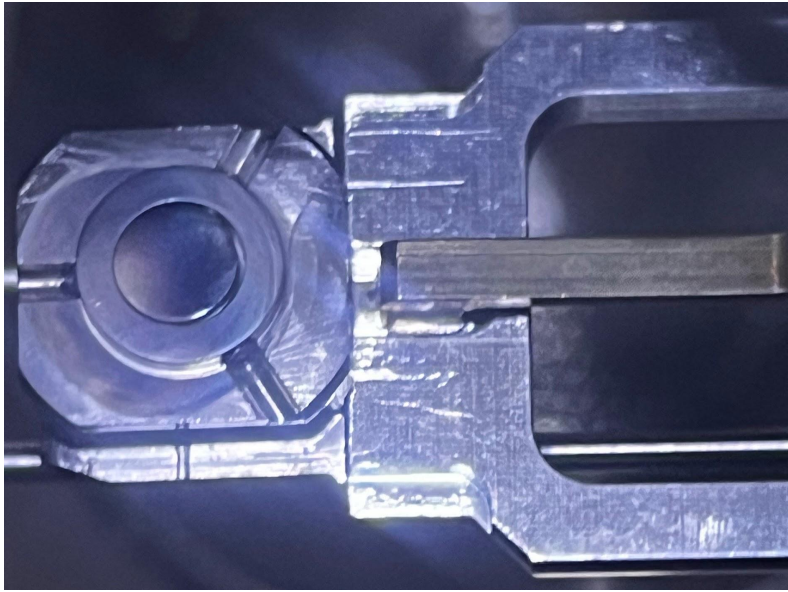
Surface Evolution of Caesiated K-Sb

XPS characterisation of an oxygen-containing precursor through caesiation and annealing



Saransh Malhotra

University of Liverpool

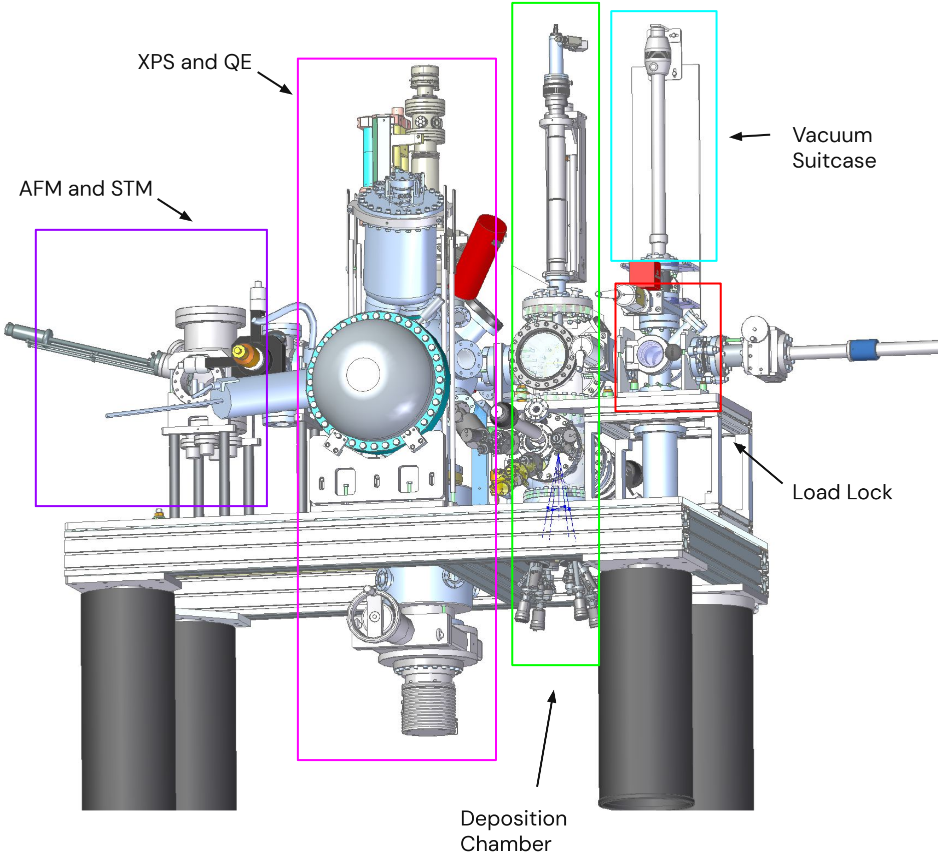
†saransh.malhotra@liverpool.ac.uk

University of Liverpool | LIV.INNO | The Cockcroft Institute of Accelerator Science and Technology | UKRI Science and Technology Facilities Council

Orsay | 09.23.26

Multiprobe: Photocathode Preparation and Characterisation.

- Integrated ultrahigh-vacuum system for thin-film preparation and surface characterisation.
- Dedicated chambers for material deposition and photoelectron spectroscopy.
- Alkali metal and antimony evaporation sources.
- Sample transfer between chambers without exposure to air.
- Sample heating (Resistive and Ebeam)and Ar sputter cleaning capabilities
- Monochromated XPS(Al kα and Non Monochromated Mg kα),
- Precise QE Measurement,
- Photocurrent Measurement during deposition
- AFM and STM



Scientific Context and Questions

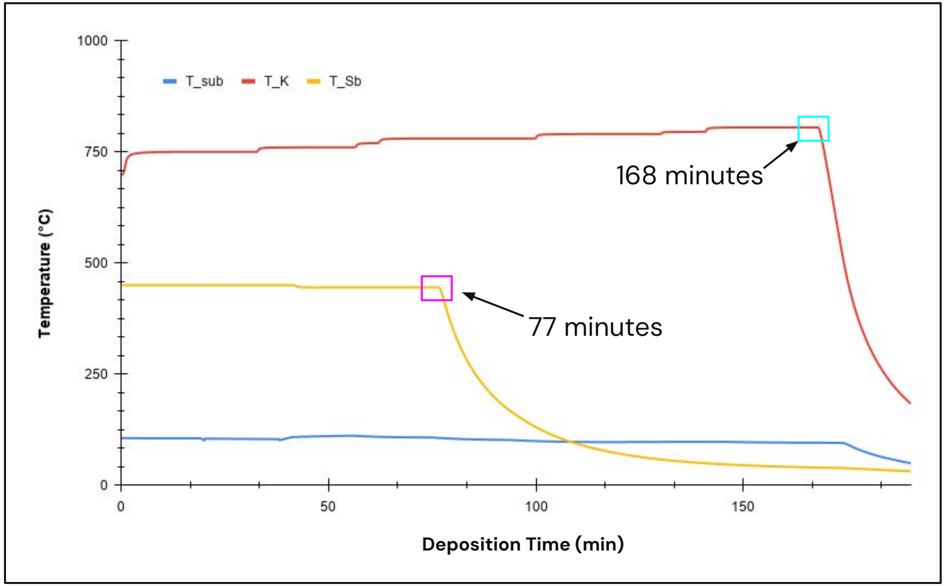
- Oxygen was already present in the K_xSb precursor, establishing a contaminated baseline before Cs activation.
- Cs deposition produced a chemically distinct activated surface, enabling direct comparison with the precursor state.
- Caesiation altered both surface composition and photoemissive response, linking chemical modification to QE behaviour.
- Annealing at 150 °C for 15 min caused further surface restructuring, with changes in elemental distribution and chemical state.
- The three-state comparison isolates the effects of Cs activation and subsequent thermal treatment.

Substrate Preparation and Cleaning

- A 6 mm polycrystalline molybdenum disc was cleaned with isopropyl alcohol (IPA) and acetone, then dried with nitrogen.
- The substrate was mounted on an Omicron-style titanium turret holder and loaded into the vacuum chamber.
- Initial heating was performed using electron-beam heating.
- The surface was cleaned by argon-ion sputtering for 15 minutes.
- Following sputtering, the substrate was degassed at 700 °C using electron-beam heating.

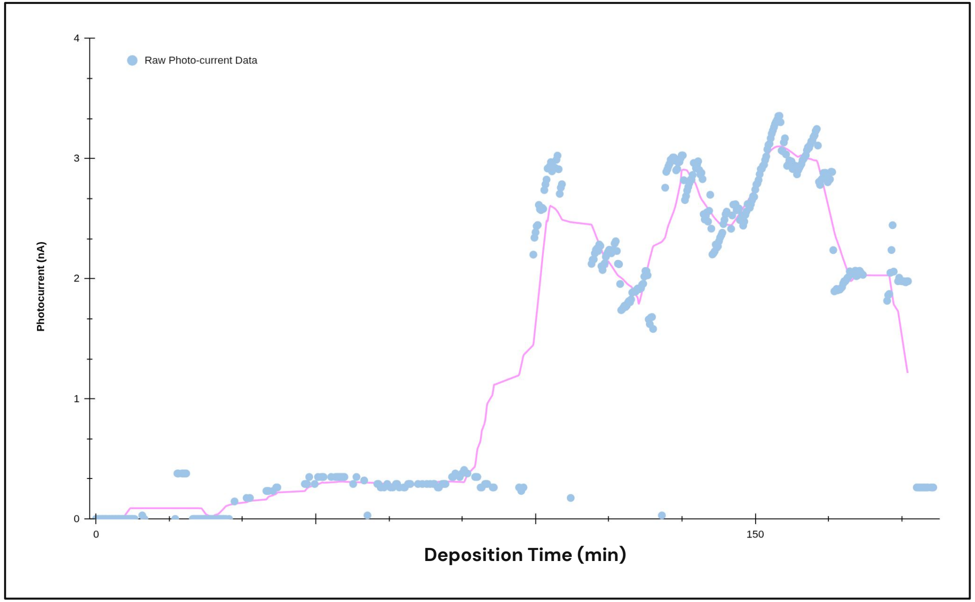
Preparation of the K_xSb Precursor

- Potassium and antimony were co-deposited onto the cleaned molybdenum substrate.
- Sb-source temperature was approximately 445–450 °C.
- K-source temperature was increased stepwise from approximately 700 to 805 °C.
- Sb-source heating stopped at 77 minutes, followed by continued K-source heating until 168 minutes.
- Substrate temperature, source temperatures, chamber pressure and lock-in photocurrent were recorded throughout preparation.



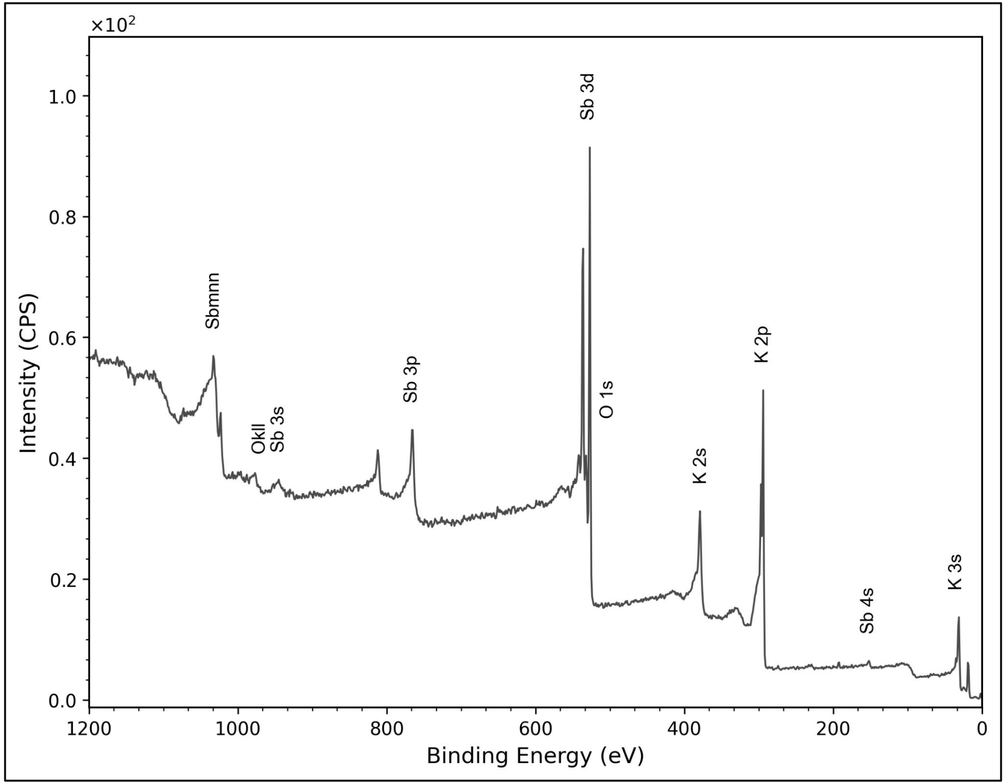
Photoemission Response During Precursor Preparation

- The photoemission signal remained low during the initial K–Sb co-deposition, indicating limited formation of a photoactive surface.
- A pronounced signal increase emerged at ~100 min after Sb deposition was terminated, suggesting a transition toward a more photoemissive surface composition.
- The photocurrent increased to ~3 nA during continued K exposure, with subsequent variations consistent with ongoing surface compositional evolution.
- XPS was subsequently used to determine the elemental composition and chemical states of the resulting K_xSb precursor.
- The as-grown precursor exhibited a final QE of ~0.1%, confirming measurable photoemission prior to Cs activation.



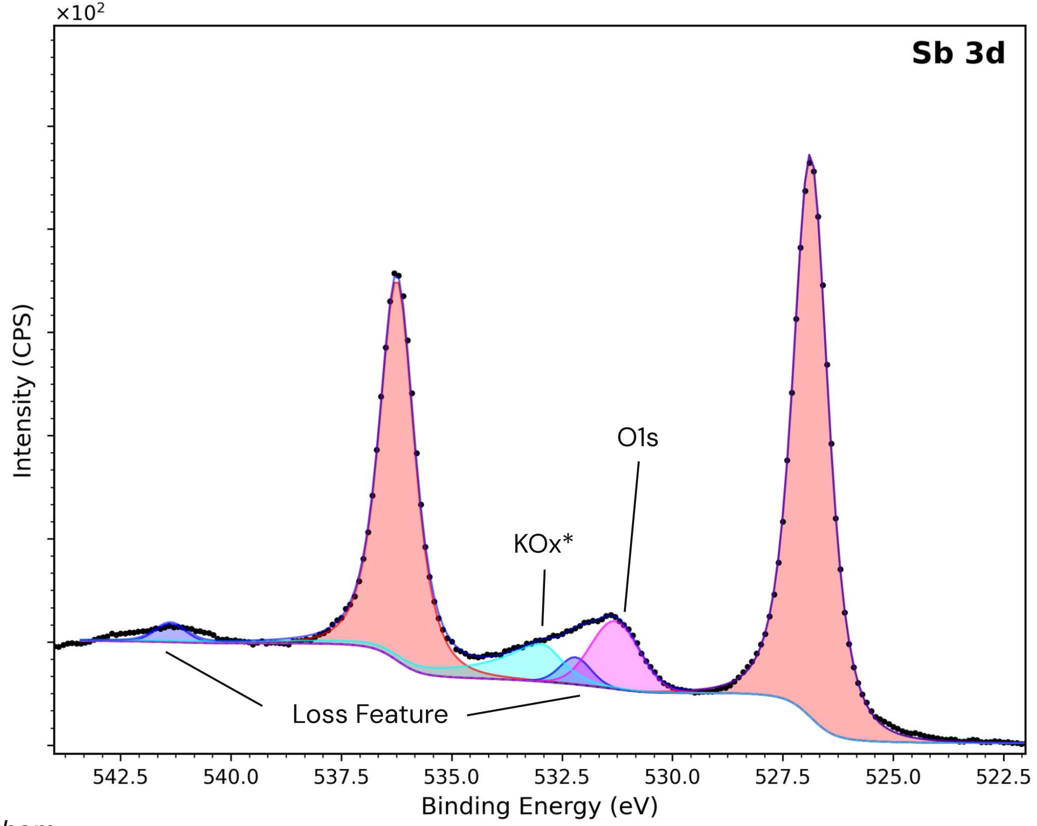
XPS Survey of the K_xSb Precursor

- K 2p, K 2s and K 3p features confirm potassium incorporation within the precursor surface.
- Sb 3p, Sb 3d and Sb 4d signals verify the presence of antimony in the deposited layer.
- The Sb 3d/O 1s region shows significant spectral overlap, requiring high-resolution fitting to resolve individual chemical contributions.
- This survey defines the pre-caesiation surface-composition baseline for subsequent comparison with Cs-activated and annealed states.
- VB/SECO measurements gave an estimated work function of 2.35 ± 0.05 eV.



Sb 3d / O 1s Core-Level Spectrum

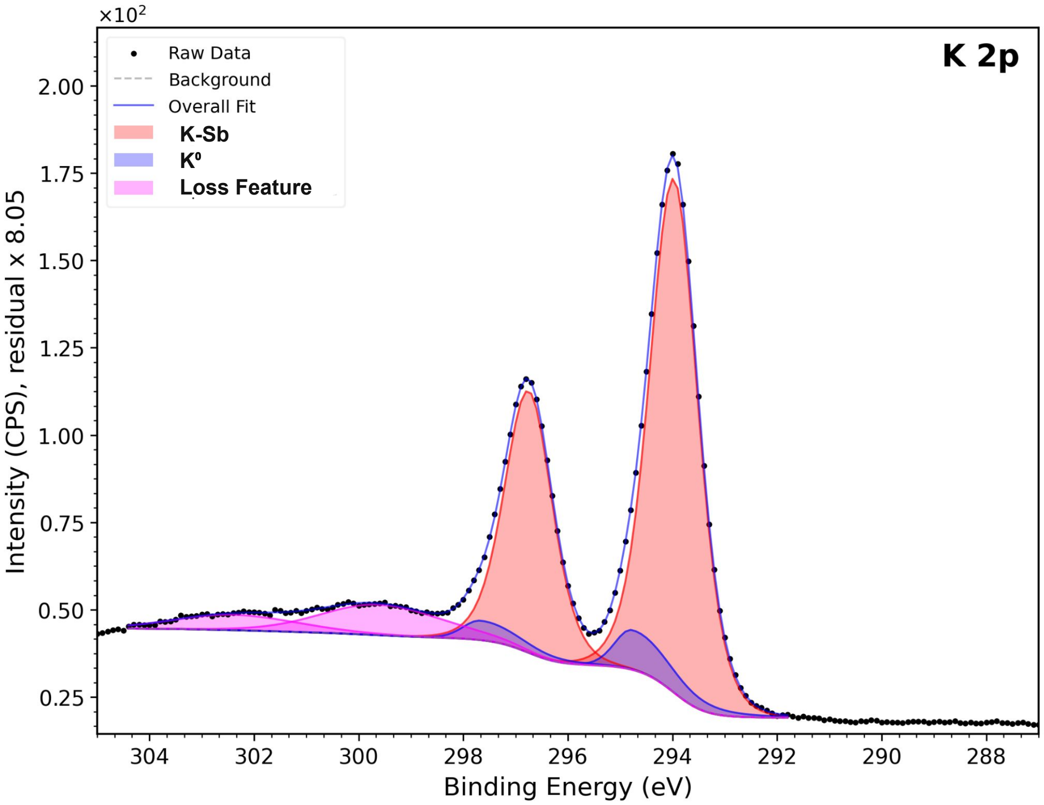
- Strong Sb 3d signal confirms the antimony-containing photocathode layer.
- Sb $3d_{5/2}$ overlaps strongly with O 1s, so chemical-state assignment from this region alone is ambiguous.
- Sb $3d_{3/2}$ is less affected by O 1s and is the cleaner region for tracking binding-energy and line-shape changes.



*R. Shi, et al.. *Chem. Int. Ed.* **2022**, *61*, e202208666; *Angew. Chem.* **2022**, *134*, e202208666.

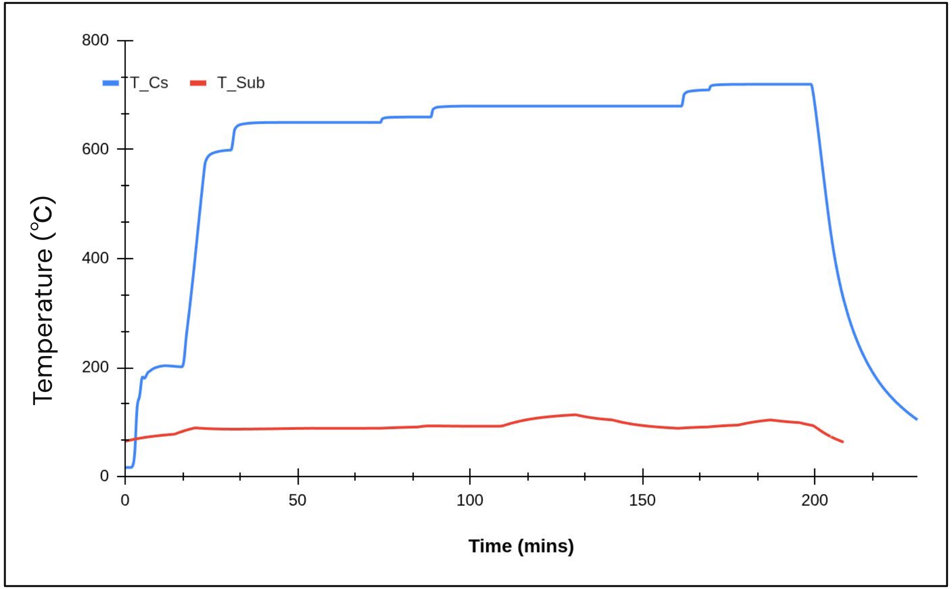
K 2p Core-Level Spectrum

- A well-resolved K 2p doublet confirms potassium incorporation into the Sb-containing precursor.
- K $2p_{3/2}$ and K $2p_{1/2}$ are centred at ~294.0 and ~296.8 eV, respectively.
- The ~2.8 eV spin-orbit splitting is consistent with the expected K 2p doublet.
- Combined with the Sb core-level spectra, the data support formation of a K–Sb precursor surface prior to Cs activation.



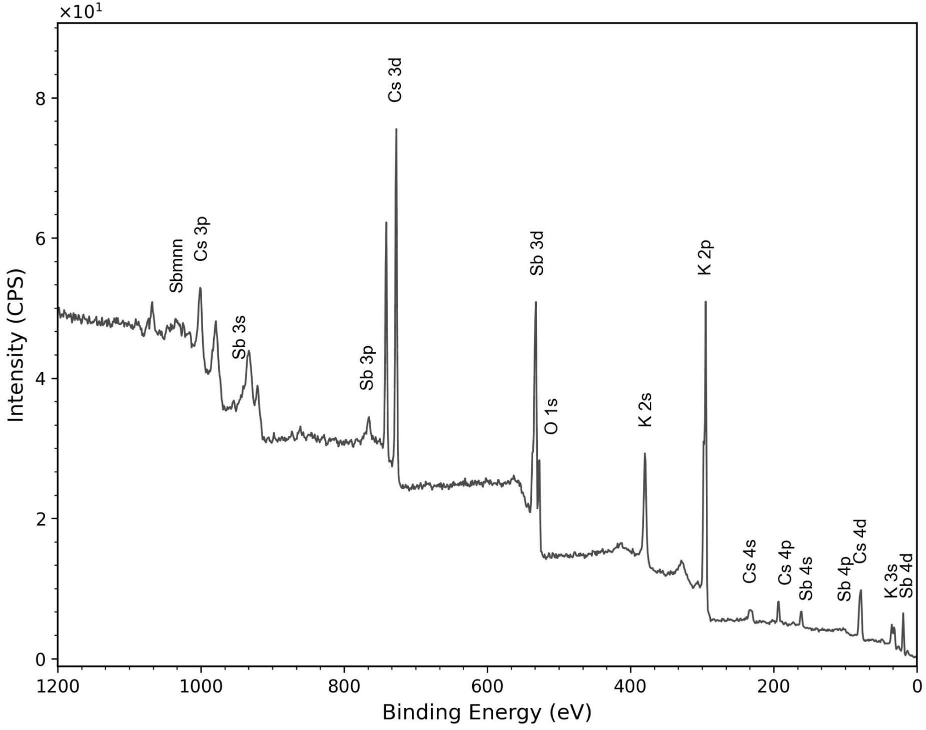
Cs Activation of K_xSb

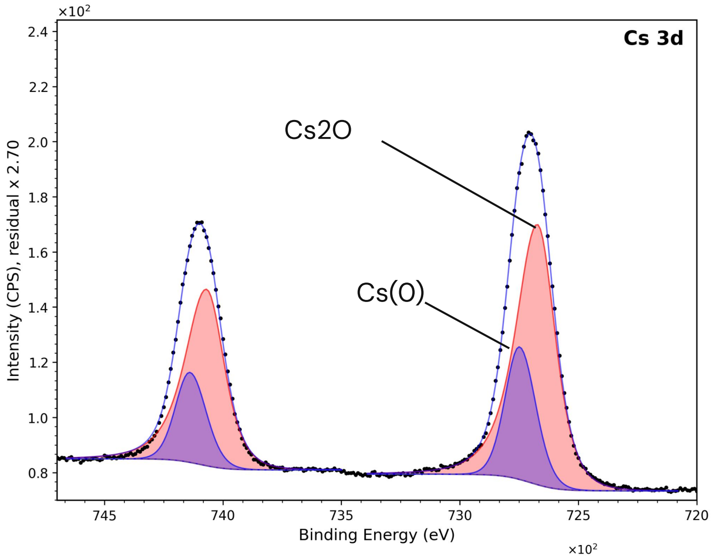
- Cs source: ramped to 720 °C
- 720 °C hold: ~25 min
- Substrate: ~93–104 °C during peak Cs exposure
- Base pressure: ~1.4 × 10^{-9} mbar
- Pressure during 720 °C Cs exposure: ~4.8 × 10^{-8} mbar
- Photocurrent: typically peaked during the 720 °C stage
- 532 nm illumination used during activation
- The final QE went down to ~0.05%, As Work Function increased to 2.52 ± 0.05 eV

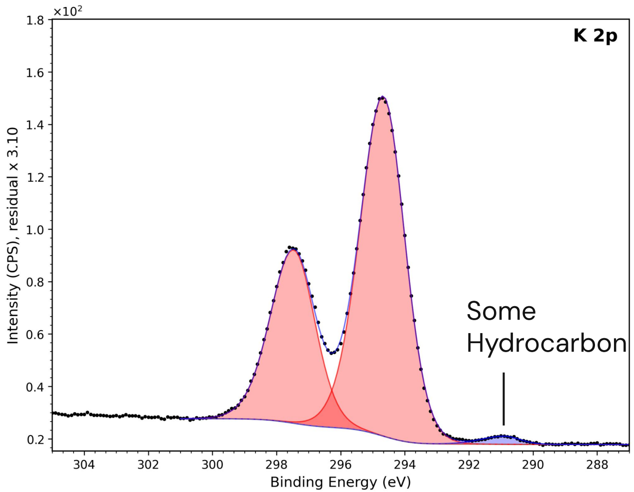


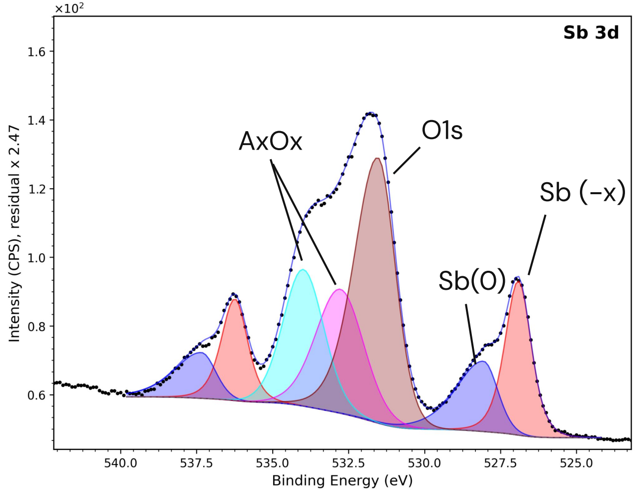
Core-Level Composition After Cs Activation

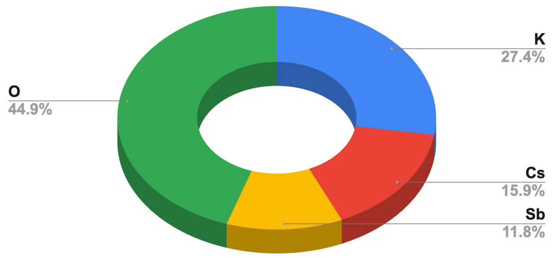
- **Cs 3d** confirms Cs incorporation.
- **K 2p** remains dominant after caesiation.
- **Sb 3d** is retained in the activated surface.
- Strong **O 1s** indicates substantial oxygen contamination.




Cs 3d
Cs2O
Cs(0)
×10²
Intensity (CPS), residual x 2.70
Binding Energy (eV)
745
740
735
730
725
720
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4

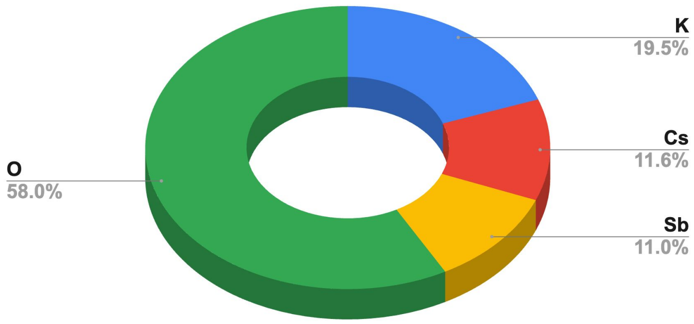

K 2p
Some
Hydrocarbon
×10²
Intensity (CPS), residual x 3.10
Binding Energy (eV)
304
302
300
298
296
294
292
290
288
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8

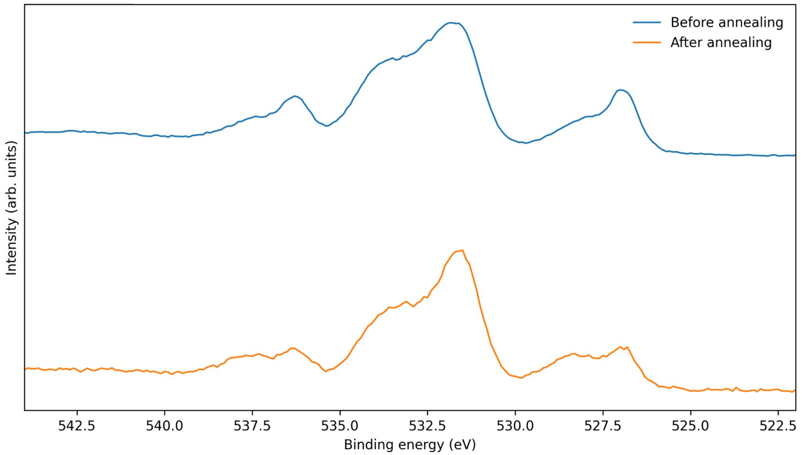

Sb 3d
AxOx
O1s
Sb (-x)
Sb(0)
×10²
Intensity (CPS), residual x 2.47
Binding Energy (eV)
540.0
537.5
535.0
532.5
530.0
527.5
525.0
0.6
0.8
1.0
1.2
1.4
1.6


K
27.4%
O
44.9%
Cs
15.9%
Sb
11.8%

Annealing and its Effects on K-Cs-Sb Surface

- Sample was annealed at 150 °C for 15 minutes
- Cs reduced after annealing
- K fraction slightly increased
- Sb fraction reduced
- Surface remained highly oxygen-rich
- Largest spectral change observed in Cs 3d
- K-Sb framework comparatively retained
- Annealing promotes Cs loss/redistribution
- QE decreased strongly after annealing to ~0.003%





Conclusions & Outlook

Conclusions

- K_xSb formation confirmed by Sb 3d and K 2p XPS
- Cs activation produced a Cs–K–Sb surface
- Surface remained strongly oxygen contaminated
- Annealing caused preferential Cs loss / redistribution
- K-containing surface was comparatively more stable
- QE decreased strongly: 0.1% → 0.052% → 0.003%

Outlook

- Reduce residual O_2/H_2O contamination during growth and transfer
- Optimise Cs source temperature, exposure time and substrate temperature
- Perform controlled O_2 degradation with sequential XPS
- Compare RT and cryogenic degradation
- Add ARXPS to probe surface vs sub-surface composition
- Correlate composition, work function and lifetime in future K–Cs–Sb growths

Acknowledgements

- **Dr Lee Jones** – supervision, guidance and support throughout the photocathode studies
- **Hugh Churn** – technical support with the experimental system and measurements
- **Dr Tim Noakes** – support and expertise in surface science

Thank You

Any Question?