MEIS studies of oxygen plasma cleaning of copper for fast response time photocathodes used in accelerator applications

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Overview

- Motivation
- Experimental Details
  - MEIS Facility
  - Data Analysis
- Effect of plasma treatment parameters on oxide composition
  - Plasma power
  - Treatment time
  - Annealing temperature
- XPS Data – comparison with MEIS
- Summary
- Further work

Photocathodes

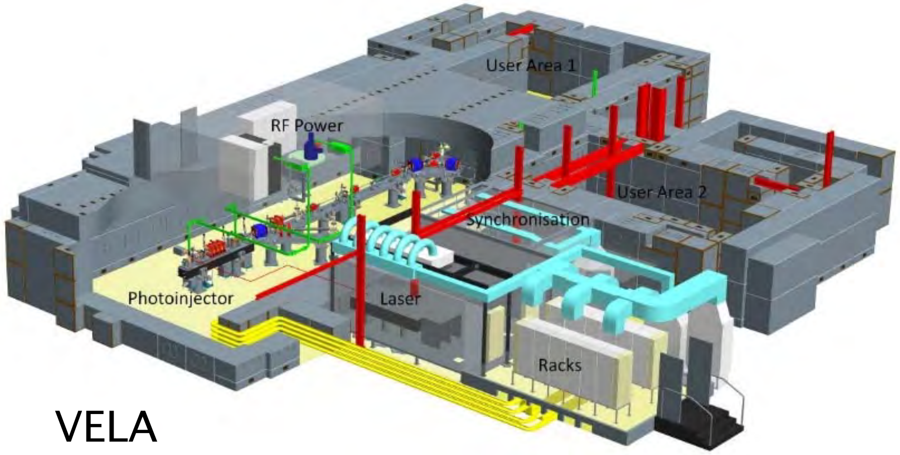
Industrial applications

- Photomultiplier tubes
- Image Intensifiers

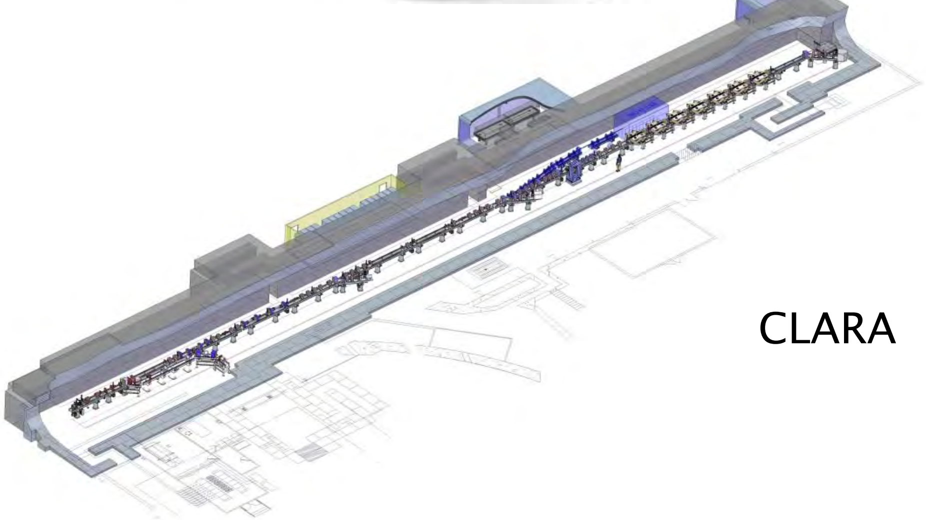
Accelerator Applications

- Light sources
- Electron accelerators for high-energy physics

<u>Test facilities at Daresbury Laboratory</u>

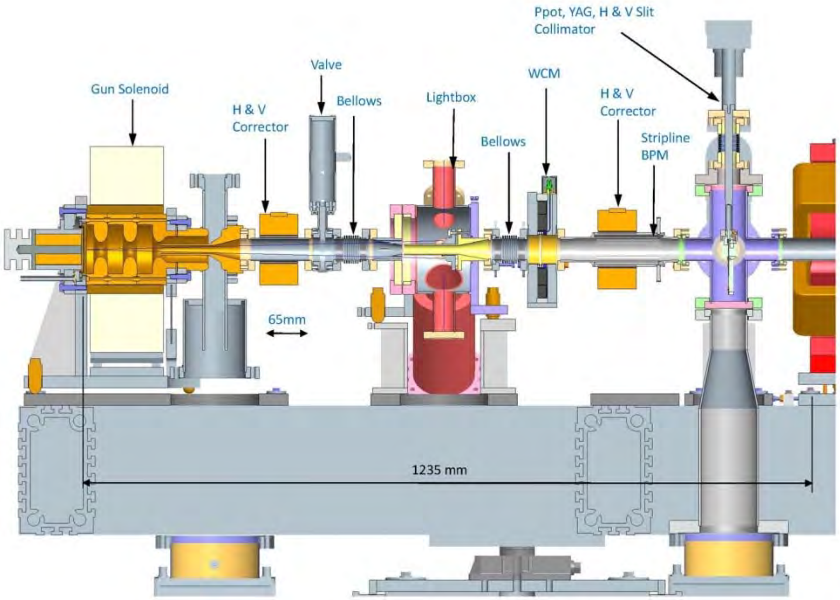


VELA

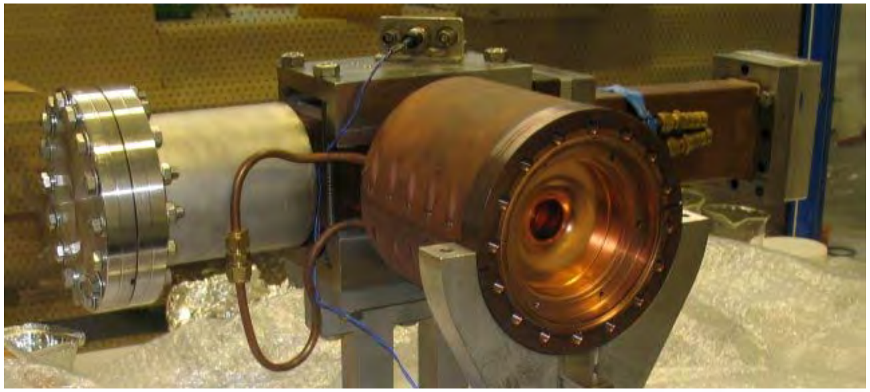


CLARA

2.5 cell S-band RF Gun



- 2.5 cell S-band RF gun
- Cu photocathode: **QE = 10^{-5}**
- Sub-100fs mode-locked laser
- Field gradient of 100 MV/m
- Max beam energy = 6.5 MeV



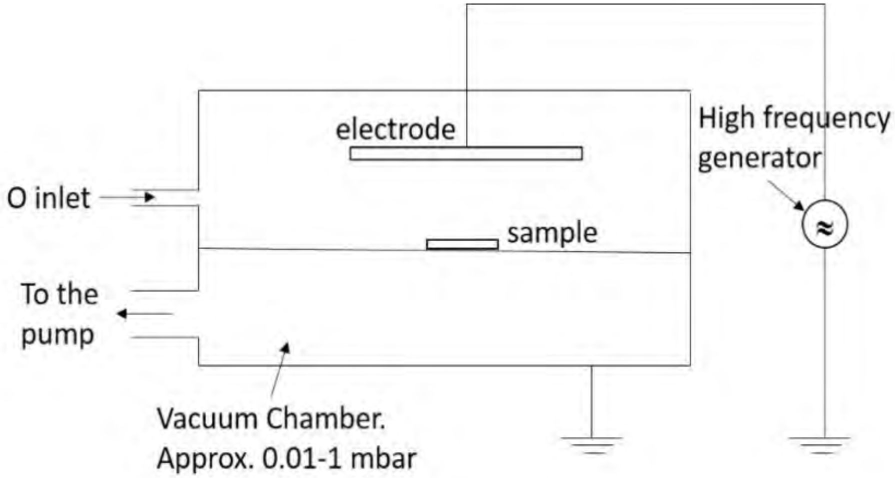
Photocathode preparation

- carried out ex-situ
- cathode transferred in-air

Cathode Preparation

VELA Cu photocathode prepared by:

- **O_2 plasma cleaning**
  - Removes hydrocarbons
  - Likely to leave a thin protective oxide layer
- **Heating to 250 ˚C (system bake)**

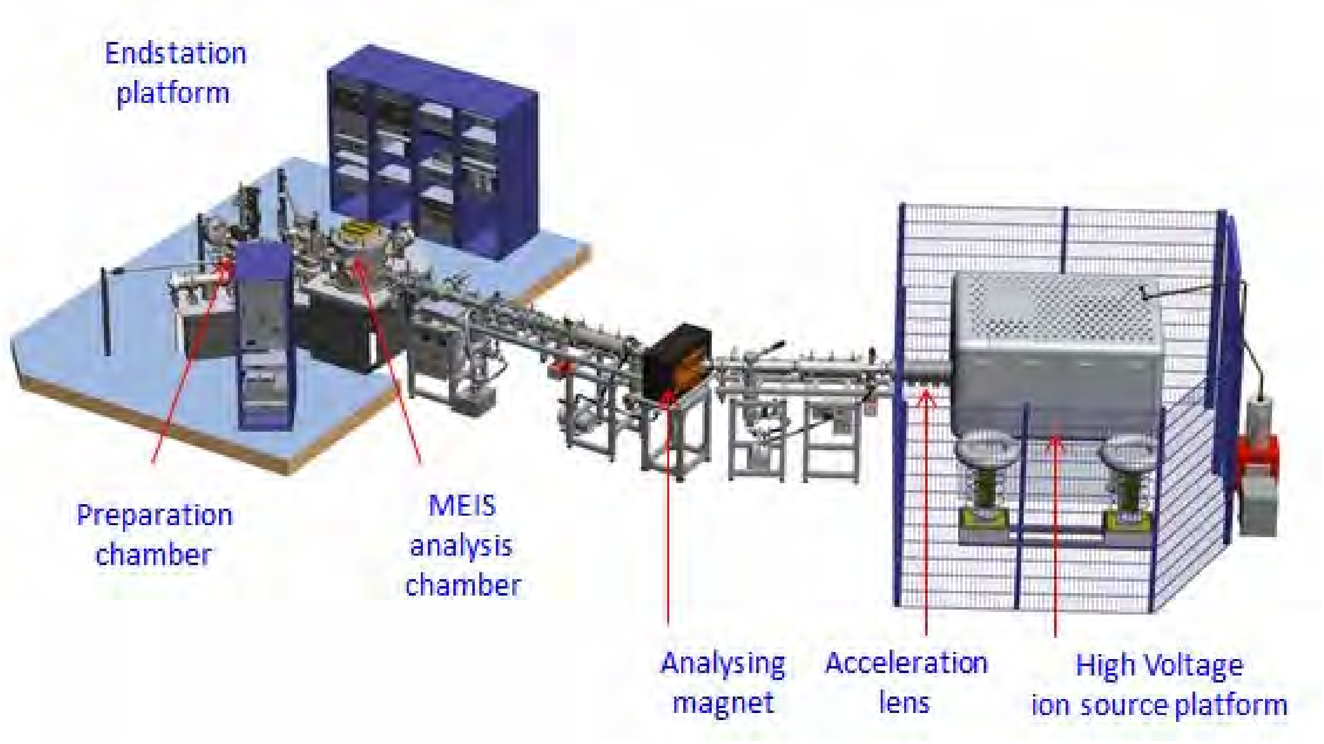


Schematic of plasma cleaner

Poor detailed understanding of the changes in composition and thickness of the oxide film in this preparation process

MEIS facility at University of Huddersfield

Use MEIS to investigate effects of oxygen plasma treatment on the thickness and composition of the oxygen film



- 100 keV He ions
- 35.3° incidence angle, 90° scattering angle
- 0.5 x 1.0 mm spot size with a dose of 1.25 μC per tile (1.27 x 10^{15} atoms/cm^2)

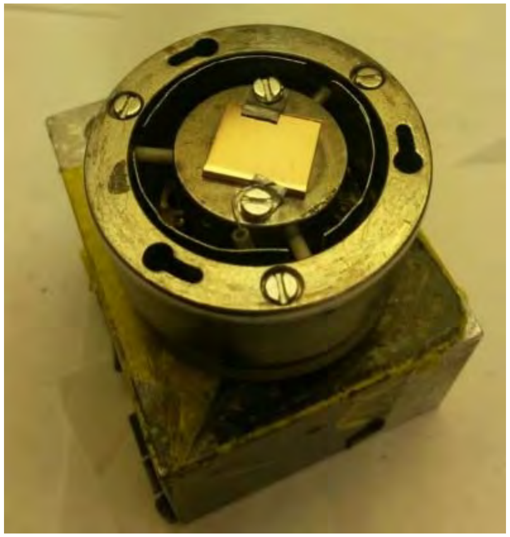
Experimental Detail

All samples cut from ‘as-rolled’ oxygen free copper cleaned with acetone and propanol

Investigate the Cu surface of samples exposed to oxygen plasma with

- Power levels between 10-100% (20-200W)
- Treatment times between 10-40 minutes

Samples mounted and transferred in-air to MEIS system



- Post heat treatment studies (in-situ - MEIS)
    - ~300˚C by radiative heating
    - ~600˚C by e-beam heating

- Temperature monitored using an IR pyrometer (probably not accurate – bottom edge of range)

MEIS Energy Spectra

Ar sputtered samples are essentially pure Cu at the surface and throughout

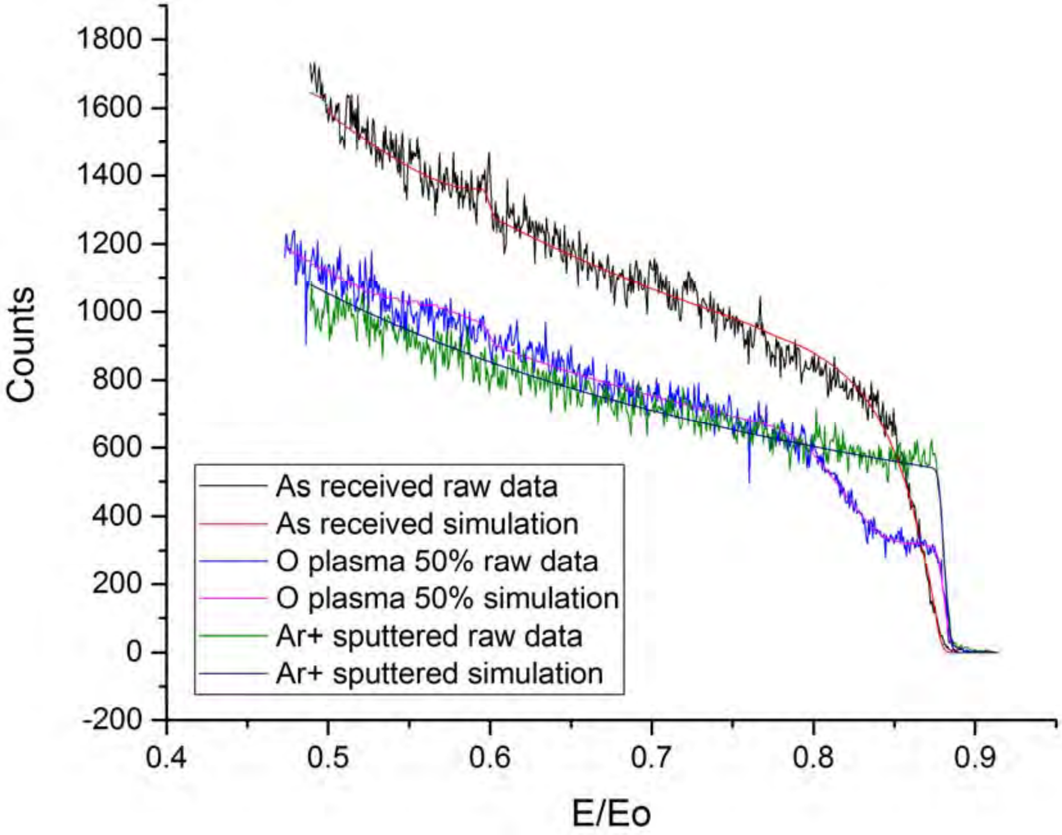
- Allows independent calibration of energy and resolution

As-loaded samples have lower energy and more inclined leading edge

- Thin (~4nm) layer of hydrocarbon contamination

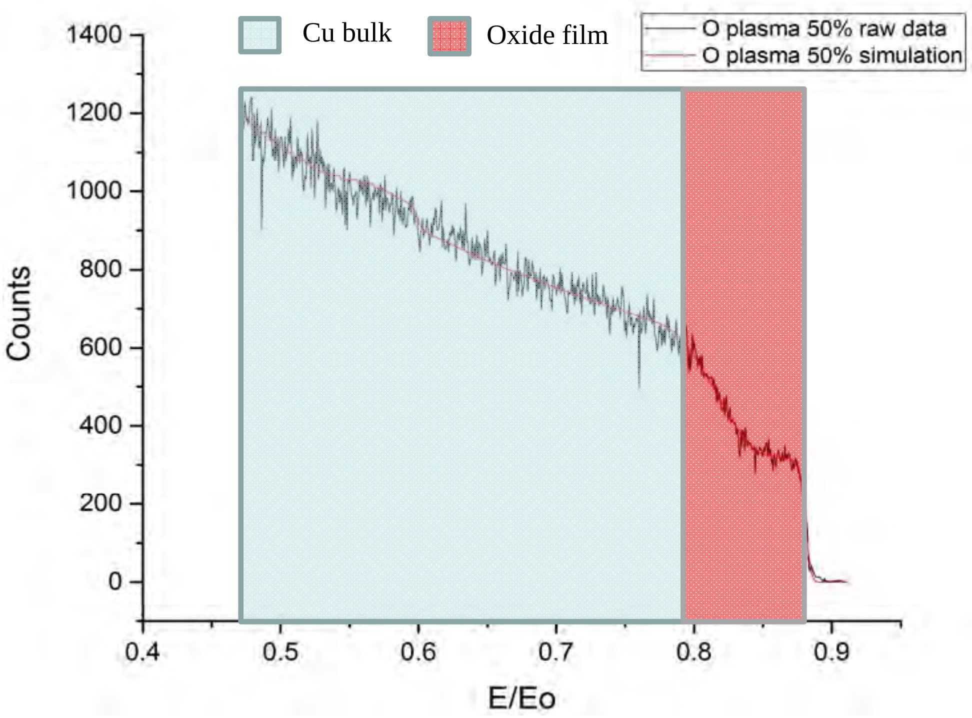
Oxygen treated samples have no hydrocarbon but thick oxide layer has been grown

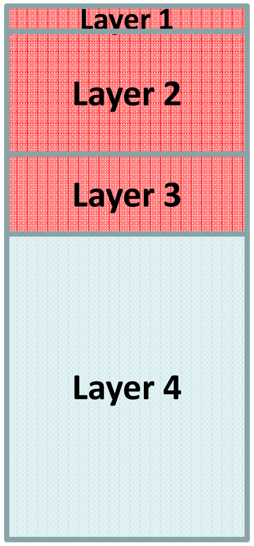
- Step width gives the thickness
- Height gives composition (O signal not large enough to influence fit significantly)



Depth Profiling

Data fitted using SIMNRA 5.02





Layer 1: Surface Layer

- Set to a couple of monolayers thickness (10×10^{15} Atoms/cm^2).
- Composition was treated as variable

Layer 2: Oxide Layer

- Composition and the thickness of this layer were treated as variable to best produce a good fit.

Layer 3: Interfacial layer

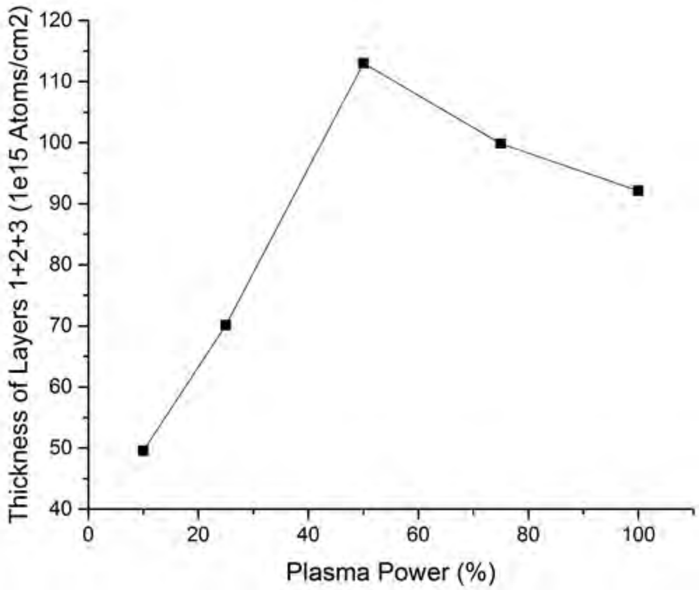
- Composition and the thickness treated as variable
- This layer probably has gradually varying composition, but is modelled by a single composition with roughness added (in layer above) to smear out the signal and improve the fit.

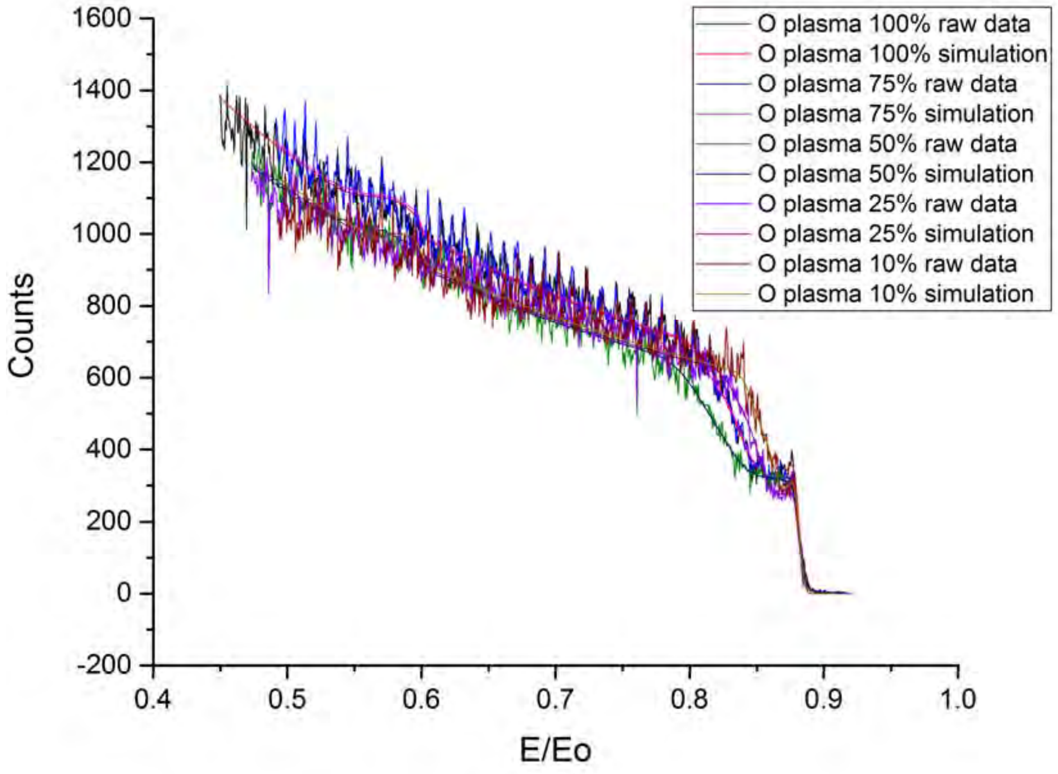
Layer 4: Cu Bulk

- Pure Copper bulk

Plasma Power Variation

Oxide film thickness increases until maximum at 50% power but decreases again above this?

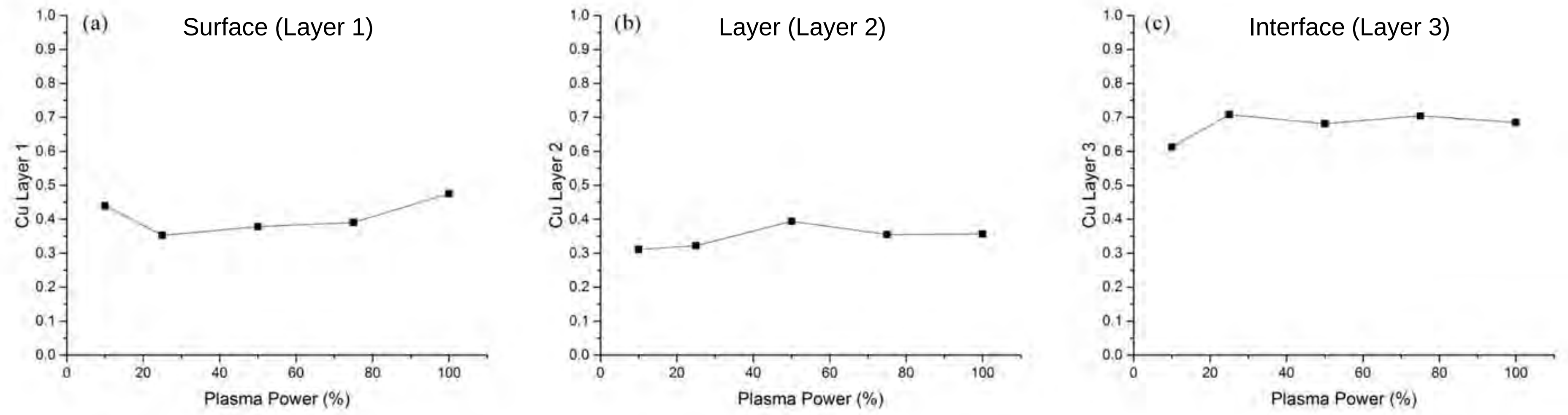




- Plasma density inhomogeneity at higher power settings?
- Sample not sitting in the highest plasma density region?

Plasma Power Variation

Copper fraction as a function of depth and plasma power



a) Surface composition slightly higher than layer beneath (40.7%)

- Anomalous surface peaks seen previously for oxides (charge fraction)*

- Small reduction in oxygen content?

b) Layer composition consistent with CuO_2 (34.8%)

- Unusual form of copper peroxide formed in highly oxidising environments?

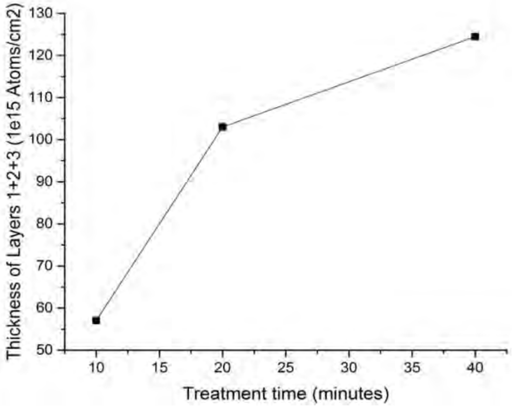
c) Interface composition Cu_2O (67.8%) on average, but more likely to be gradually changing composition from higher oxygen content to bulk metal

* See for example Kido, Nishimura and Fukumura, PRL 82 (1999) 3352

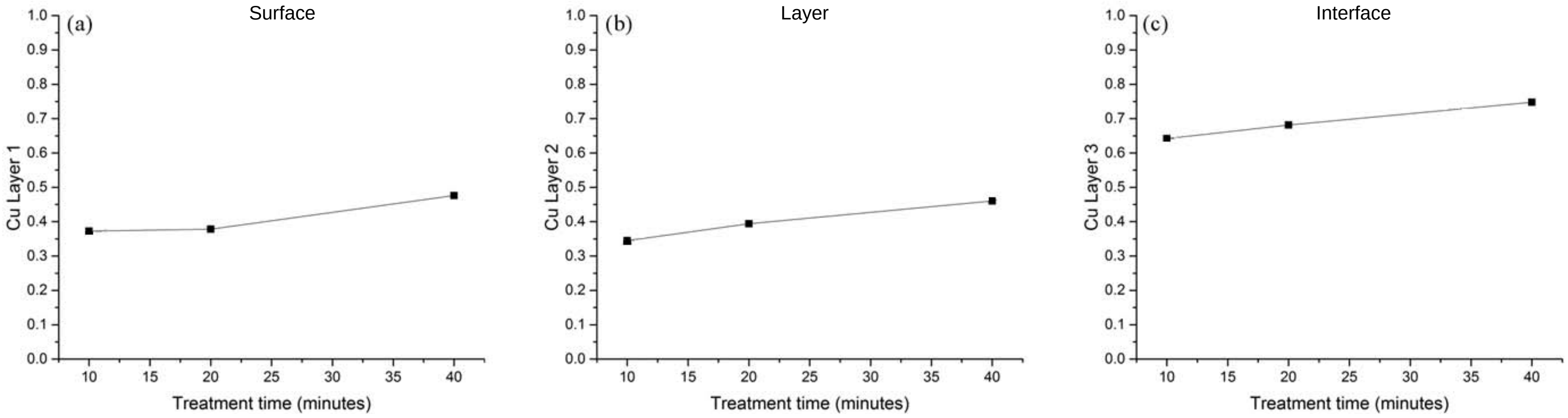
Treatment time Variation

Film thickness increases with treatment time broadly as expected

- Initial rapid increase with time
- As thickness increases diffusion and/or penetration of energetic species limits further increase



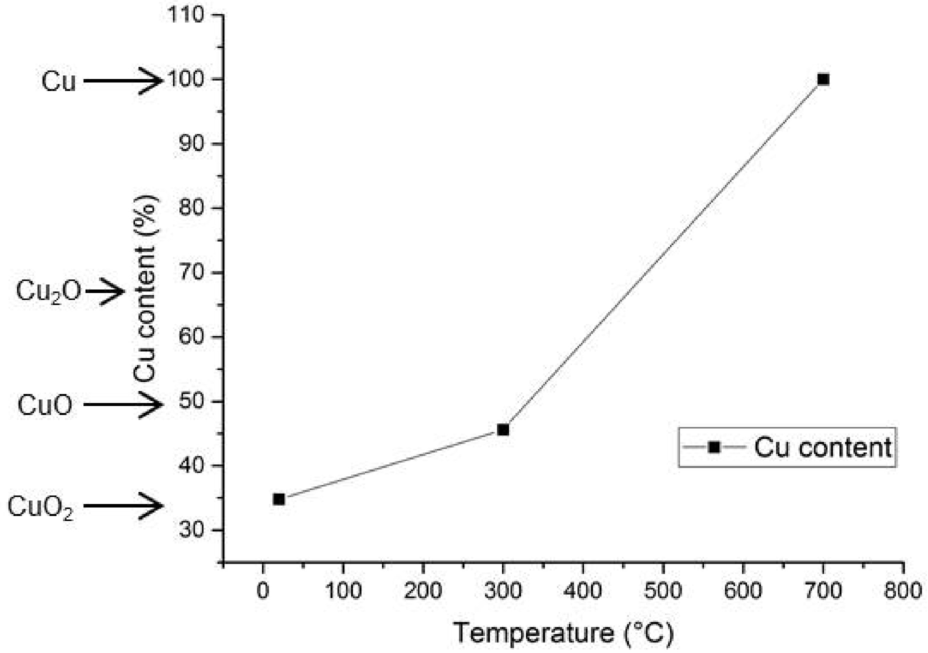
Copper fraction as a function of depth and treatment time



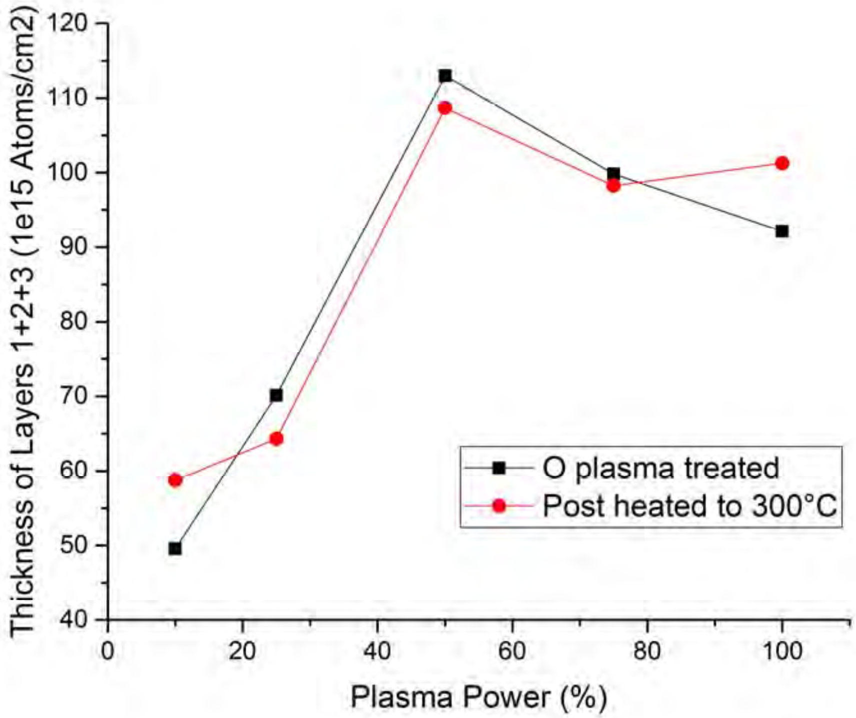
Composition data essentially shows the same behaviour as power variation data

Annealing

Film thickness unaffected by 300°C anneal (but completely removed by 600°C treatment)



Further data required to accurately assess the minimum temperature for complete oxygen removal



Film composition moves to an average of 45%, closer to CuO (second layer of the model)

XPS Analysis

Depth Profiling with Thermo K-alpha instrument

Al K alpha monochromated source (1486.6 eV)

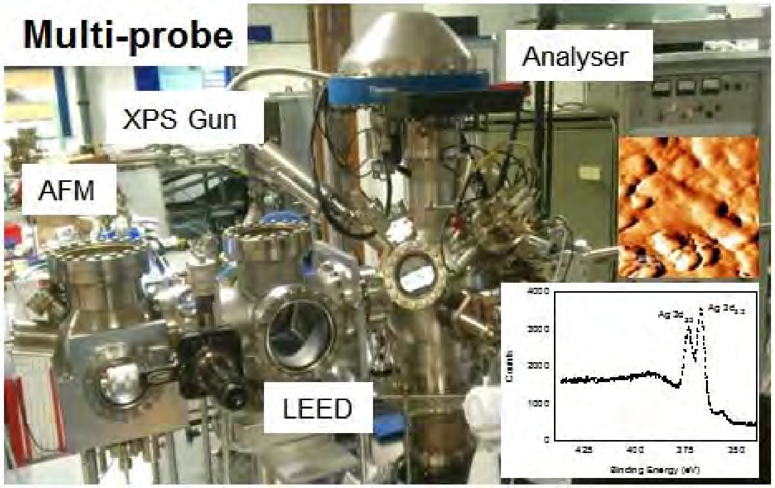
Flood gun for charge compensation 300 micron spot size

Snap scans with 128 channels, 151.2 eV pass energy, 5 scans at 1s (total time is 5s)

Etching: 200 eV Ar^+ ion beam, 1.2 mm raster, 0.03nm/s based on Ta_2O_5 etch rate.

The peak fitting with a Lorentzian(70%)/ Gaussian(30%) mix and Shirley background.

Scofield Relative Sensitivity Factors for quantification.



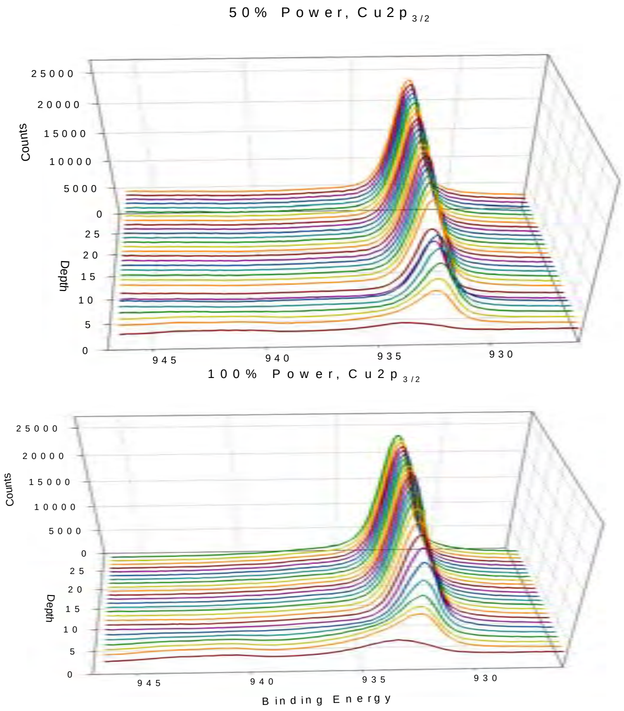
High Resolution spectra from Multiprobe instrument at Daresbury

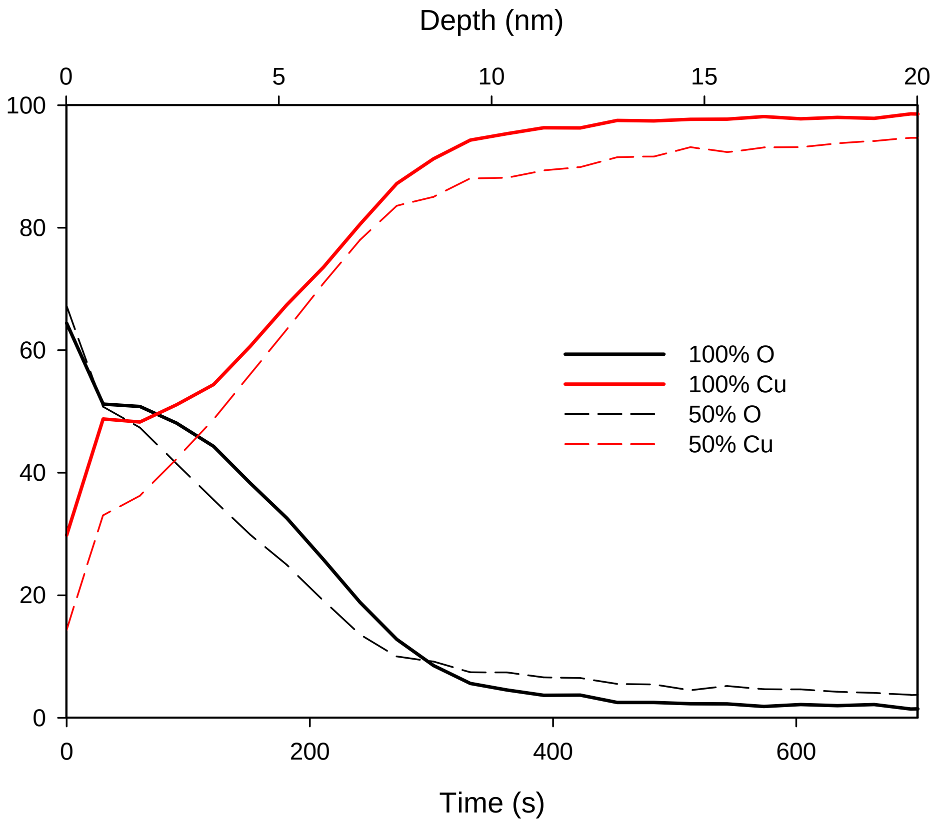
Mg K alpha source (1253.6 eV)

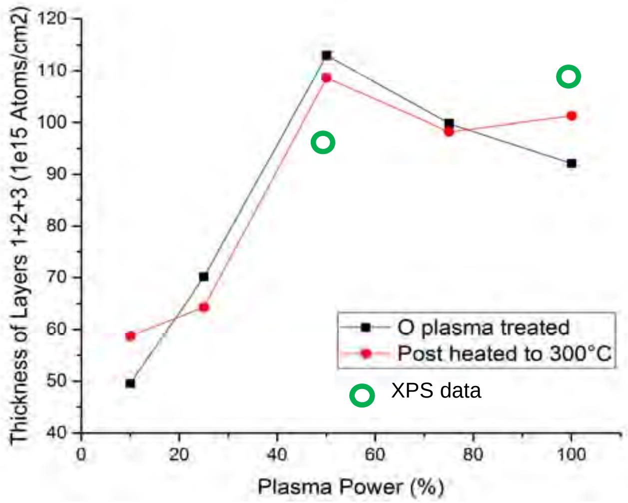
Alpha110 analyser with 1.1 eV resolution average of 5 scans

CasaXPS analysis (Shirley background, Scofield RSFs)

XPS Depth Profile Cu $2p_{3/2}$







- XPS sputter depth profiling for 50 and 100% power shows similar depths although 100% now marginally thicker.
- XPS data is consistent with previous MEIS analyses

High Resolution XPS Data

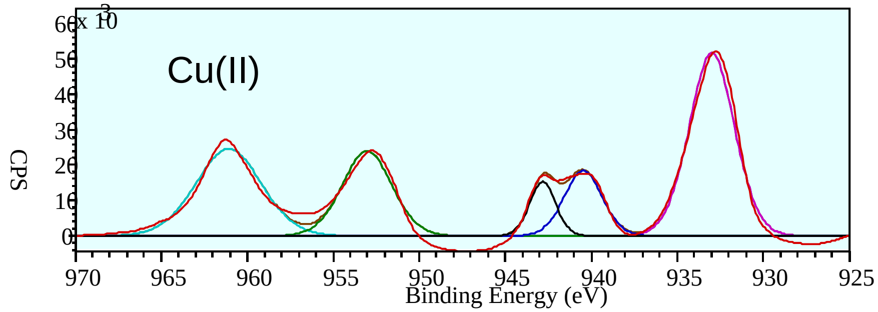
University of Huddersfield
International Institute for Accelerator Applications

Compositional analysis shows very high oxygen content

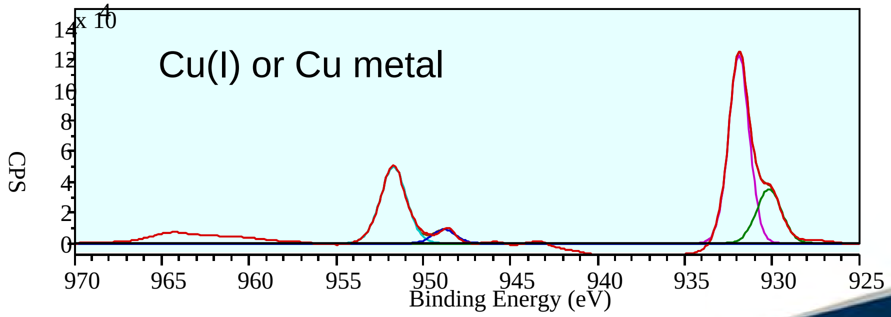
- Hydrocarbon contamination in as received is confirmed
- O_2 plasma treatment removes a significant amount (~95%) of this contamination

Metal	QE	XPS (%)		
		Cu $2p_{3/2}$	O 1s	C 1s
Cu				
Received	4.2E-6	0.6	40.4	59.0
O_2 plasma	0	16.8	80.1	3.1
Anneal 250°C ½ hrs	1.6E-4	16.8	76.7	6.5

Copper region oxygen plasma cleaned



Copper region post annealed 250°C



- Chemical shift data shows Cu(II) for the plasma treated sample (CuO_2 and CuO both have copper in the 2+ oxidation state)
- However, annealed sample indicates Cu(I) or metallic Cu, not consistent with compositional analysis or MEIS data?
- QE after anneal: 1-2 orders up

Science & Technology
Facilities Council

Summary

Oxygen plasma treatment removes hydrocarbon contamination and leaves an oxygen rich film (CuO_2!)

- Increasing treatment time increases thickness; composition remains the same
- Increasing power increases thickness until 50% above which it may be position sensitive?

Annealing to 250-300°C changes composition (less oxygen), however oxide thickness remains unchanged

- Doesn't appear to give metallic surface
- Oxide surfaces have higher work function
- Additional 'cleaning' from high power UV photoinjector laser during operation (QE of 2×10^{-5} seen)?

XPS results are largely consistent with the MEIS analysis

- Similar depth profiles and precise composition with the exception of an annealed sample
- XPS does agree with the high oxygen content
- Indicates the necessity for further work investigate the effect of the annealing process on the precise composition

Further Work

More detailed evaluation of annealing behaviour

- More accurate temperature measurement (thermocouple)
- More data points at different temperatures

Single crystal studies to determine the effect of surface orientation

- (111), (110) and (100) surfaces

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