# Growth of Thin Platinum Films on the Cu(100) Surface

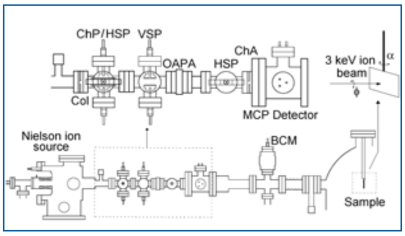
M. Walker, C.R. Parkinson, M. Draxler and C.F. McConville *
Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom.

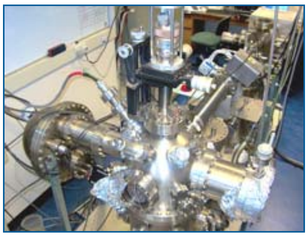
## Introduction

- Pt and Cu are widely used materials in catalytic processes. Aim to investigate new alloy and thin film structures to potentially aid such processes.
- Use co-axial impact collision ion scattering spectroscopy (CAICISS) [1-3], low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) to investigate the characteristics of the clean Cu(100) surface, Pt deposition, and subsequent annealing. This combination of surface sensitive techniques allows us to probe the compositional and structural properties in a layer-by-layer fashion.
- At room temperature, Pt deposition leads initially to the formation of a disordered Cu-Pt alloy in the surface region. Further Pt deposition leads to the formation of a Pt-rich surface, possibly an indication of the onset of layer-by-layer Pt film growth.
- Observe changes to the lattice structure due to the incorporation of the larger Pt atoms.
- Annealing to temperatures in excess of 300 °C leads to the diffusion of Pt into the bulk Cu(100) structure, as well as some re-ordering of the lattice.

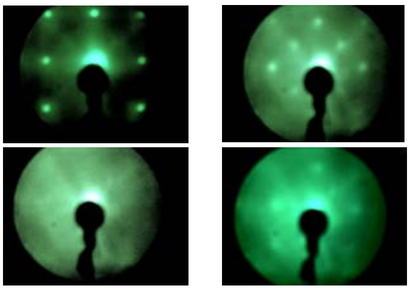
## Experimental Details

- Low energy ion bombardment & annealing was used to clean the surface (typically bombarded with 3 keV $Ar^+$ for 30 minutes, followed by an 800 °C anneal for 1 hour).
- Pt deposition was carried out using a home-made Pt evaporation source, with coverages calculated using XPS. A deposition rate of approximately 1 ML per hour was used throughout.
- LEED was used to monitor the surface periodicity and to enable accurate sample alignment for CAICISS.
- CAICISS details - 3 keV $He^+$ beam; polar angle scans taken in <110> azimuth, in 1.8° steps with 100 s step duration.



## LEED Observations



Clean surface (1x1), 65 eV

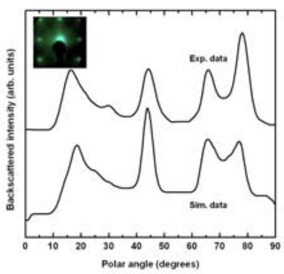
0.55 ML c(2x2), 120 eV

2.75 ML no pattern, 120 eV

300 °C anneal weak c(2x2), 120 eV

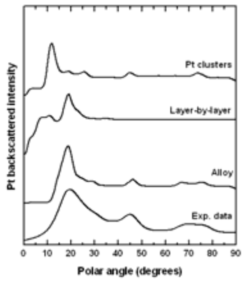
## CAICISS Data - Clean Cu(100)

- A (1x1) LEED pattern and contaminant-free XPS spectra (not shown) were recorded before CAICISS experiment.
- Simulations of data using the FAN package [3] revealed a 1.6% contraction in the outermost interlayer spacing, $\Delta_{12}$, to 1.78 Å (bulk value = 1.81 Å).
- $\Delta_{23}$ expanded by 1.6% to 1.84 Å.
- Deeper layers unchanged relative to the bulk spacing.
- Observations in agreement with previous data [4].



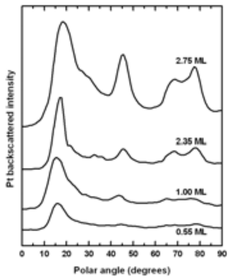

## CAICISS Data - 0.25 ML Pt Deposition

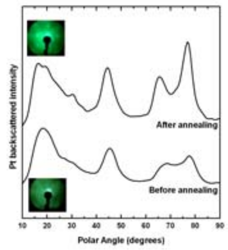
- Pt deposited at 300 K.
- XPS data taken ⇨ Pt coverage of 0.25 ML.
- Simulations discount Pt clusters on the surface and the growth of a Pt thin film on top of the Cu(100) structure.
- FAN indicates a Cu-Pt alloy in the top three layers of the structure. Majority of Pt remains in outermost layer (see table below).
- Expansion of the interlayer spacings in the surface region (see table), is due to incorporation of Pt in to the structure.




## Pt Deposition to 2.75 ML & Annealing

- Pt deposition continued, with CAICISS data taken at coverages of 1.00, 2.35 and 2.75 ML.
- Initially, Pt resides mainly in the surface layer. However, it begins to penetrate as far as the fifth layer of the Cu(100) structure at coverages of 2.35 ML and higher.
- Pure Pt surface layer observed at 2.75 ML, in conjunction with a 0.12 ML Pt overlayer, 2.2 Å above the surface layer (and required for the feature observed at ~ 30°).
- Observations indicate the onset of layer-by-layer growth of a disordered Pt film (disorder indicated by LEED).
- Annealing at 300 °C leads to some degree of ordering, seen in the sharpening of CAICISS features and the recovery of a weak c(2x2) LEED pattern.
- Annealing at 300 °C leads to the diffusion of Pt in to the bulk Cu lattice. Layer compositions are shown in the table below.
- Observations in qualitative agreement with previous data [5].




| Pt coverage | 0.00 ML | 0.25 ML | 0.55 ML | 1.00 ML | 2.35 ML | 2.75 ML | 300 °C anneal |
|---|---|---|---|---|---|---|---|
| Pt in overlayer | - | 0 | 0 | 0 | 0.12 ML | 0.12 ML | 0.05 ML |
| Surf. layer Pt | - | 18% | 45% | 80% | 87% | 100% | 50% |
| Layer 2 Pt | - | 5% | 5% | 10% | 85% | 90% | 33% |
| Layer 3 Pt | - | 2% | 5% | 10% | 50% | 55% | 25% |
| Layer 4 Pt | - | 0 | 0 | 0 | 0 | 5% | 25% |
| Layer 5 Pt | - | 0 | 0 | 0 | 0 | 15% | 25% |
| Surf. - overlayer | - | - | - | - | 2.20 Å | 2.20 Å | 2.20 Å |
| $\Delta_{12}$ | -1.6% | +7.7% | +10.5% | +10.5% | +10.5% | +10.5% | +10.5% |
| $\Delta_{23}$ | +1.6% | +1.6% | +2.2% | 0 | 0 | 0 | 0 |
| $\Delta_{34}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

- Total Pt coverages from XPS, accurate to ± 0.05 ML.
- Interlayer spacings and layer compositions from CAICISS, accurate to ± 0.02 Å and ± 5% respectively.

## Conclusions

- Clean Cu(100) surface shows small relaxations in the outermost layers.
- Initial deposition of Pt on to the Cu(100) surface at room temperature leads to the formation of a disordered, substitutional Cu-Pt alloy in the three outermost layers of the Cu(100) structure. The majority of the Pt atoms reside in the surface layer at sub-monolayer coverage.
- At Pt coverages in excess of 2 ML, the surface and second layers were observed to be Pt-rich, with a 0.12 ML Pt overlayer. This indicates the onset of the layer-by-layer growth of a disordered Pt film.
- Annealing the structure containing 2.75 ML of Pt to 300 °C leads to the diffusion of Pt in to the Cu bulk structure, with some ordering observed at the surface.

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* *Corresponding author (e-mail: C.F.McConville@warwick.ac.uk)*

The University of Warwick

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