Corrosion of nuclear fuel: radiolysis driven dissolution at the UO_2/water interface

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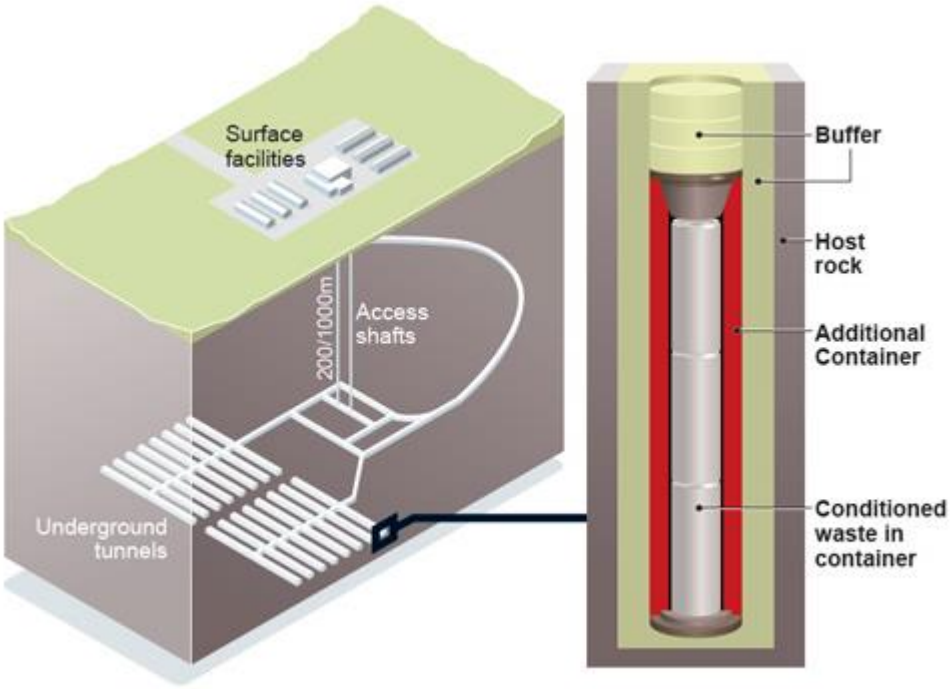
Research Motivation

High level nuclear waste (HLW) is increasing globally, by around **12,000 tonnes** each year [1].

Polycrystalline UO_2 accounts for the majority of HLW generated by modern society.

Storage within a geological disposal facility, is the most viable solution.

A repository has multiple barriers: durable metal containers, a clay buffer and a deep stable geologic environment.



Problem: corrosion of the surface of stored UO_2 on exposure to ground water, resulting in the release of radionuclides [2].

[1] World Nuclear Association ,(2013) .
[2] U. Strandberg and M. Andren, Journal of Risk Research **12**, (2009).
[3] West Cumbria MRWS Partnership (2015).

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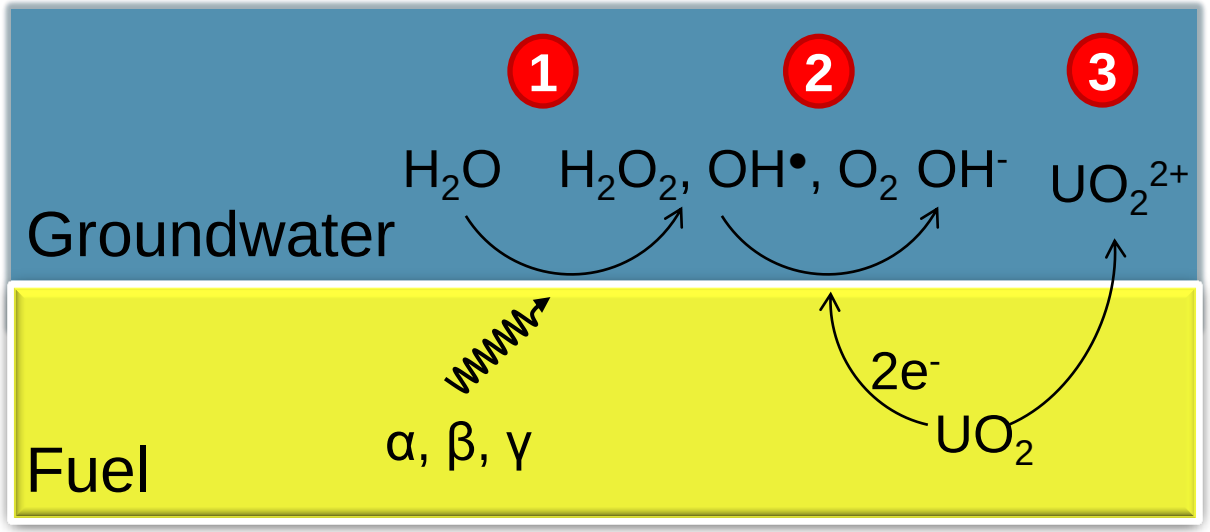
Corrosion of UO_2

The primary mechanism of UO_2 corrosion is **oxidative dissolution** [4]:

$$UO_2 \rightarrow UO_{2+x} \rightarrow UO_2^{2+}$$

1. Radiolytic production of oxidants.
2. Cathodic reduction of oxidants.
3. Anodic oxidation and dissolution of the fuel.



[4] D. W. Shoesmith, J. Nucl. Mater. **282**, (2000).

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Oxidative Dissolution of UO_2 Thin Films

The oxidative dissolution of UO_2 was investigated by exposing thin films of single crystal oriented UO_2 to radiolytically produced oxidation products (H_2O_2, $OH^\bullet$, O_2).

Why single crystal thin films?

Thin films replace the complexity of bulk materials with idealised, homogenous surfaces.

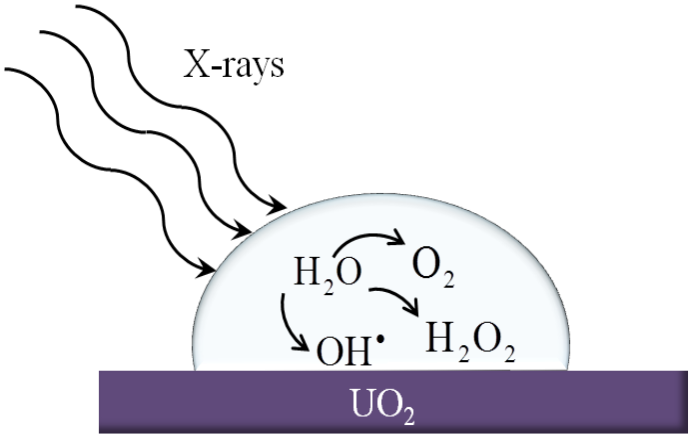
Provide greater surface sensitivity.

Low activity, allows transportation to large facilities

Reproducing the corrosive environment

Thin films of UO_2 were exposed to a droplet of pure water.

Radiolysis of the water droplet was achieved using a focussed, high energy X-ray beam.



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Thin Film Growth

Grown via Reactive DC Magnetron Sputtering

Advantages

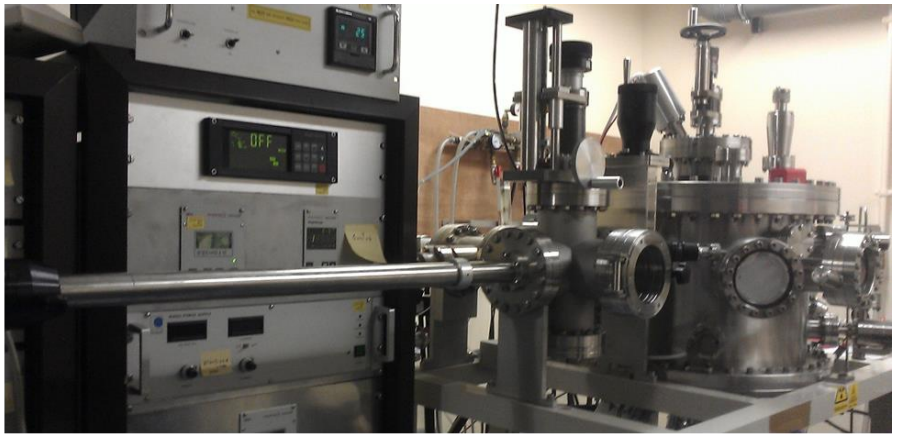
- High deposition rates
- Uniform growth
- Good control of stoichiometry

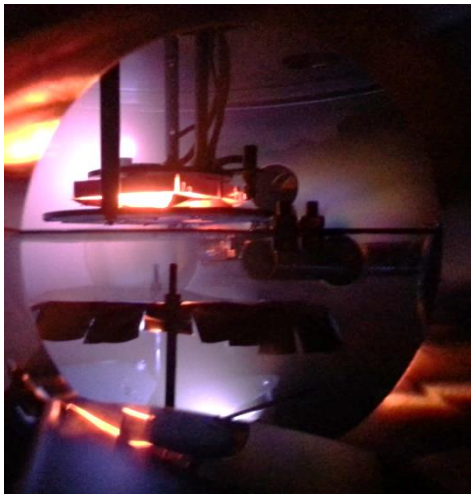
Growth Conditions

Temperature: ≈ 550 °C

Oxygen Pressure: 2 x 10^{-5} mbar

Argon Pressure: 7 x 10^{-3} mbar





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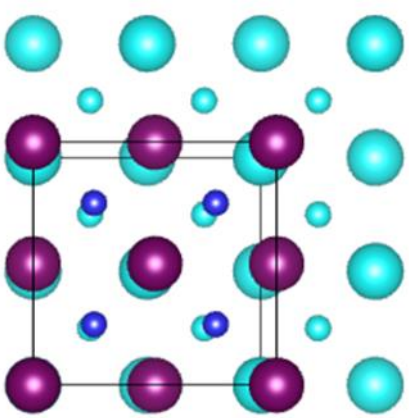
Single Crystal Growth

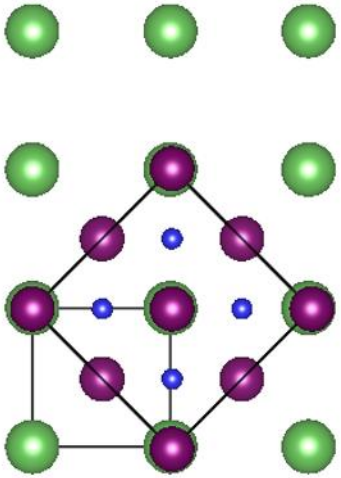
Substrate Matching: UO_2 [001]

A good substrate match is required to achieve a high quality film.

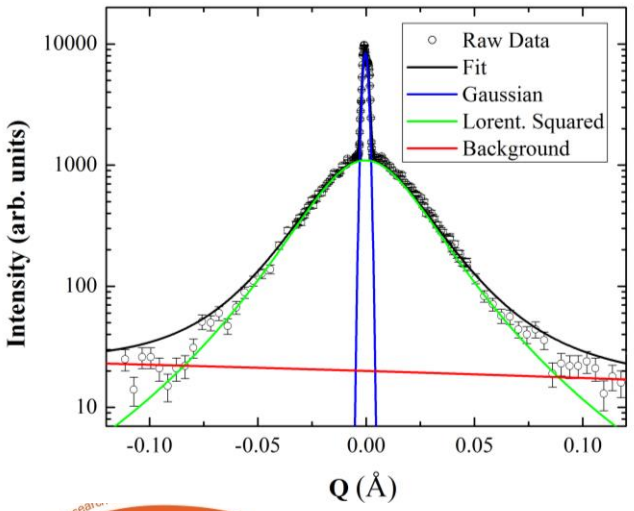
Reduced strain leads to improved mosaicity and roughness.

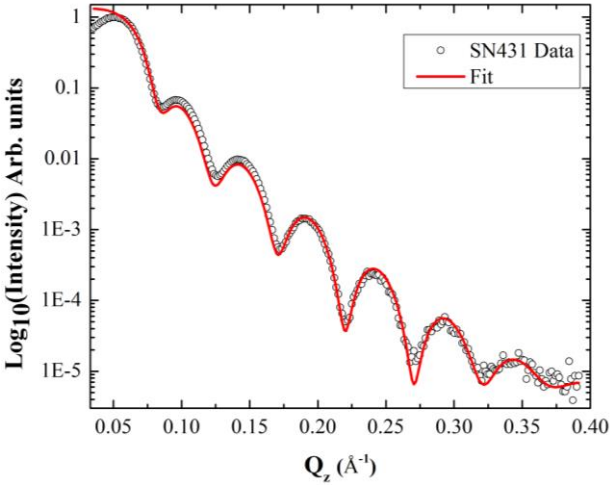


YSZ: 6.3% Mismatch



LSAT: 0.2% Mismatch





Rocking curves show good mosaicity, with widths in the region of 0.05°.

Reflectivity curves show reproducible film thicknesses, giving a deposition rates of 1.3 $Å s^{-1}$.

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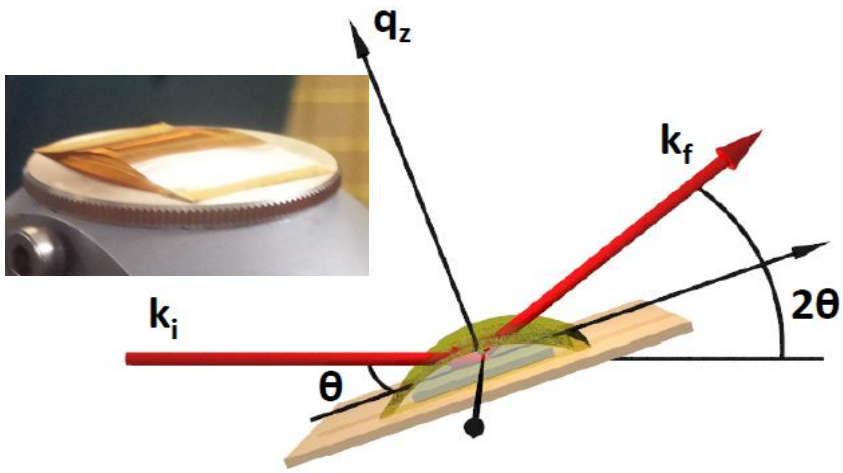
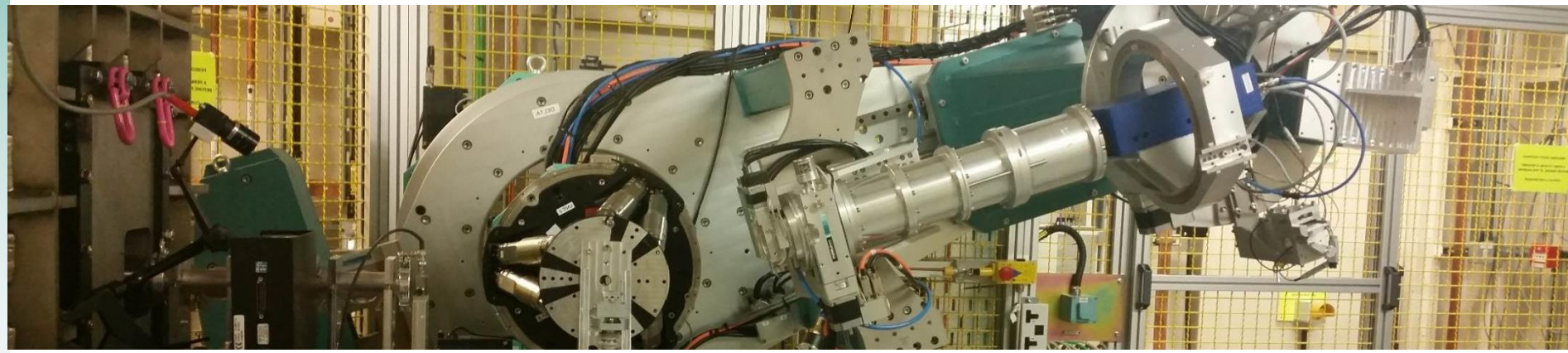
Synchrotron Experiments

Experiments were conducted at the ESRF, BM28 and Diamond Light Source I07.

The x ray beam was used as:
A source – to radiolyse the water,
A probe – to investigate changes in surface morphology using XRR and XRD.





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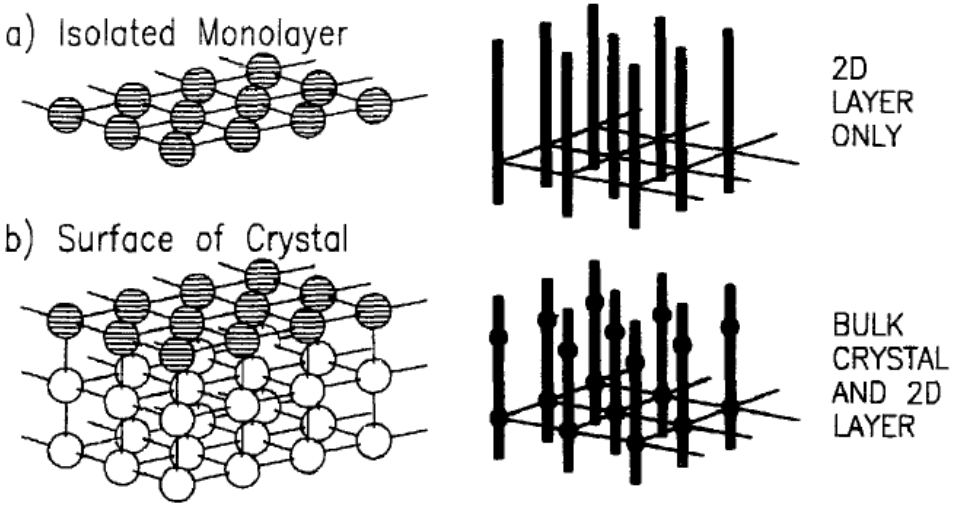
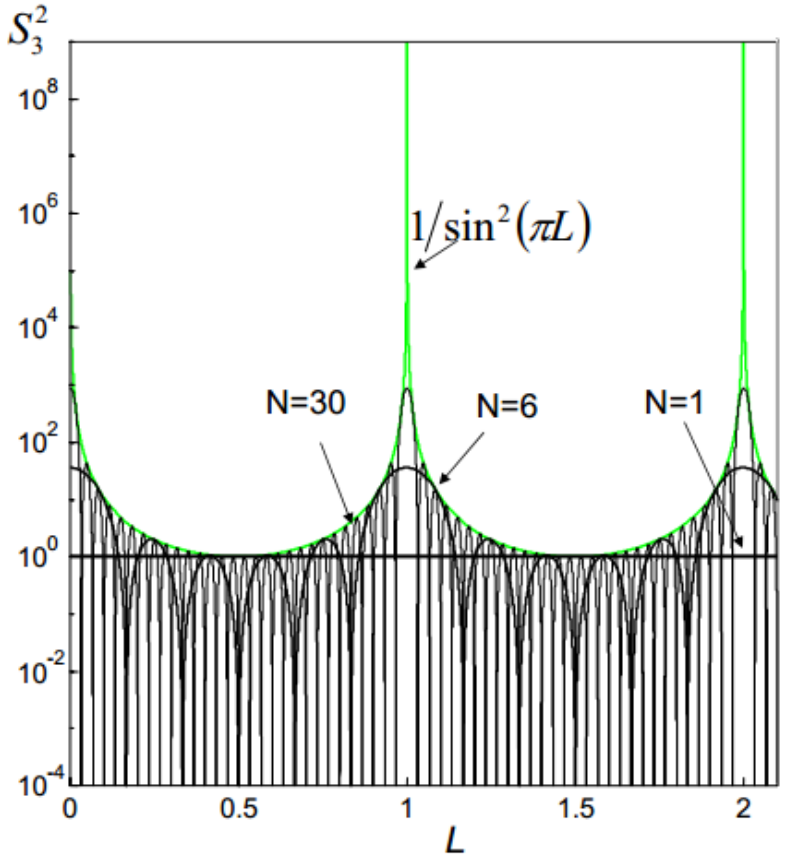
X-ray Diffraction: Surface Effects



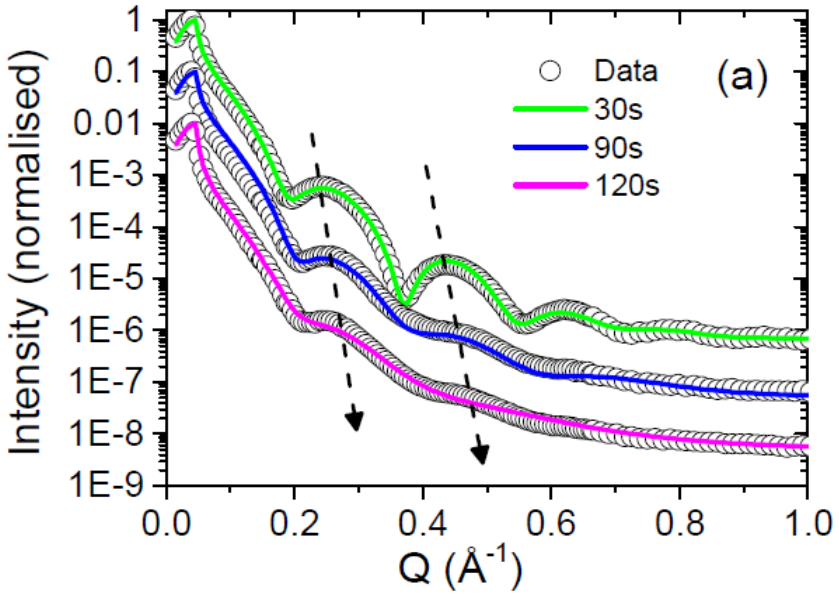
A termination of the crystal gives rise to additional scattering between the bulk Bragg peaks.

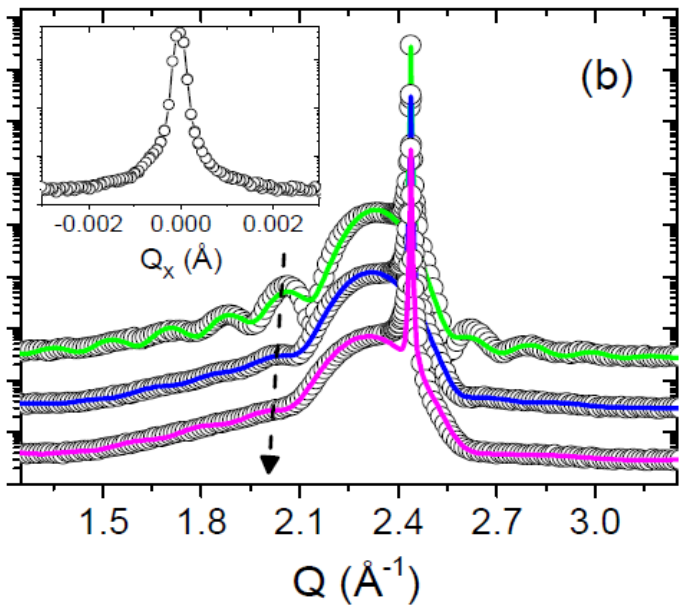
For a thin film, surface effects are seen as fringes around the Bragg peak. Fringes are a result of interference between x-rays scattering from the film interfaces.

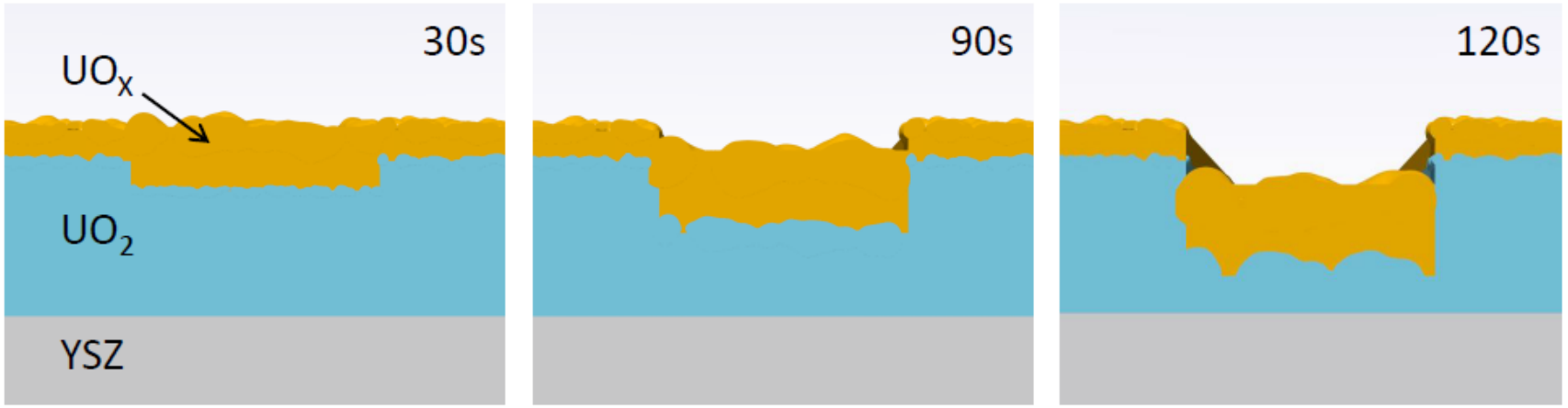
A high flux of X-rays are required to observe surface effects.



Synchrotron Results







[5] R. S. Springell et al., Faraday Discussions (2015) DOI: 10.1039/C4FD00254G.

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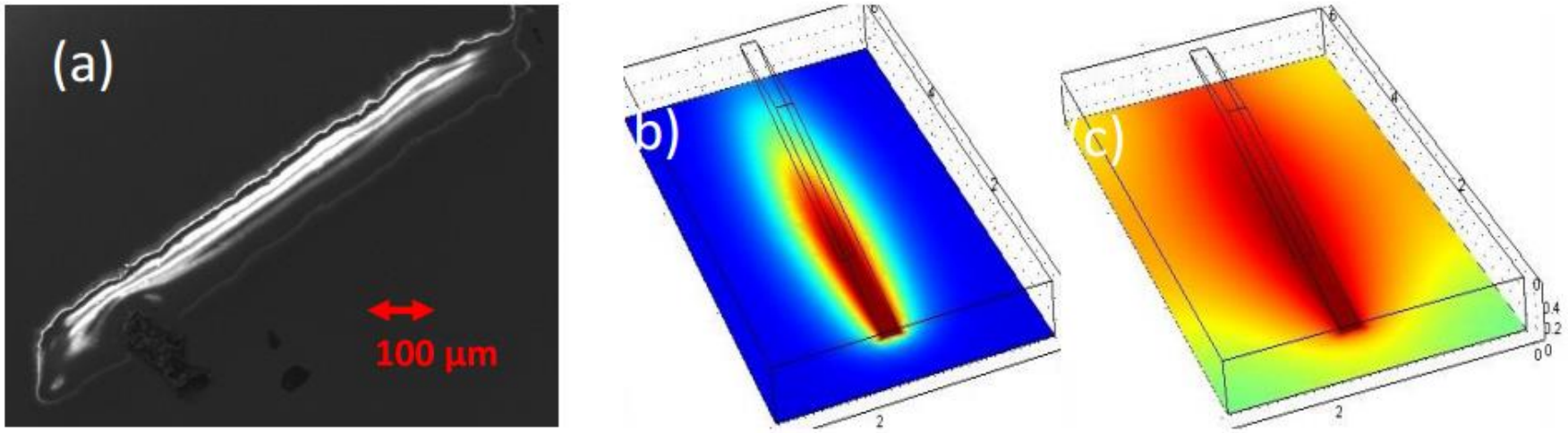
Diffusion of Oxidant Species



(a) SEM image of a corroded UO2 single crystal thin film,(b) and (c) are images of the corrosion footprint after 500 s, as calculated using finite element modelling, including H_2O_2 surface diffusion and bulk diffusion constants, respectively [5].

Why surface diffusion?

1) Beam enhanced surface effect – photocatalysis?
2) A more reactive short lived oxidising species

[5] R. S. Springell et al., Faraday Discussions (2015) DOI: 10.1039/C4FD00254G.

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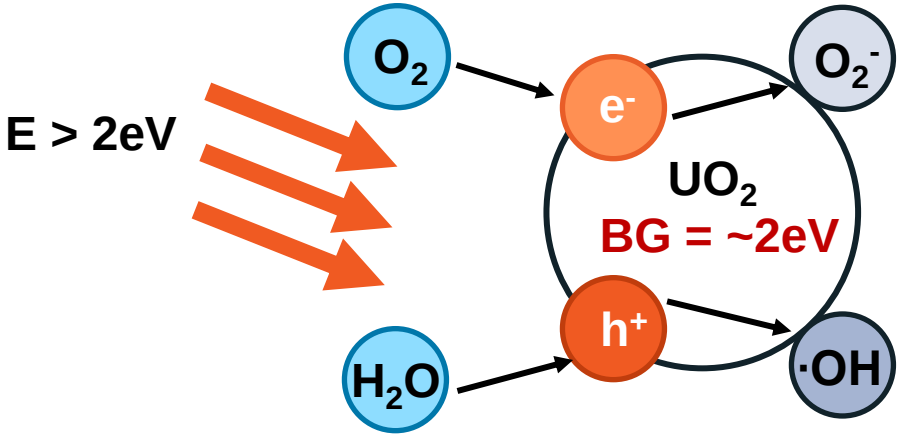
Investigating Photocatalysis

Measured the rate of change in Bragg peak intensity before (17.116 keV), at (17.166 keV) and after (17.216 keV) the uranium L3 absorption edge.

Expected the enhancement in the number of electrons excited to the continuum at such an absorption edge, to have a significant effect on any photocatalytic process.



However, we did not observe any difference in the rate of decrease in Bragg peak intensity, within experimental errors.

What is the mechanism responsible for the increased corrosion seen in the beam footprint?

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Conclusions

Successfully developed a technique to induce oxidative dissolution of UO_2 using synchrotron radiation to mimic residual radiation fields of nuclear material in storage.

On exposing single crystal UO_2 thin films to the radiolytic products, a loss of single crystal UO_2, and growth of a higher UO_{2+x} phase is observed.

Finite element model suggests the corrosion is dependent on a surface interaction, as no significant corrosion is seen from bulk diffusion of radiolytic oxidants.

Future work: Investigate further the corrosion mechanism, by trying to identify the corrosion species.

Publications: R. S. Springell et al., Faraday Discussions (2015) DOI: 10.1039/C4FD00254G.

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Acknowldegments

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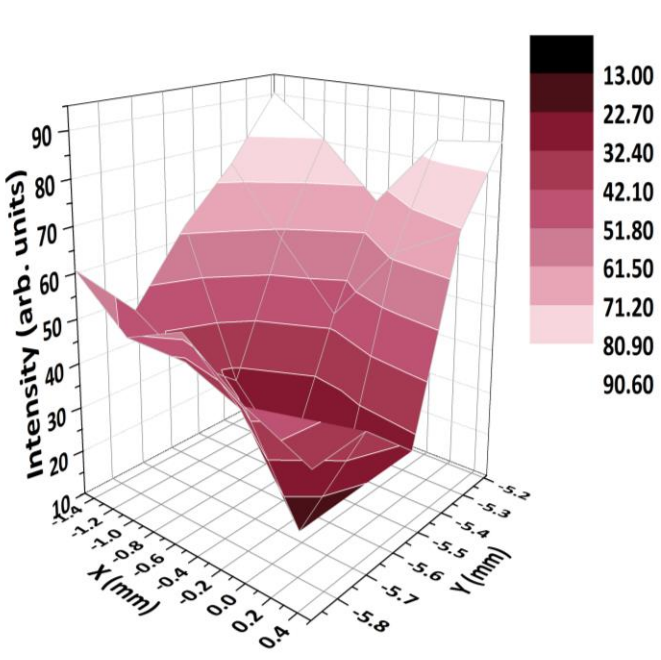
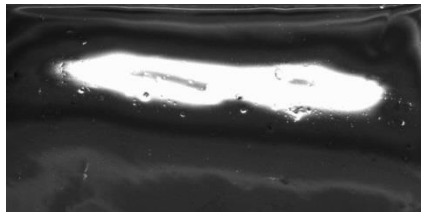
Post Exposure Analysis: EDX

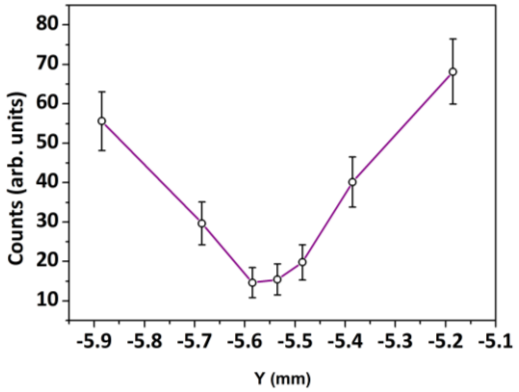
Energy dispersive X-ray spectroscopy was used to map the uranium content over the exposed area. A loss of uranium was seen over an area corresponding to the beam footprint.

This supports the synchrotron data, showing that oxidative dissolution reduces the thickness of UO_2 thin films

EDX image indicates charged substrate areas in white *(top right)*







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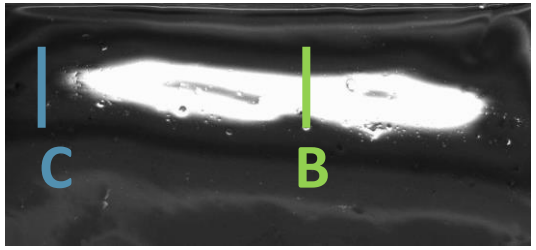
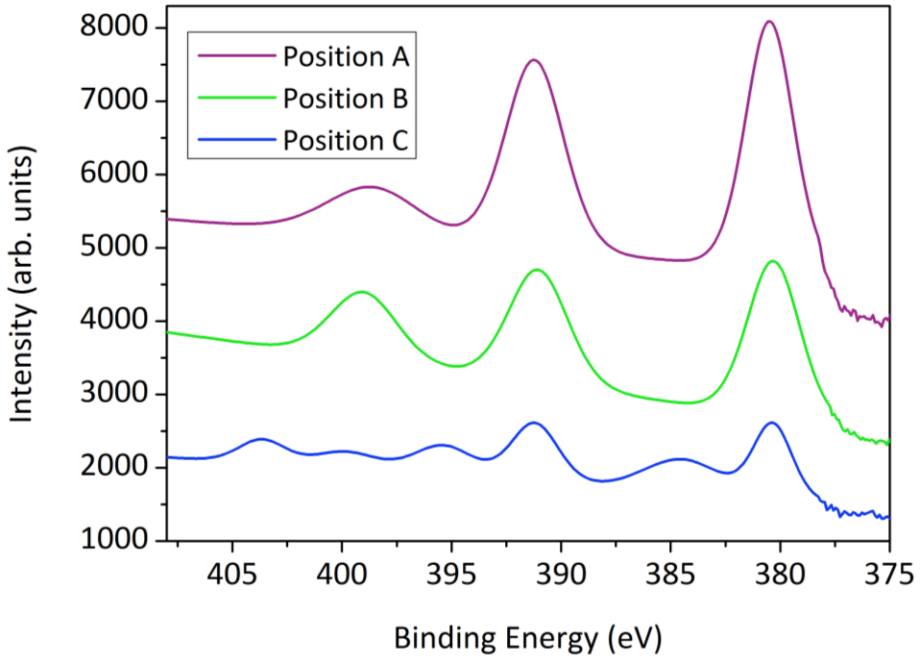
Post Exposure Analysis: XPS

X-ray photoelectron spectroscopy (XPS) was used to compare the composition of the film at three different locations. Position A – 'clean film' and positions B and C as indicated on the EDX image.

Scans of the U 4f region showed a significant loss in intensity is found in the UO_2 peaks (380.3 eV, 391.1 eV) at regions exposed to radiolytic products.

At region C a further two peaks can be seen (384.5 eV, 395.1 eV), these can be attributed to higher oxides (e.g. UO_3) deposited at the outer edge of the exposed region.





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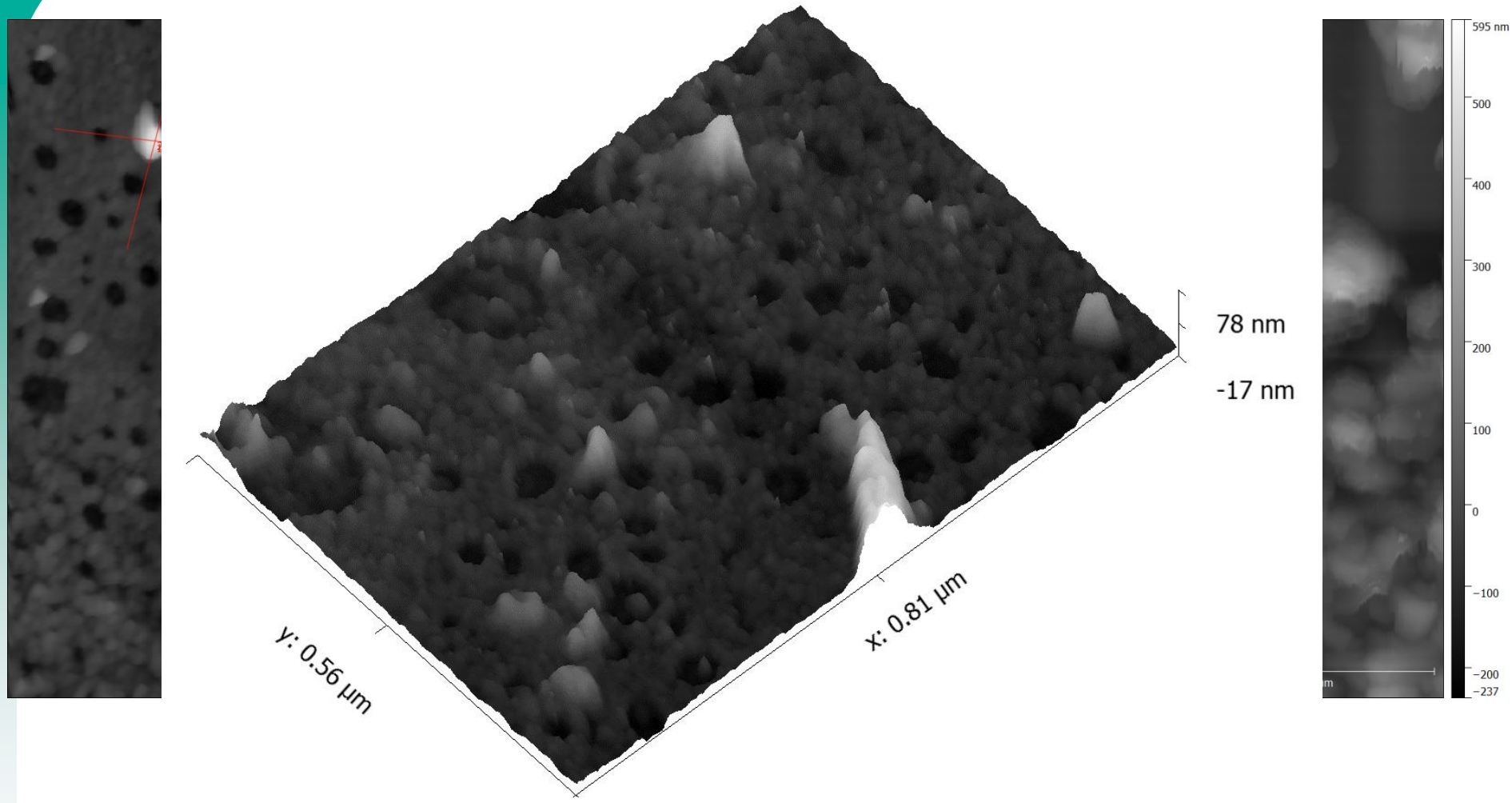
Post Exposure Analysis: AFM



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