ARTICLE

Supplementary: Mixed H_2O/H_2 Plasma-Induced Redox Reactions of Thin Uranium Oxide Films under UHV Conditions

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Peak fitting details

The following table contains information about U4f XPS peak parameters which were used as references in the fitting routine.

Oxidation states	Binding energy (eV) of U4f7/2	Binding energy (eV) of U4f5/2	Spin orbit splitting of U4f main lines (eV)	FWHM (eV) of U4f7/2	Satellite peaks separation from U4f5/2
U(IV)	380.1	390.9	10.7	1.5	6.7
U(V)	380.4	391.3	11.2	1.46	8.1
U(VI)	381.1	391.8	10.7	1.2	4.4 and 9.9

O1s XPS spectra

The O1s spectra of the different conditions applied to UO2, U2O5 and UO3 films are plotted after being shifted to the same low binding energy of the unexposed film.

Each spectrum corresponding for the different conditions is also plotted separately with the spectrum of the unexposed film.

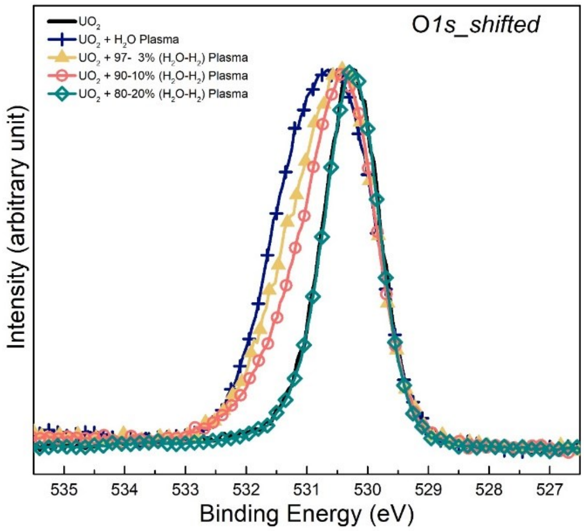

Figure 1 X-ray photoemission spectra of the O*1s* core level line recorded for the precursor and plasma treated films after being shifted to the lower binding energy side of UO_2 film. Films exposed to pure water plasma and mixed gas plasma of water and hydrogen.

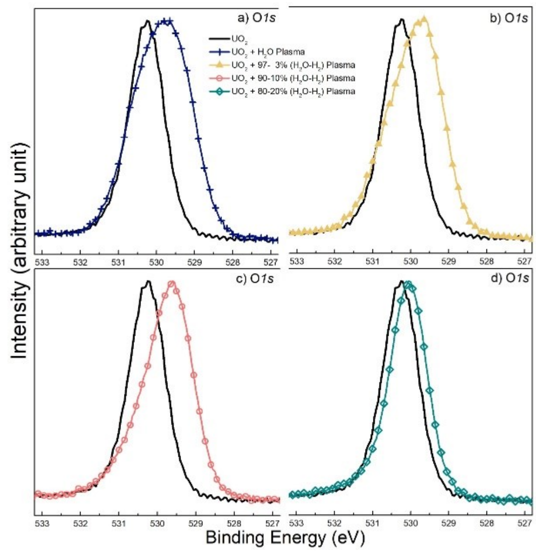

Figure 2 X-ray photoemission spectra of the O*1s* core level line recorded for

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the precursor and plasma treated films. Films exposed to pure water plasma and mixed gas plasma of water and hydrogen.

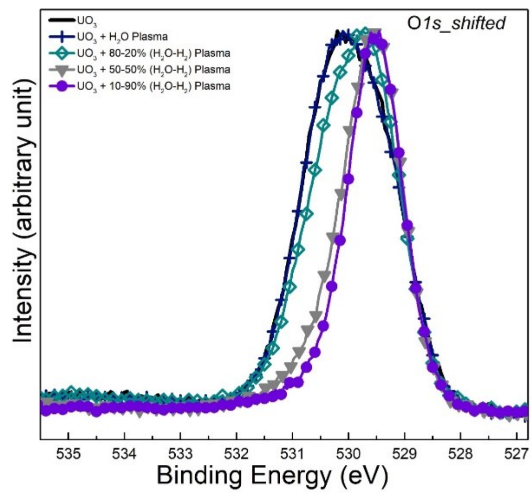

Figure 3 X-ray photoemission spectra of the O1s core level line recorded for the precursor and plasma treated films after being shifted to the lower binding energy side of UO_3 film. Films exposed to pure water plasma and mixed gas plasma of water and hydrogen.

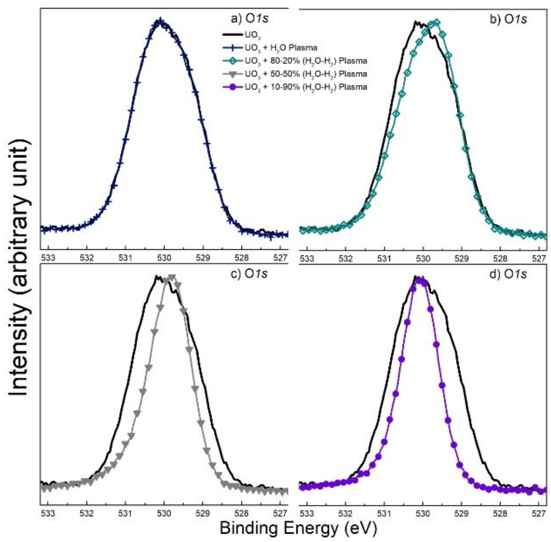

Figure 4 X-ray photoemission spectra of the O*1s* core level line recorded for the precursor and plasma treated films. Films exposed to pure water plasma and mixed gas plasma of water and hydrogen.

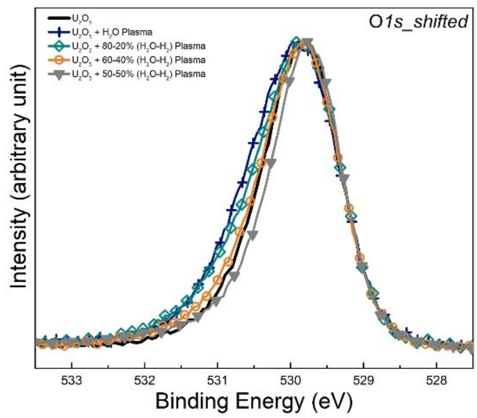

Figure 5 X-ray photoemission spectra of the O*1s* core level line recorded for the precursor and plasma treated films after being shifted to the lower binding energy side of U_2O_5 film. Films exposed to pure water plasma and mixed gas plasma of water and hydrogen.

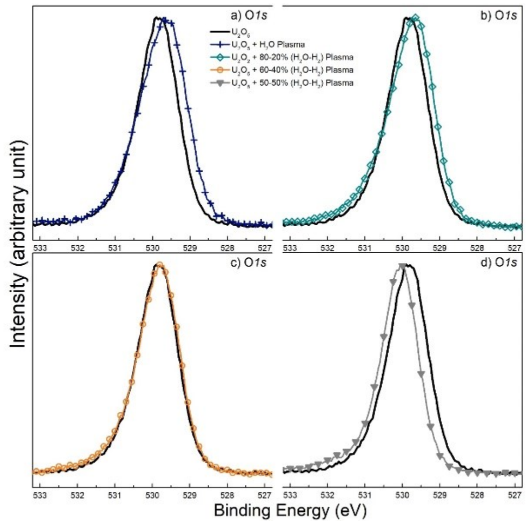

Figure 6 X-ray photoemission spectra of the O*1s* core level line recorded for the precursor and plasma treated films. Films exposed to pure water plasma and mixed gas plasma of water and hydrogen.

Crystal structure of different uranium oxides

In the text when we refer to the similar structures of UO_3, U_2O_5 and U_3O_8, we refer to the lamellar and orthorhombic structure in contrast to the cubic structure observed for UO_2. Indeed UO_3 displays more reported polymorphism than any of the other oxides, with a reported seven crystalline polymorphs and one amorphous phase [Hoekstra et al. *Journal of Inorganic & Nuclear Chemistry*, 1970, 32(10), 3237-3248. Siegel et al. *Acta Crystallographica*, 1966, 20, 292-295]. *γ*-UO_3 is reported as the most thermodynamically most stable UO3 polymorph. As supplementary information, a table will report the structure of UO_2, g-UO_3, d-UO_3, d-U_2O_5, a-U_3O_8, b-U_3O_8 together with atomic position in the cell.

Table 1 The structure of UO_2, g-UO_3, d-UO_3, d-U_2O_5, a-U_3O_8, b-U_3O_8 with lattice parameters.

Compound	Space group	Unit cell	a	b	c
UO2 [1]	Fm-3m	fcc	5.46380		
g-UO3 [2]	Fddd	orthorhombic	9.81300	19.93000	9.71100
d-UO3 [3]	Pm-3m	cubic	4.16500		
d-U2O5 [4]	Pnma	orthorhombic	6.84900	8.27400	31.70600
a-U3O8 [5]	Amm2	orthorhombic	4.14800	11.96600	6.71700
b-U3O8 [6]	Cmcm	orthorhombic	7.06900	11.44500	8.30300

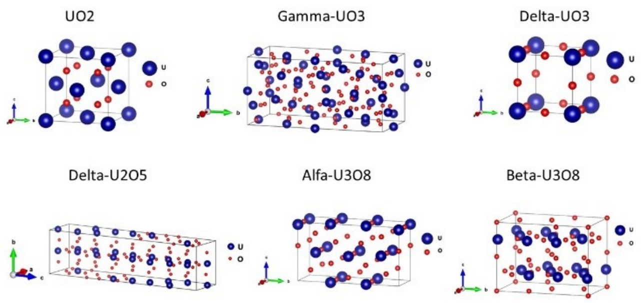

Figure 7 The atomic position in the cell of UO_2, g-UO_3, d-UO_3, d-U_2O_5, a-U_3O_8, b-U_3O_8.

Notes and references

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