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

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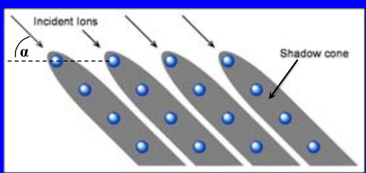
Abstract

The formation of an alloy upon room temperature deposition of Pt on the Cu(100) surface has been observed by co-axial impact collision ion scattering spectroscopy (CAICISS), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS). Simulations of the CAICISS results are given to support the proposed alloy structures at a Pt coverage of 0.55 ML, with comparisons between layer-by-layer, alloy and Pt surface cluster models. With increasing Pt coverage the surface region becomes Pt-rich, with the formation of a Pt overlayer observed at coverages of 2.35 ML and above. This indicates the onset of layer-by-layer growth of a pure Pt film. LEED observations indicate that the film is disordered. The effects of annealing at temperatures up to 300 °C are also shown for a Pt coverage of 2.75 ML, where CAICISS clearly demonstrates the penetration of Pt in to the Cu substrate.

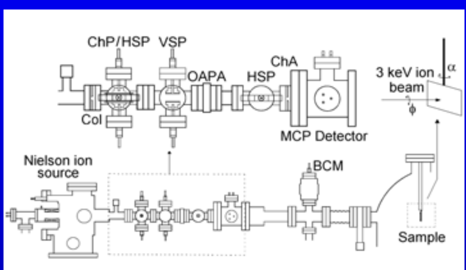
CAICISS

- Unique surface science technique giving both chemical and structural information which is highly surface specific.[1-3]
- 3 keV He^+ ions scattered through 180°. Shadow cones block contributions from sub-surface layers in specific scattering geometries.
- Beam directed across a small aperture → pulses of ~ 60 ns incident on the sample
- Scattered ions and neutrals are detected in time-of-flight mode
  → energy spectrum of scattered particles
  → mass of scatterer and hence chemical composition.
- Ion-atom interaction potential (ZBL function or Molière approximation to the Thomas-Fermi model)
  → shadow cones → trajectory focusing at cone edges
  → large peak when directed on to another target atom
  → intensity vs. polar angle (α) profile
  → structural information

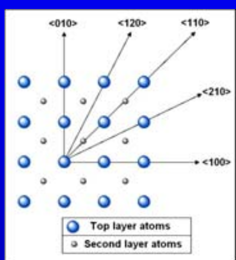


Experimental Detail

- The Cu(100) surface was cleaned by cycles of Ar^+ bombardment at 3 keV followed by annealing the sample to 800 ˚C. XPS was used to confirm a 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 coverages up to 2.75 ML (as determined by XPS and CAICISS, relative to the Cu surface).
- Annealing treatment at 300 °C for 10 minutes to observe any changes in the composition and structure of the surface region as a result of annealing the surface.



The experimental arrangement of the Warwick modular CAICISS apparatus (described in detail elsewhere[1]). 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-right of the image.



All presented data, collected in the <100> azimuth (shown above), have been analysed with the help of the FAN simulation package[4].

References

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4. H. Niehus, FAN simulation software, Humboldt-Universität zu Berlin, Institut für Physik, Berlin (http://asp2.physik.hu-berlin.de/).
5. R. Belkhou, J. Thiele and C. Guillot, Surface Science 377- 379 (1997) 948.

Results

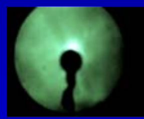
LEED Observations and CAICISS Data

(Pt coverages determined by CAICISS and XPS, accurate to ± 5% ; Interlayer spacings from CAICISS are accurate to ± 0.02 Å)

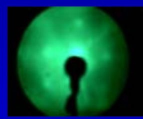
LEED Observations

clean surface, (1x1)
(at 65 eV)

0.55 ML, c(2x2)
(at 120 eV)

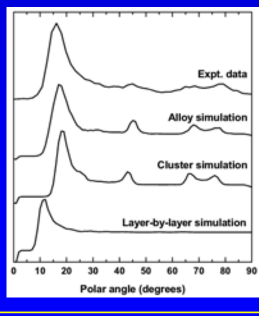


2.75 ML, no pattern
(at 120 eV)



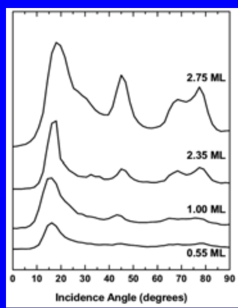
300 °C anneal, weak c(2x2)
(at 120 eV)

Study of growth mode



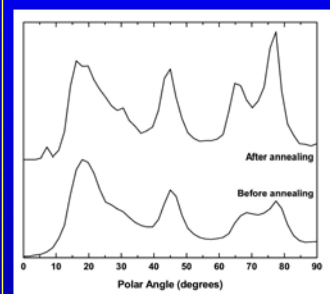
- Experimental Pt coverage calculated to be 0.55 ML by CAICISS and XPS.
- Peaks at 45°, 67° and 75° indicate a small amount of Pt which does not reside in the surface layer. All features best reproduced by the alloy model. The weak c(2x2) pattern observed suggests some disorder in the alloy.
- FAN simulation results show the Pt concentration to be approximately 5% in both the second and third layers of the sample. The surface layer comprises 55% Cu and 45% Pt in a random alloy arrangement.

Pt deposition up to 2.75 ML



- Sub-surface Pt at sub-monolayer coverage (45°, 67° & 75° peaks).
- Observe feature at ~ 32° at 2.35 ML coverage and above, due to 0.12 ML overlayer of Pt situated 2.20 Å above the surface.
- Surface Pt enrichment with increasing coverage. Top layer observed to contain 80% Pt at 1.00 ML, 87% at 2.35 ML and 100% Pt at 2.75 ML. Drift in surface peak from 16° to 18° due to incorporation of larger Pt atoms in to the alloy structure.
- Change in spacing between the surface layer and second layer. Spacing is 1.79 Å for clean surface and 2.00 Å at 2.75 ML coverage. Seen as a shift in peak positions to larger polar angles with increasing coverage.
- No LEED pattern observed, therefore a disordered film at 2.75 ML.

Annealing of 2.75 ML Pt film at 300 °C



- Increase in the relative intensity of the central peaks show significant migration of Pt from surface to bulk during annealing at 300 °C.
- Surface layer changes from purely Pt to an average CuPt composition. Second layer changes from 90% Pt to an average Cu_2Pt composition.
- Increase in amount of Pt in deeper layers. Alloy with average Cu_3Pt composition is formed in layers three, four and five. CAICISS cannot penetrate deeper in to the sample in this azimuth.
- Amount of Pt above the surface is reduced from 0.12 ML to 0.05 ML.
- Weak c(2x2) LEED pattern observed. Some ordering is also indicated by the general sharpening of the peaks following annealing.

Conclusions

- Sub-surface Pt found at sub-monolayer Pt coverages, exhibiting a weak c(2x2) LEED pattern at a coverage of 0.55 ML.
- Formation of Cu-Pt alloy, with surface becoming more Pt-rich with increasing amount of deposited Pt. Possible onset of layer-by-layer growth above coverage of 2.35 ML and above, in agreement with Belkhou et al[5].
- Annealing at 300 °C results in Pt diffusing in to the bulk. Annealing a sample with 2.75 ML of Pt resulted in a CuPt surface layer, Cu_2Pt second layer and Cu_3Pt in layers 3, 4 and 5. Some ordering is indicated within the alloy.

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