Growth of Thin Platinum Films on Ni(100) and Ni(110) : A CAICISS, LEED and XPS Study

M. Walker, C.R. Parkinson and C.F. McConville

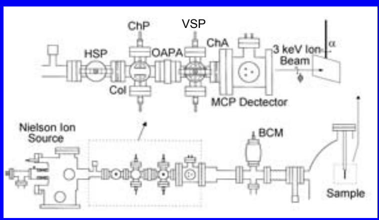
Department of Physics, University of Warwick, Coventry, CV4 7AL, UK

Abstract

Coaxial impact collision ion scattering spectroscopy (CAICISS), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) have been used to study the growth of Pt films on Ni(100) and Ni(110) up to a total deposition of 2.0 ML. The formation of surface alloys upon room temperature Pt deposition, in pressures of approximately 10^{-9} mbar, is observed by CAICISS on Ni(110) from Pt coverages of 0.25 ML upwards. Upon deposition of 2.0 ML, a Ni-Pt alloy is formed in the top five layers of the Ni(110) crystal. Evidence at a coverage of 1.0 ML on Ni(110) is given to support the formation of a surface alloy in contrast to layer-by-layer and island growth modes. Growth of a 0.25 ML Pt film on the Ni(100) surface did not show any sub-surface Pt immediately following deposition. The effects of annealing a 0.25 ML Pt film on Ni(100) at temperatures up to 600 °C are shown, with CAICISS clearly demonstrating the penetration of Pt in to the Ni substrate upon annealing.

Instrumentation

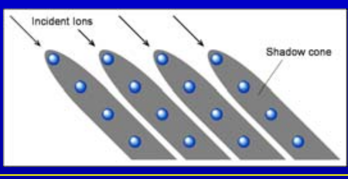
- Equipment includes: CAICISS system (see below), retractable LEED optic, dual anode X-ray source and a 100 mm concentric hemispherical electron analyser.
- Manipulator capable of x,y,z translation, azimuthal and polar rotation, heating to 800 °C.
- Inert gas ion gun for sample cleaning.
- Pt e-beam evaporation source for Pt deposition at approximately 1 ML per hour.



The experimental arrangement of the Warwick modular CAICISS apparatus. The deflection plates and the collimating apertures are also shown in cross-section. Several components are labelled: MCP, micro-channel plate detector; OAPA, off-axis port aligner; ChP, chopping plates; ChA, chopping aperture; BCM, beam current monitor; HSP and VSP, horizontal and vertical steering plates; Col, collimator. The detector-to-sample separation is 80 cm. The scattering geometry adopted for the CAICISS experiments and the rotation axes for the incident polar (α) and azimuthal (ϕ) angles are shown in the upper image.

CAICISS

- Unique surface science technique giving chemical and structural information which is highly surface specific.[1-4]
- 3 keV He^+ ions scattered through 180°. Shadow cones block out contributions from sub-surface layers at specific incidence angles (see diagram below).
- Beam directed across small aperture → He^+ pulses of 60 ns incident on the sample
- Scattered ions and neutrals detected in time-of-flight mode
  → energy spectrum of scattered particles
  → mass of scatterer (from energy and momentum conservation)
  → chemical composition.
- Ion-atom interaction potential → shadow cones
  → trajectory focusing at cone edges
  → large peak when directed on to another target atom
  → intensity vs. incidence angle profile → structural information

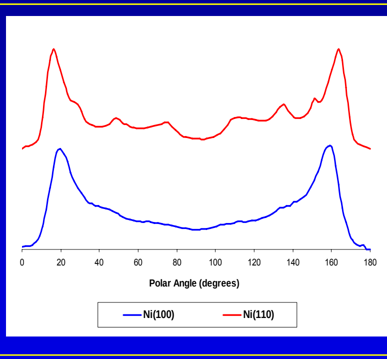


Experimental Detail

- Ni surface cleaned by cycles of Ar^+ bombardment at 3 keV followed by annealing the sample to 800 ˚C.
- XPS to confirm clean surface after a (1x1) LEED pattern had been observed and to calibrate Pt deposition source.
- CAICISS data from the clean surface taken for reference before Pt was deposited at room temperature at coverages up to 2.0 ML (as determined by XPS, relative to the Ni surface).
- 10-minute annealing treatments were carried out in 50 ˚C steps from 200 ˚C to 650 ˚C to observe any changes in the composition and structure of the surface region as a function of annealing temperature.

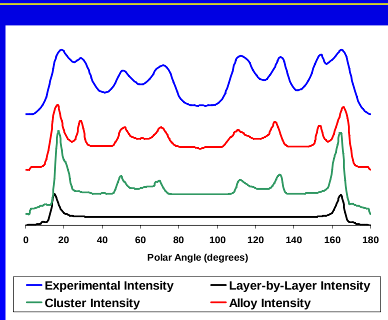
Results

CAICISS Data (Pt coverages determined by XPS)



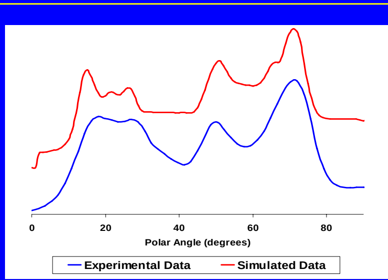
0.25ML Pt on Ni(100) and Ni(110)

- Pt signal from Ni(100) sample shows no peaks due to sub-surface Pt (expected at 45°, 66° and 77°). No LEED pattern was observed. Therefore all Pt is in surface layer in a random alloy with average Ni_3Pt composition.
- Pt signal from Ni(110) sample shows peaks at 27°, 51° and 75° which are due to sub-surface Pt atoms in a random alloy structure. The sample has a surface layer with 20% Pt, 3% Pt in the second layer and 2% Pt in the third layer.
- Therefore, CAICISS shows a difference in the growth modes of Pt on Ni(100) and Ni(110).



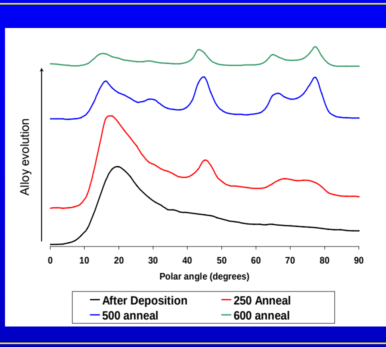
1.0ML Pt on Ni(110)

- Peak at approximately 27˚ in CAICISS data only reproduced by simulations[5] of a random surface alloy in the top 3 layers.
- Layer-by-layer growth and Pt cluster models do not reproduce this feature.
- Formation of a random alloy in the surface region. 25% Pt in the surface layer, with 50% Pt and 25% Pt in the second and third layers.
- No discernable LEED pattern → random alloy.



2.0ML Pt on Ni(110)

- Bulk peaks (50° and 70°) indicate Pt in at least the first 5 layers of the Ni(110) crystal. Find alternating Ni_2Pt and NiPt layers.
- Large bulk peaks (relative to surface peak) reveals relatively large concentrations of subsurface Pt.
- Broadness of surface peak indicates a small Pt overlayer (0.20 ML in this case), which suggests the onset of layer-by-layer growth at coverages above 2.0 ML on Ni(110).



Annealing of a 0.25 ML Pt film on Ni(100)

- Data after deposition shows no sub-surface Pt. Peaks appear at 29°, 45°, 66° and 77° after 250 °C anneal, indicating a small amount of sub-surface Pt (0.05 ML spread over layers 2 and 3).
- Sub-surface peaks continue to increase relative to the surface peak (18°) with annealing treatments up to 500 °C.
- Intensity of all peaks decrease after 600 °C anneal, indicating significant Pt diffusion in to the substrate.

Conclusions

- Difference in initial growth mode of Pt on Ni(100) and Ni(110).
- Random alloy forms at Pt coverages from 0.25 ML to 2.0 ML on Ni(110). Results at higher coverages suggest the formation of Pt overlayers above a total Pt deposition of 2.0 ML.
- On Ni(100), sub-surface Pt is seen in the CAICISS data only after annealing at 250 °C, with significant Pt migration to sub-surface regions starting at 500 °C. The majority of the Pt had diffused in to the substrate after annealing to 600 °C.

References

1. C.R. Parkinson, M. Walker and C.F. McConville, Surf. Sci. **545** (2003) 19.
2. T.C.Q. Noakes, D.A. Hutt, C.F. McConville and D.P. Woodruff, Surf. Sci. **372** (1997) 117.
3. R.J. Dixon, C.F. McConville, S.J. Jenkins and G.P. Srivastava, Phys. Rev. B **57** (1998) R12701
4. H. Niehus, W. Heiland and E. Taglauer, Surf. Sci. Rep. **17** (1993) 213.
5. H. Niehus, FAN simulation software, Humboldt-Universität zu Berlin, Institut für Physik, Berlin (http://asp2.physik.hu-berlin.de/).