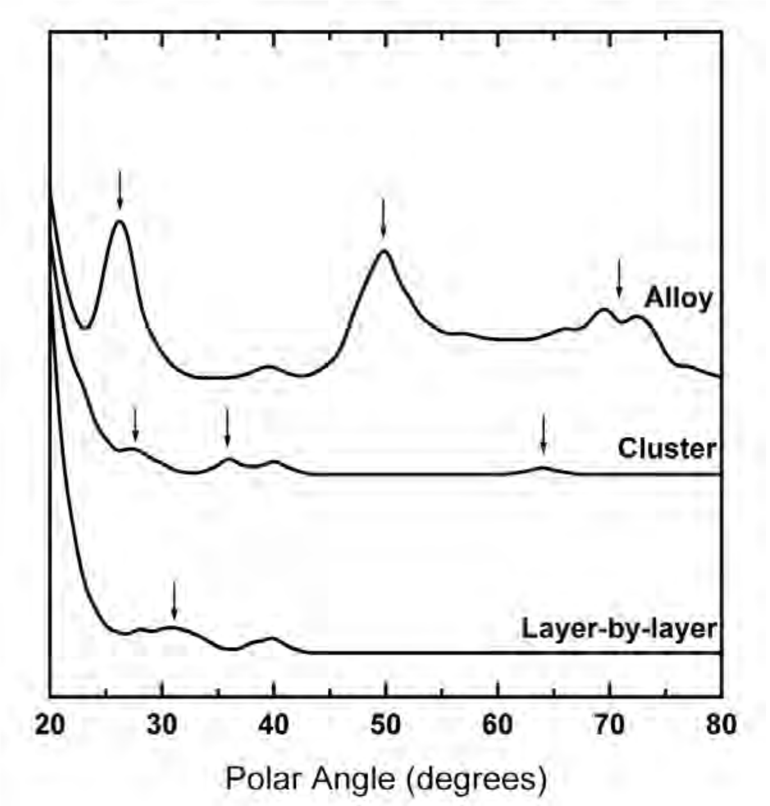
CAICISS in $<\bar{1}10>$ azimuth

# Pt deposition on clean Ni(110)

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

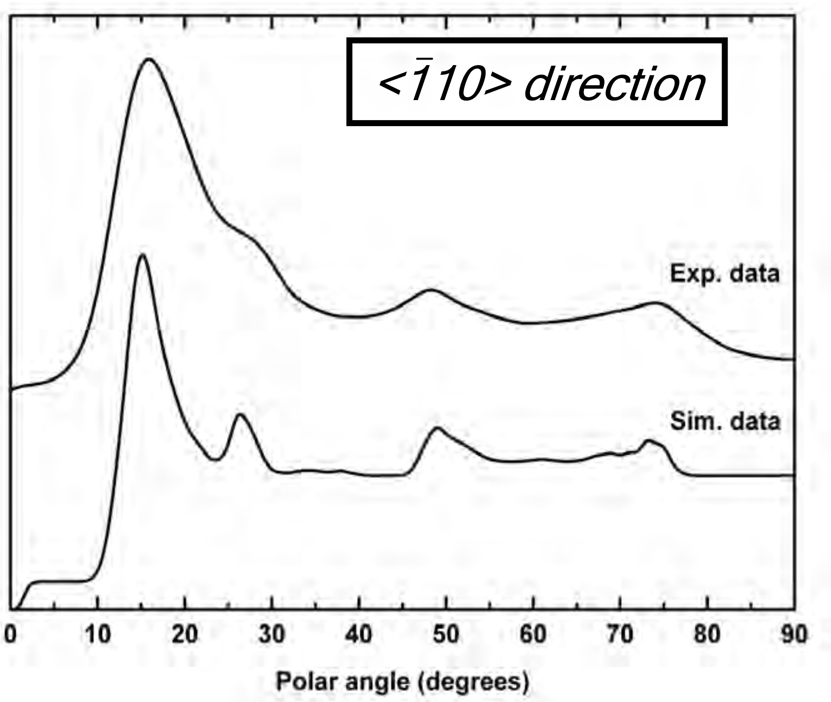
- *Models simulated include:*
  - *Layer-by-layer Pt film growth.*
  - *Ni-Pt alloy in top three layers.*
  - *3D Pt clusters formed on the surface.*

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



# Pt deposition on clean Ni(110)

- *0.22 ML 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.*

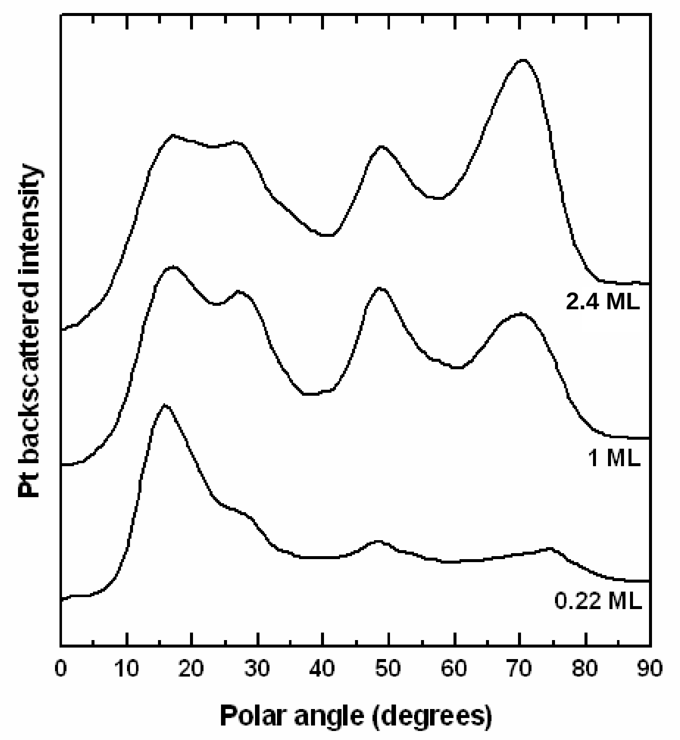


# Pt deposition on clean Ni(110)

- *Continued deposition up to coverage of 2.41 ML (from XPS).*
- *No LEED patterns observed ➢ disorder at the surface.*

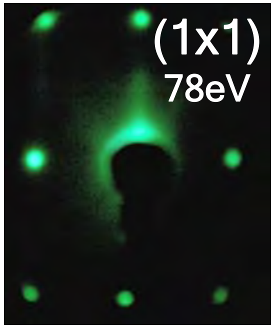
| Pt Coverage | 0.22 ML | 1.07 ML | 2.41 ML |
|---|---|---|---|
| Layer 1 Pt | 15% | 12% | 32% |
| Layer 2 Pt | 5% | 35% | 85% |
| Layer 3 Pt | 2% | 22% | 48% |
| Layer 4 Pt | 0% | 15% | 15% |
| Layer 5 Pt | 0% | 13% | 18% |
| Layer 6 Pt | 0% | 0% | 18% |

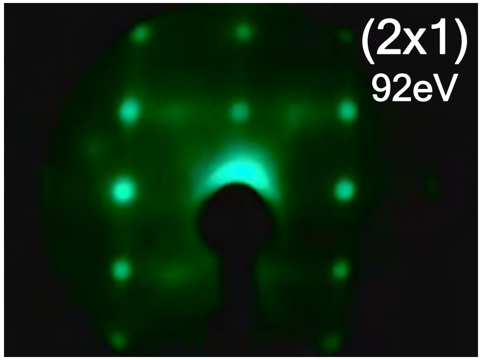
➢ *Room temperature Pt deposition yields a disordered extended Ni-Pt alloy.*

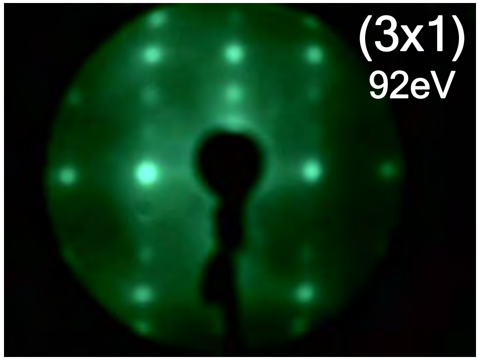


# Oxidation of Ni(110) - LEED

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







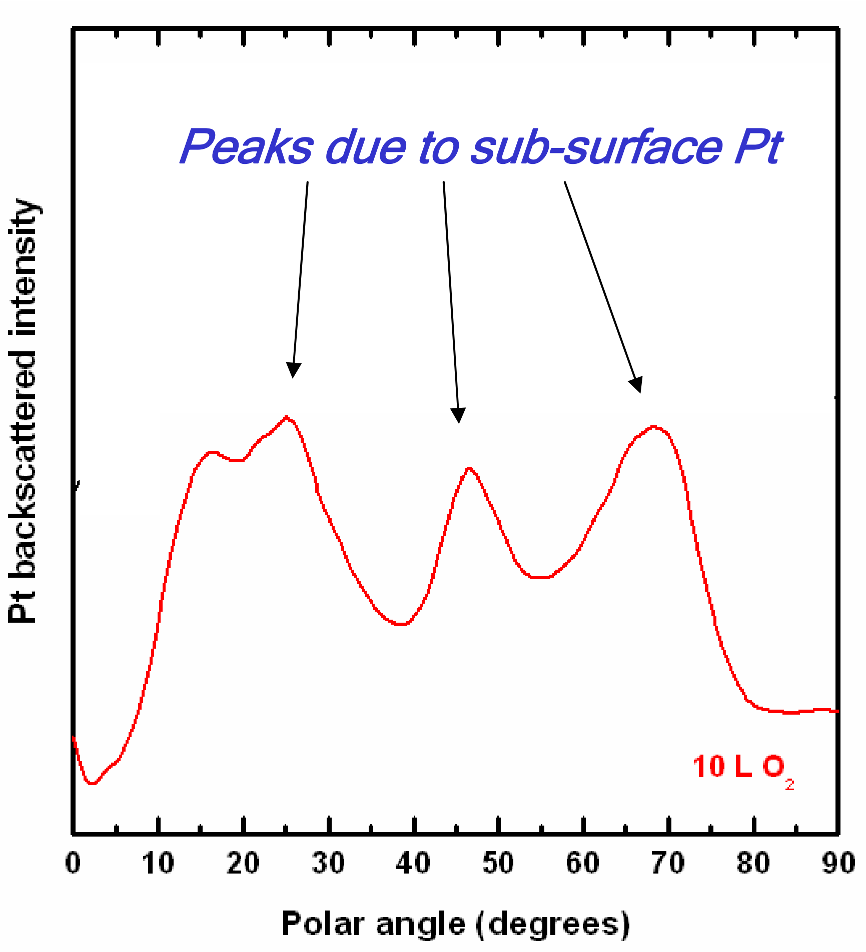
*[2] K. Yagi-Watanabe et al., Surf. Sci. 482-485 (2001) 128.*
*[3] P.R. Norton et al., Surf. Sci. 175 (1986) 313.*

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

- *Deposited ~ 0.5 ML 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.*

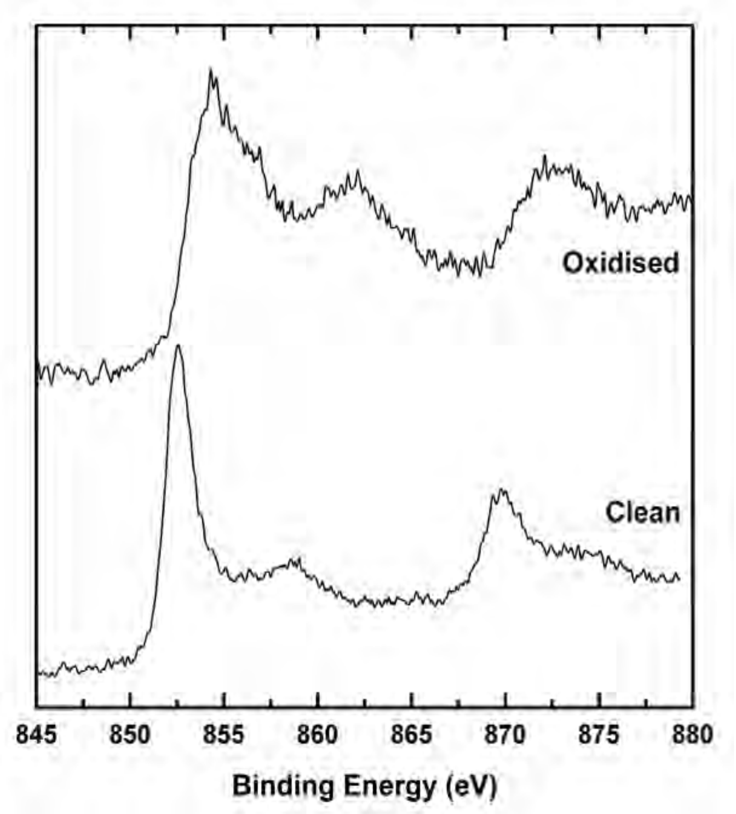
- *Use higher doses of atomic oxygen to form a thick NiO film prior to Pt deposition.*



# 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 |

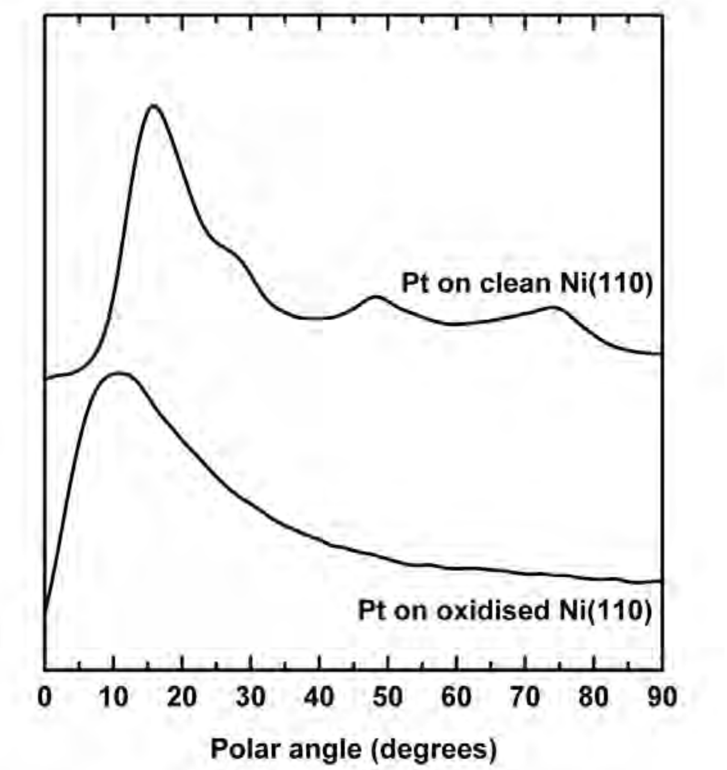


- *No evidence of metallic Ni signal in XPS measurements.*

# Pt deposition on oxidised Ni(110)

- *0.31 ML 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 growing layer-by-layer on top of the NiO film.*



# Pt on oxidised Ni(110) - XPS

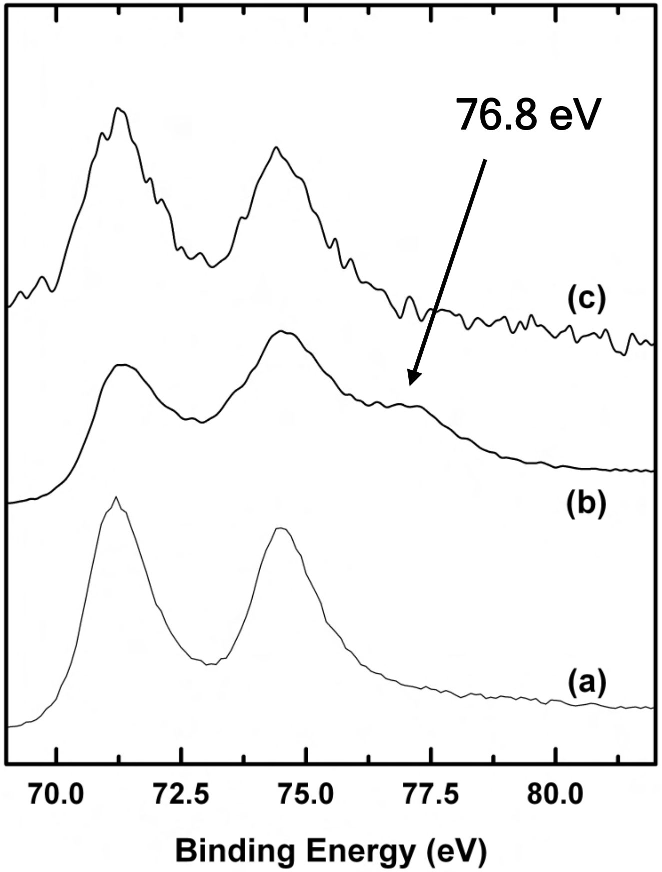
- *Compare Pt 4f peaks to previous work [4].*

- *(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 layer-by-layer Pt film 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 grows layer-by-layer on heavily oxidised surface, in contrast to the alloy formation observed on the clean surface.*

# Acknowledgements

- *Co-workers: Chris McConville (supervisor), Charles Parkinson, Markus Draxler and Rob Johnston (technician).*
- *EPSRC for Doctoral Training Account award [MW].*
- *Austrian Science Fund (FWF), Erwin Schrödinger Fellowship (Project Number J2417-N08) [MD].*

*REFERENCES*

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

*[2] - Ni oxidation - K. Yagi-Watanabe et al., Surf. Sci. 482-485 (2001) 128.*
*[3] - Ni oxidation - P.R. Norton et al., Surf. Sci. 175 (1986) 313.*
*[4] - Clean Pt & PtO data - C.R. Parkinson et al., Surf. Sci. 545 (2003) 19.*

EPSRC Engineering and Physical Sciences Research Council

FWF Der Wissenschaftsfonds.

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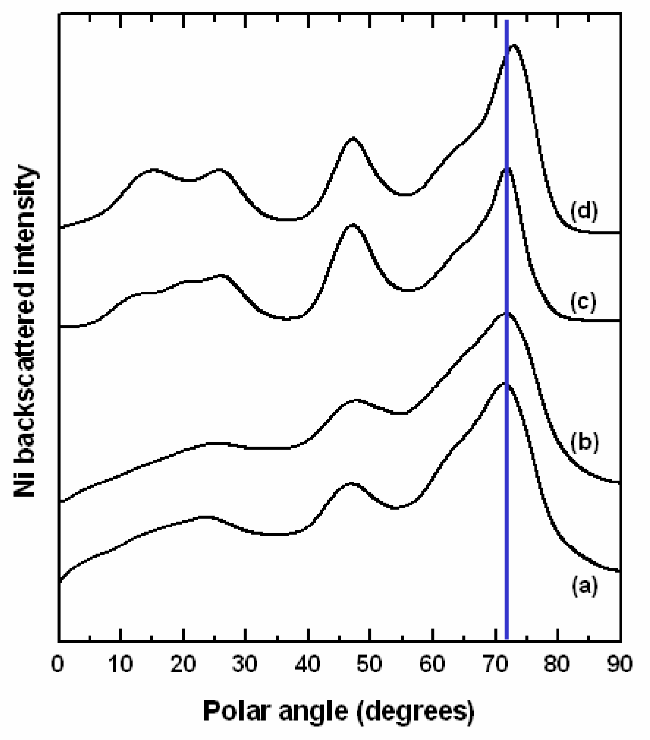
# Pt on oxidised Ni(110) - CAICISS

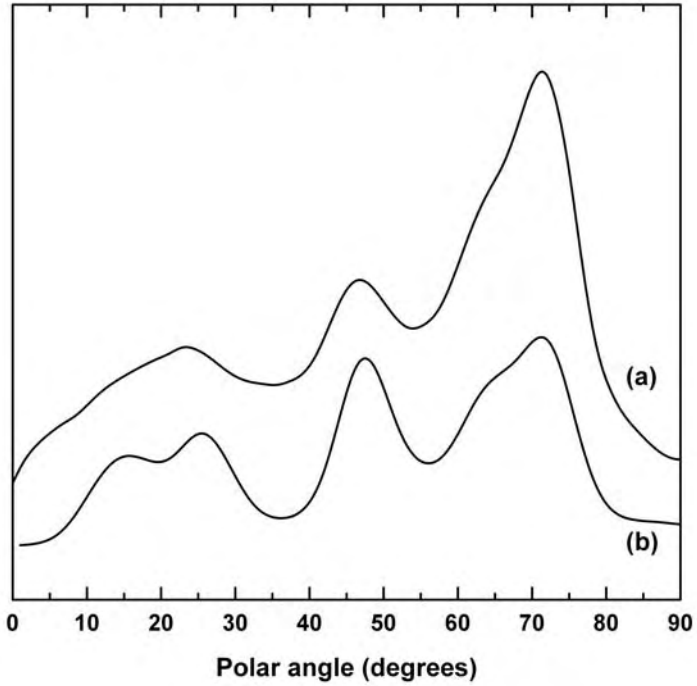
- *Inclusion of Pt in to the NiO film would change interlayer spacings.*
- *Look for changes in the Ni signal before and after Pt deposition.*
  - ➢ *(a) - NiO surface.*
  - ➢ *(b) - Pt-covered NiO surface.*
  - ➢ *(c) - Simulation of (b).*
  - ➢ *(d) - Pt on clean Ni(110).*
- *Little change as a result of Pt deposition.*
- *No expansion in $\Delta_{12}$, 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.*



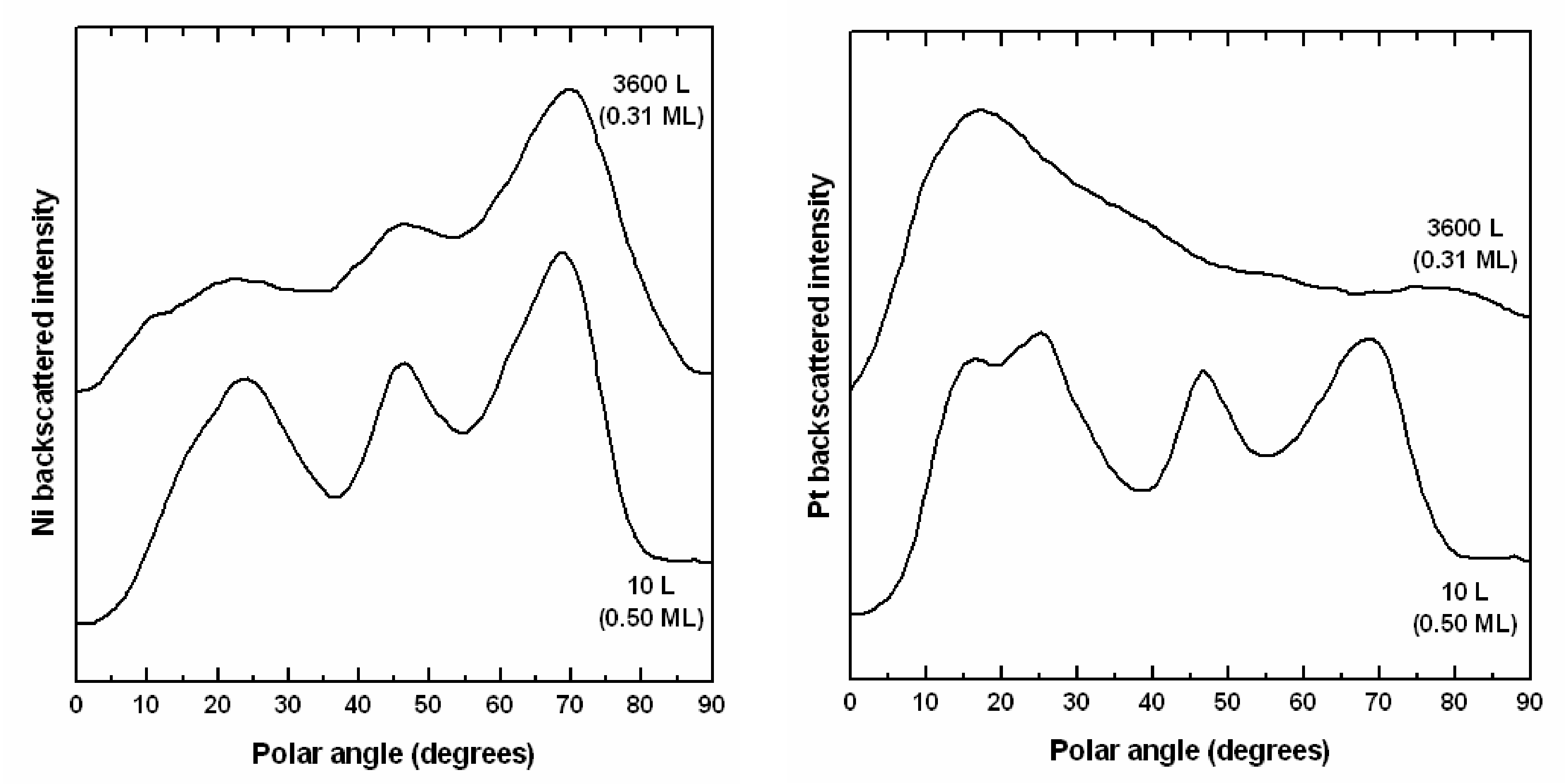
# Oxidation of Ni(110) - CAICISS

- *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).*
- *$\Delta_{12}$ 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.*



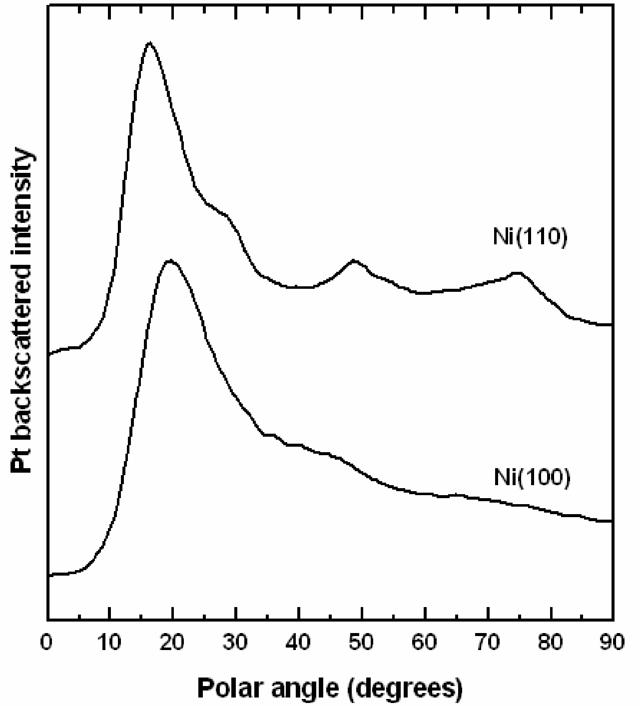
# Pt deposition on clean Ni(100)

- *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).*

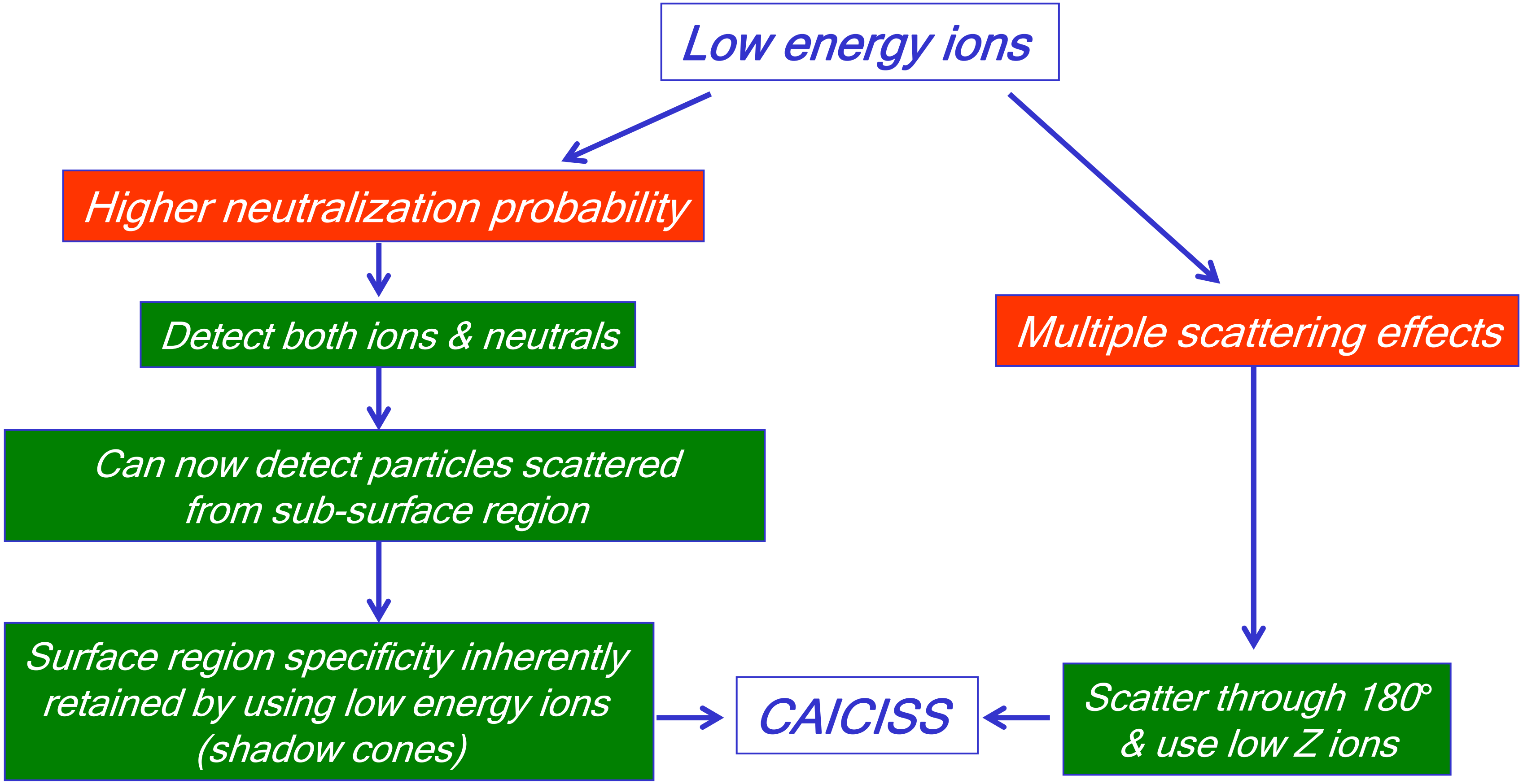
➢ *Suggests layer-by-layer growth.*

➢ *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.*



# 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*

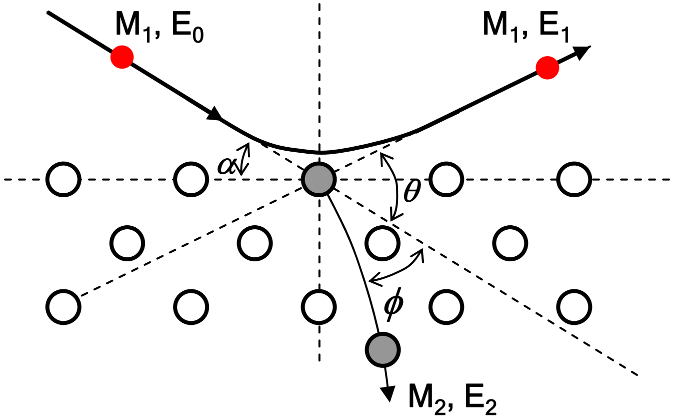
*CAICISS*

# 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:*

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

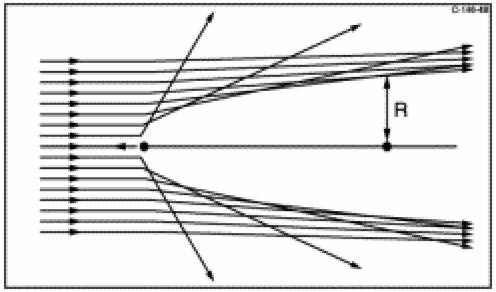
➢ *Measuring $E_1$ leads to determination of $M_2$.*

# Shadow cones

- *Scattering process also described using a Coulombic ion-atom interaction potential.*
- *Have long interaction times at low incident ion energies, so must also consider screening of nuclei by electrons ⇨ screening factor.*
- *Interaction potential ⇨ region in to which ions cannot penetrate.*
  - *Shadow cones*
- *Forward scattering through small angles*

*⇨ increased flux at shadow cone edge*

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

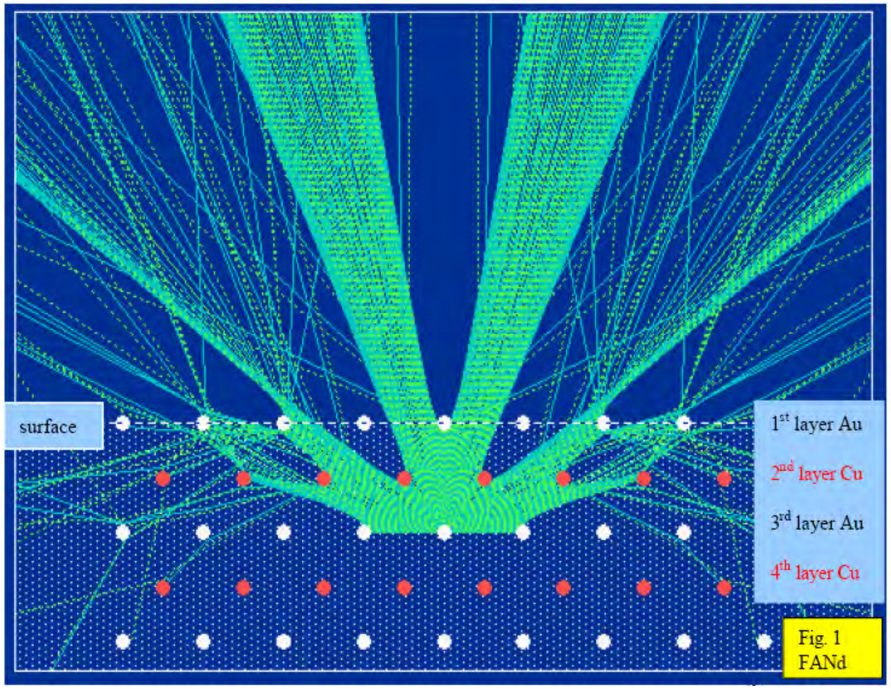


# The FAN simulation program

- *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.*