Valence-band spectra of tin oxides interpreted by $X\alpha$ calculations

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The two tin oxides, SnO and SnO_2, are not easily distinguished by their core x-ray photoelectron spectroscopic regions, but have significantly different valence-band regions. In addition, significant differences exist in the separations between the near-core region and the valence-band region. These differences are well explained by $X\alpha$ calculations.

INTRODUCTION

Tin has a large difference in binding energy between the metal and the oxides in the Sn $3d$ x-ray photoelectron spectroscopic (XPS) core region, but only a small difference between the oxides (SnO and SnO_2) themselves. This presents a problem since the chemical nature of oxidized tin surfaces is important in many practical situations. In fact the Sn $3d$ to O $1s$ separation is nearly the same in the two oxides.[1,2] Thus, in both our work[1] and that of Lau and Wertheim, SnO_2 had a separation from the O $1s$ peak of only 0.1 eV more than SnO. We argued, on the basis of experiments where a tin metal electrode was electrochemically oxidized, that there was a real separation of 0.5 eV between the Sr $3d$ core regions of the two oxides. Clearly such small differences in the core XPS region make the use of core XPS difficult for distinguishing between tin oxidation state, especially bearing in mind difficulties associated with spectral calibration and uncertainties associated with oxide surface composition of any oxide standards. Lau and Wertheim[2] identified many disagreements in the literature and pointed out the problems associated with ready oxidation of SnO to SnO_2 and the ready hydration of both oxides.

Lau and Wertheim showed[2] that SnO and SnO_2 can be distinguished by a very different valence-band spectrum. Their work suggests that valence-band XPS is the best method for unambiguously distinguishing between SnO and SnO_2.

In this paper the valence-band spectra are interpreted by transition-state $X\alpha$ calculations. For comparative purposes we have run our own valence-band spectra and included the near-core region in our study. The $X\alpha$ calculations support the main differences in the valence-band spectra of the two oxides and show that clear differences in the two spectra are to be expected.

EXPERIMENTAL

XPS measurements were made using a Vacuum Science Workshop VSW-HA-100 spectrometer with a base pressure in the 10^{-10}-Torr region using Al $K\alpha$ x radiation. Spectra were recorded to achieve maximum instrument resolution (better than 0.8 eV) and data were usually collected with at least 17 points per eV in order to be sure to identify any subtle features that might be lost at lower resolution and a larger step size.

High-purity tin metal from Goodfellow's metals were used. Our SnO_2 spectra were obtained from a heavily oxidized sample of this metal. The oxidation of tin has been fully studied e.g., Refs. 2–7. At low oxygen exposures intermediate species and mixtures of oxides may result; for example, Lau and Wertheim[2] showed that tin metal exposed to 10^4 to 10^6 L of oxygen consisted of both SnO and SnO_2, but our sample was air oxidized for a very extended time and may be assumed to be SnO_2. [1 langmuir $(L) \equiv 10^{-6}$ Torr sec.] To obtain an SnO sample, we argon-ion etched the SnO_2-covered tin surface (using 5 keV argon ions) until some underlying tin metal was seen. We have previously[8] found that such etching conditions can lead to oxide reduction. The Sn $3d$ binding energies were similar to those for two oxides reported in our previous work.[1] In the case of both oxides only a single O $1s$ peak at a binding energy corresponding to oxide was seen (there was no hydroxide oxide peak). The purpose of running these spectra was to generate our own data for comparison with the calculations and to extend the range of the spectra that were previously reported by Liu and Wertheim.[2] The valence-band spectra were smoothed and had a nonlinear background subtracted using our previously reported methods.[9,10]

RESULTS AND DISCUSSION

The valence-band region

Robertson[11] published a band-structure calculation for SnO_2, and the electronic structure of SnO_2 has been discussed by Cox and Hoflund.[12] In order to understand the important differences in the valence-band spectrum between SnO and SnO_2, we have carried out transition-state $X\alpha$ calculations on clusters representing these two solids. SnO_2 has a rutile structure where the tin is octahedrally surrounded by six oxygen atoms, whereas SnO (in its usual blue-black form) has the tetragonal PbO structure where each tin atom is surrounded by four oxygen atoms in a C_{4v} arrangement. One assumes a lone pair of electrons occupying the apex of a tetragonal pyramid in the SnO structure.

Figure 1 shows the valence-band region of SnO_2 compared with the results of a transition-state $X\alpha$ calculation on an octahedral $SnO_6{}^{8-}$ cluster. Figure 2 shows the

TABLE I. Parameters used and features of the $X\alpha$ calculations.

α values: Tin 0.700 00, Oxygen 0.744 47	
Outer = Intersphere 0.73558 (SnO), 0.73812 (SnO$_2$)	

Maximum l value: Tin 4, Oxygen 1		
Oxide modeled:	SnO$_2$	SnO
Cluster:	SnO$_6$$^{8-}$	SnO$_4$$^{6-}$
Symmetry:	O_h	C_{4v}
Sn—O bond lengths:	2.054 Å	2.224 Å
Tin sphere radius:	1.384 Å	1.544 Å
Oxygen sphere radius:	1.184 Å	1.236 Å
Watson sphere radius:	2.054 Å	2.224 Å
Outer sphere radius:	3.238 Å	3.263 Å
Virial ratio $(-2T/V)$:	1.000 455	1.000 198

Convergence:	When the difference in potentials at the beginning and end of the iteration was less than 10^{-5} of the potential at the start of the iteration. This gives energy levels that differed by less than 10^{-6} Ry between the last two iterations.
Core electrons:	"Thawed" so that they retained atomic character while being fully included in the iterative process. Sn 1s, 2s, 3s, 2p, 3p, and 3d electrons and O 1s electrons were treated as core electrons.

FIG. 1. (a) XPS valence-band region for SnO$_2$ after smoothing and removal of a nonlinear background. (b) Calculated XPS valence-band region from transition-state $X\alpha$ calculation for SnO$_6$$^{8-}$. The component peaks represent the calculated energy levels adjusted for the XPS photoelectron cross section.

valence-band region of SnO compared with the results of a transition-state $X\alpha$ calculation on a C_{4v} SnO$_4$$^{6-}$ cluster.

The parameters used and the features of the $X\alpha$ calculations are indicated in Table I. Calculations were performed with the Watson sphere set equal to the Sn—O bond length and set equal to the outer sphere radius, but only th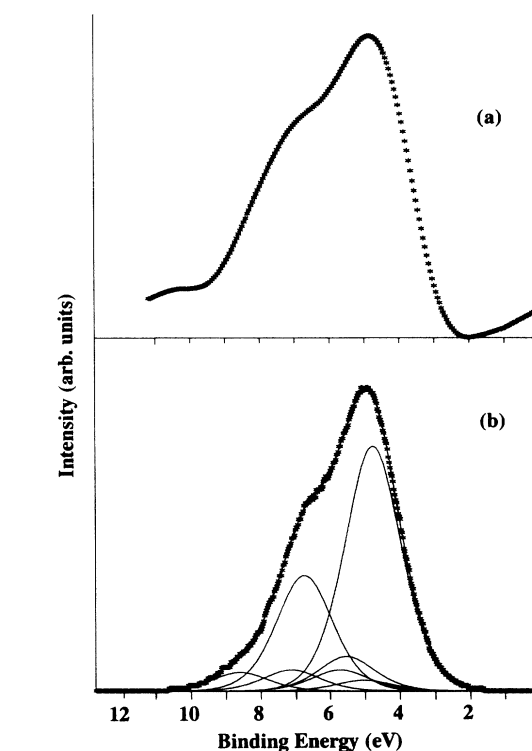e former data were used in the figures since there was little difference when the larger Watson sphere radius was used. The geometry and bond lengths were taken from the well-known crystallographic information for these compounds.[13] Atomic spheres that overlapped by about 25% were used. A full set of transition-state calculations for each energy level in the outer valence-band region was carried out. In this process half an electron is

TABLE II. Orbital energies and atomic populations for valence levels from transition-state calculations for SnO (SnO$_4$$^{6-}$).

Orbital	Transition-state Energy (eV)	Atomic populations[a]				
		Sn 4d	Sn 5s	Sn 5p	O 2p	O 2s
A_1	−18.26	0.154	0.250	0.070	0.326	0.085
A_2	−15.80	0.058	0.001	0.039	0.588	0.032
E	−15.58	0.080		0.078	0.661	0.055
B_1	−15.56	0.024			0.764	
E	−14.79	0.016		0.005	0.782	0.012
B_2	−14.06	0.032			0.844	0.016
E	−13.73	0.027		0.009	0.831	0.028
A_1	−13.43	0.113	0.007	0.108	0.403	0.021
B_2	−13.34	0.056			0.887	0.029
A_2	−13.31				0.909	

[a]Atomic populations are shown for the SnO$_4$$^{6-}$ stoichiometry. Remaining charge is mostly due to intersphere charge. The outer sphere charge was generally less than 0.01 and never greater than 0.03 for the levels shown.

TABLE III. Orbital energies and atomic populations for valence levels from transition-state calculations for SnO_2 (SnO_6^{8-})

Orbital	Transition-state Energy (eV)	Sn 4d	Atomic populations[a]			
			Sn 4s	Sn 4p	O 2p	O 2s
A_{1g}	−26.16		0.295		0.539	0.147
T_{1u}	−24.54			0.100	0.674	0.061
T_{2g}	−24.14	0.024			0.771	
T_{2u}	−23.03				0.822	
T_{1u}	−22.84			0.053	0.816	0.020
T_{1g}	−22.28				0.890	
E_g	−21.98	0.086			0.851	0.036

[a]Atomic populations are shown for the SnO_6^{8-} stoichiometry. Remaining charge is mostly due to intersphere chare. The outer sphere charge was generally less than 0.007 and never greater than 0.01 for the levels shown.

removed from each energy level to account for ionization in a series of different calculations, one for each energy level. The calculated spectrum was obtained by fitting each energy level to a 50% Gaussian-Lorentzian product function,[14] with each peak having a full width at half maximum of 2 eV and an area given by the sum of each level's atomic populations multiplied by their atomic photoelectron cross section.[15] The atomic populations

used for the component peak areas were adjusted for the stoichiometry of SnO or SnO_2 (rather than the cluster stoichiometry SnO_4^{2-} or SnO_6^{8-}). Tables II and III list the calculated energy levels for the two clusters.

Clearly the agreement is good, and the main features of the spectrum are well represented (in Fig. 2 the experimental spectrum has some contribution from metal which increases the intensity of the lowest-binding-energy–peak adjustment for this would give even better agreement). Our experimental valence-band spectra are similar to those of Liu and Wertheim.[2] It should be noted that our spectra are background subtracted for comparison with the calculations. Any background-removal method has some error associated with it, so there is some uncertainty regarding relative intensities. The main prediction of the calculations is that SnO has three nearly equal intensity overlapping features, whereas SnO_2 has three overlapping features with the lowest-binding-energy peak of much greater intensity than the other two peaks, with the highest-binding-energy feature of lowest intensity. Tin is a case where the valence band is much less intense than that for transition metals where the high XPS cross section for d electrons dominates the spectrum. In fact the tin valence-band spectra are dominated by those levels that have a small amount of Sn 4d character which has a much higher XPS cross section than tin 5s and 5p electrons—the main components of the valence band.
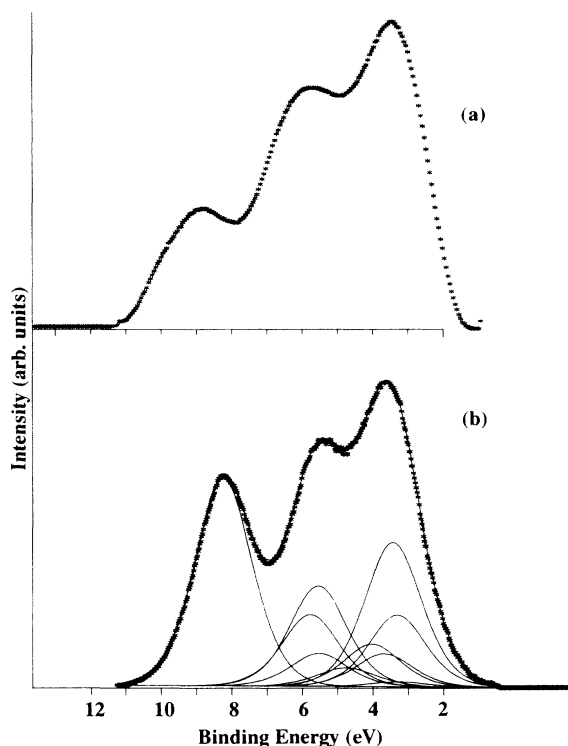

FIG. 2. (a) XPS valence-band region for SnO after smoothing and removal of a nonlinear background. (b) Calculated XPS valence-band region from transition-state $X\alpha$ calculation for SnO_4^{6-}. The component peaks represent the calculated energy levels adjusted for the XPS photoelectron cross section.

Positions of the valence-band peaks with respect to the near-core region

The separation of the features in the valence band from the near-core region also provides significant differences between the two tin oxides. Thus, we find that in SnO the most intense peak in the valence band is separated by 23.7 eV from the Sn 4d core peak, but this separation falls to 21.1 eV in SnO_2. The transition-state calculations predict a separation of 23.8 and 21.5 eV, respectively. All this suggests that *shifts in the near–valence-band region can be much more sensitive to differences in oxidation state than in the core region.* An advantage of using separations in the spectra is that the values obtained are independent of any calibration method, since separations

are measured within the same spectrum, leading to much more accurate values.

CONCLUSIONS

We report the first $X\alpha$ calculation of the tin-oxide XPS valence-band spectrum. We find that these $X\alpha$ calculations give excellent agreement with the experimental valence-band spectrum and to separations between near-core region features and the valence band. The results support the experimental evidence that tin oxides can be reasonably distinguished by valence-band XPS.

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