Satellite Structure in the U 4f *X*-Ray Photoelectron Spectrum of Uranium Dioxide

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Summary When UO_2 is oxidised to UO_{2+x} a second 'shake-up' satellite is identified at 8·2 eV to the high binding energy side of each U 4f core level in the photoelectron spectrum; these satellites are attributed to the development of oxygen clusters in the UO_2 lattice structure.

IT has recently been reported by various authors[1-5] that a satellite structure is observed to accompany the U 4f *X*-ray photoelectron (XPS) signals of UO_2, but the results are confusing. For $UO_{2\cdot001}$ our early studies[1] noted a weak structure positioned at 6·9 eV to the high binding energy side of each of the U 4f core lines. Two satellites within 10 eV of each U 4f signal from UO_2 were subsequently reported by Pireaux *et al.*[2] and measurements by Baer and Schoenes[3] and Beatham *et al.*[4] in this region identified only one set of satellite signals each separated from the principal U 4f peaks by 7·1 and 6·7 eV respectively.

To explain these observations we have reinvestigated the U 4f photoelectron spectrum characteristic of carefully prepared stoicheiometric UO_2[5] using a Kratos ES 300 photoelectron spectrometer with both a standard Al-K_α exciting source and monochromatic Al-K_α radiation. As before and in agreement with Beatham *et al.*[4] we find only a single 'shake-up' satellite in this region accompanying each of the principal core lines at a separation of 6·8 eV for the pure compound. This we assign to a transition involving the predominantly O 2p and U 5f molecular orbitals.

On exposing the stoicheiometric $UO_{2\cdot00}$ surface to O_2 (*ca.* 5×10^{-3} Torr) for 16, 32, and 120 h at room temperature, however, we observe significant alterations in the satellite positioned at 6·8 eV, notably the progressive generation of a second satellite at 8·2 eV (Figure). This new feature appears while there is no indication in the spectrum of surface contamination by carbonaceous species or water vapour during the oxidation process.

The surface oxide structure responsible for these spectroscopic features may arise from several processes which can be generalised into two alternatives. Either a new oxide grows as a separate phase from the underlying UO_2 or excess of oxygen is incorporated into the lattice to form a surface phase of 'UO_{2+x}'. In the former alternative the new oxide may be a known oxide such as U_4O_9, U_3O_7, U_3O_8, or UO_3 but measurements of the shift in position of the U $4f_{7/2}$ peak and comparison with data recorded previously[1] indicate a relatively low degree of oxidation corresponding to the formula $UO_{2\cdot07}$. Although these results could derive from a new oxide formed as a very thin or incomplete layer on the UO_2 surface, recent measurements from freshly prepared and characterised samples of the higher oxides reveal distinctly different peak profiles and satellite structures in the U 4f region compared with those reported here. Moreover, inhomogeneous oxide mixtures would be expected to give broad U 4f peaks and ill defined satellites.

Of special interest is the observation that on leaving the U_4O_9 sample in the spectrometer for 4 days at room temperature and 1×10^{-9} Torr the surface disproportionates to give a spectrum very similar to that of UO_{2+x} in the Figure. Oxidation of UO_2 is known to take place through the incorporation of oxygen at interstitial sites.[6] As a consequence a neighbouring lattice oxygen is forced from its original site creating a composite centre or 'cluster'. Above *ca.* 400 °C the phase diagram of the uranium–oxygen system shows that the product of such oxygen dissolution is hyperstoicheiometric UO_{2+x}. At the lower temperatures of this experiment though, UO_{2+x} disproportionates into a less oxidised form of UO_{2+x} and into U_4O_9 or, more exactly, into non-stoicheiometric U_4O_{9-y}, the latter having a structure very similar to UO_{2+x} and 'y' being very small.[7]

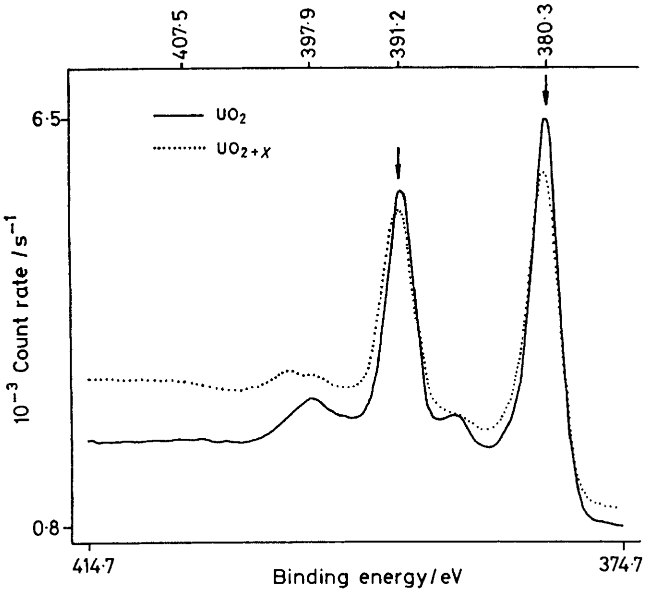

FIGURE. Uranium 4f region of the X-ray photoelectron spectrum of UO_2 and UO_{2+x}.

Only the U 4f photoelectron spectrum has been considered so far but the O 1s region would also be expected to reflect these changes. In accord with previous observations,[1] the O 1s peak moves to lower binding energy on oxidation, from 530·3 to 530·0 eV, consistent with a less covalent oxygen co-ordination. Moreover, among non-stoicheiometric compounds only $Fe_{1-x}O$ has been as thoroughly studied as UO_{2+x} and it is interesting to note therefore, that in an XPS study of $Fe_{1-x}O$, Oku and Hirokawa[8] considered that the relatively large width of the O 1s peak implied vacancy clustering. Here also an increase in the half-height peak width is observed but only to the extent of *ca.* 3%.

Thus we conclude that the development of a satellite at 8·2 eV could be related to the formation of a diphasic surface oxide containing Willis-type clusters in which an individual oxygen atom has a total negative charge less than in the isolated oxygen ion. The new feature in the XPS spectrum may therefore be assigned to the shake-up (charge-transfer) of an electron from the oxygen cluster to metal 5f or 6d levels following photoionisation and hence satellite structure may be a delicate monitor of surface stoicheiometry.

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