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Oxygen 2s spectroscopy of tin oxides with synchrotron radiation-induced photoemission

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Abstract: Oxygen 2s spectroscopy can be especially useful in studies using synchrotron radiation (SR) where the deeper O 1s level frequently can not be excited. For tin oxides (SnO and SnO₂), the weak emission from the O 2s levels has been previously found degenerate with the intense photoemission peak from Sn 4d levels around a binding energy (BE) of 26 eV. By working at the Cooper minimum of the interfering tin signal, a distinct peak near BE ≈22.5 eV could be unambiguously attributed to emission from O 2s levels in tin oxides considering photoionization cross-section arguments. The O 2s intensity could now be used for the quantitative evaluation of the near-surface oxygen-species concentration. We have used the O 2s in combination with the Sn 4d areas to study the variations of the [Sn]/[O] ratio as a function of the preparation of a SnO₂ single crystal. Although the dominant formal valence state for tin determined from a Sn 4d lineshape analysis remains essentially Sn⁴⁺, we show that this [Sn]/[O] ratio can vary from simple to double. This can be explained by oxygen interstitials buried in a sub-surface region during ion bombardment, which segregate at the surface upon annealing.

1. INTRODUCTION

In detailed photoemission studies, we have recently addressed the electronic structure of tin oxides (SnO and SnO₂) using UPS [1] and XPS [2]. The low-energy region (0 eV < Binding Energies (BE) < 35 eV) has proved particularly useful for discriminating between stannous and stannic oxide. Using XPS, the deconvolution of the Sn 3d peak in terms of Sn²⁺ and Sn⁴⁺ formal valence states can be usefully guided [2] by considering characteristic features of the VB (which derives from O 2p, Sn 5s and 5p levels), e.g. the energy difference between the VB leading peak and the shallow Sn 4d levels found at BE ≈ 26 eV. With UPS which allows better resolving power, the direct deconvolution of these Sn 4d levels is usually possible [3]. Oxygen 2s spectroscopy [4] can be especially useful in studies using synchrotron radiation (SR) where the deeper O 1s level frequently can not be excited. However, other s or p levels often hybridize with O 2s levels while the high intensity from more localized d or f levels may also hide the low-intensity O 2s emission, found between binding energies of 14 and 33 eV. This is dramatically true for systems involving oxygen and tin, since the O 2s levels have been reported to be degenerate [5] with the intense Sn 4d signal, strongly favoured by its electron occupancy (10 electrons vs 2 electrons for O 2s) and its partial photoelectron cross section [6] $\sigma_{\text{Sn } 4d} > 10 \sigma_{\text{O } 2s}$ in most of the X-ray and UV regimes). Nevertheless, both in our UPS and monochromatized-XPS spectra, we have noticed on the low-BE side of the Sn 4d peak a very small bump at BE ≈ 22 eV. In order to identify this unknown structure, which, we think, could be due to O 2s levels, we have tried to reduce the intensity of the interfering tin signal. This has been possible by working at the Cooper minimum of the Sn 4d levels. This minimum, which occurs for states with nodes in their radial wave function [7], has been calculated [6] for Sn at about 140 eV.

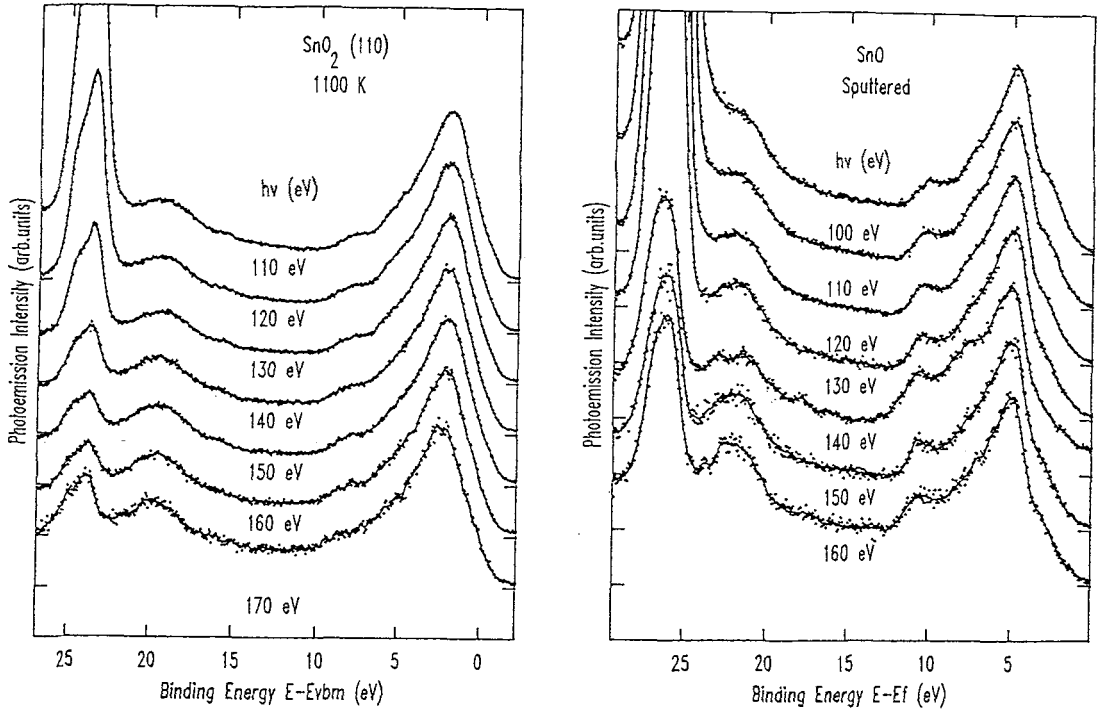


Fig.1: VB and near-core region EDC's for photon energies in the vicinity of the Cooper minimum of the Sn 4d levels, for SnO₂ (110) annealed at 1100K (left panel) and sputtered SnO (right panel).

2. RESULTS

Fig.1 shows representative UPS spectra of SnO₂ and SnO taken at various photon energies in the vicinity of the Cooper minimum. The overall degradation of the signal-to-noise ratio for increasing $h\nu$ reflects the general decrease of the partial σ_i . To compensate for this overall decrease and to ease comparison, each spectrum has been normalized to the intensity of the prominent peak of the VB, derived from levels which have mainly an O 2p character [8], and is easily located in the VB of both oxides. For tin dioxide (Fig.1, left panel), the Sn 4d intensity rapidly decreases with $h\nu$ up to 150 eV where it appears as intense as the unknown structure. The same trend is reproduced for tin monoxide, except that the Sn 4d area does not decrease below ≈ 3 times the unknown structure area. As a general trend, it is visible that the unknown structure intensity slightly increases with respect to the O 2p intensity between 110 and 170 eV.

3. INTERPRETATION

The hypothesis of a satellite associated with Sn 4d levels can directly be ruled out since the unknown-structure intensity does not follow the large variations of the Sn 4d peak intensity. Assuming that the unknown structure could be due to emission from the O 2s levels, we have plotted in Fig.2 the ratio of its intensity and the O 2p intensity (extracted from the VB). These points correlate rather well with the theoretical ratio of the partial photoionization cross sections $\sigma_{O\ 2s} / \sigma_{O\ 2p}$ between 110 and 170 eV. The same type of argument has been previously used to identify an O 2s-derived structure in the VB photoemission spectra of high-temperature superconductors [9]. We therefore unambiguously attribute the weak emission at $BE \approx 22.5$ eV in tin oxides to O 2s levels. This energy lies in the range where O 2s levels have been reported for other oxides, e.g. from 20.3 eV for BaO [10] to 24.5 for SiO₂ [4].

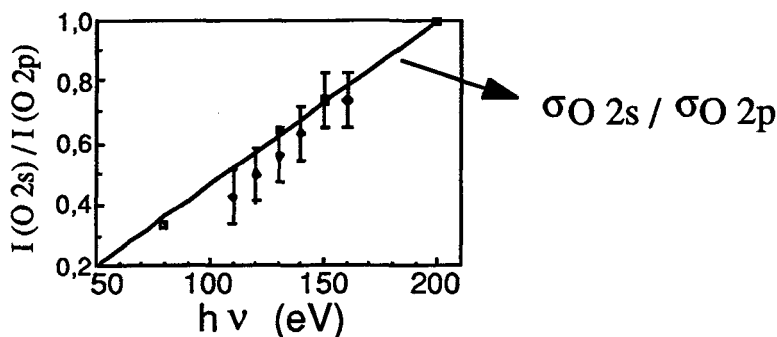


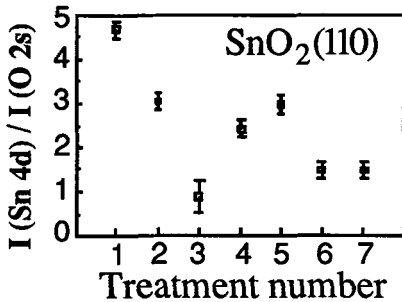
Fig.2: Correlation between the intensity ratio (solid points) of the unknown structure (supposedly O 2s-derived) and the O 2p structure in the VB of SnO₂ (110) with the calculated partial photoionization cross sections ratio $\sigma_{O\ 2s} / \sigma_{O\ 2p}$ between 110 and 170 eV (solid line).

We have now a direct access to an oxygen core level intensity and we can use the O 2s intensity or its area to compare it with the Sn 4d intensity, without relying on the hybridized O 2p orbitals which are much more difficult to isolate in the valence band of the oxides. This allows the determination of the relative concentrations of oxygen and metal within the photoelectron sampling depth. It also cancels a drawback of UPS applied to oxides, which, considering the low photon energies implied, does not usually allow electrons from the O 1s to be excited above the vacuum level. For example, one can now understand qualitatively why the intensity ratio $I(\text{Sn } 4d) / I(\text{O } 2s)$ is higher for tin monoxide (3.5 for SnO vs 1.5 for SnO₂), since it simply reflects the stoichiometry of the oxide. In what follows, we will illustrate the usefulness of our ability to estimate the [Sn]/[O] ratio through the O 2s and Sn 4d area measured at the Cooper minimum.

4. APPLICATION

We have measured in this way the $I(\text{Sn } 4d) / I(\text{O } 2s)$ intensity ratio for a fresh SnO₂ (110) single crystal face prepared in the usual way using successive Ar-ion bombardment and UHV annealing treatments. Although the Sn 4d levels and the VB show only minor changes [3], Fig.3 denotes substantial changes of the [Sn]/[O] ratio, and particularly, an irreversible decrease of the post-sputtering ratio with the number of sputtering/annealing cycles. This appears rather surprising if one considers the usually reported trends for most oxides which are easily reduced [11] by preferential sputtering of the light oxygen atoms under Ar-ion bombardment. Such a trend is of course locally valid here since ion bombardment effectively increases the [Sn]/[O] ratio, which increases further with a larger ion dose (treatments n°4 and 5). This is also confirmed by the analysis of the Sn 4d detailed peak shape and by the VB which show evidence of some limited reduction (evolution towards an SnO stoichiometry) upon ion bombardment [3]. Annealing, on the contrary, restores near-core and VB spectra characteristic of stoichiometric SnO₂, which is reflected by the (local) decrease of the [Sn]/[O] ratio.

In the present case, we believe that the net [Sn]/[O] decrease may be explained by the creation, during ion bombardment, of a subsurface layer enriched in oxygen. Part of this oxygen diffuses towards the surface upon annealing, causing the progressive decrease of the [Sn]/[O] ratio. We describe this mechanism in more detail hereafter. The dominant defect in SnO₂, the doubly ionized oxygen vacancy, has been determined using electrical methods [12]. We propose, therefore, that the oxygen species detected here are neutral atomic oxygens, which are virtually undetectable in a conductivity experiment. The creation of such an "anti-frenkel" disorder [13] where both oxygen vacancies and oxygen interstitials coexist is likely to happen upon Ar-ion bombardment. Considering momentum conservation arguments, the oxygen primaries hit by Ar⁺ ions are displaced towards the bulk, resulting in the formation of a subsurface layer enriched in neutral atomic oxygen interstitials. The latter remain undetected in UPS due to the short sampling depth. Upon annealing, these oxygen species could well diffuse towards the surface through the microdomains reduced by the ion bombardment [3], and even along the c-axis of the native rutile structure of SnO₂ (diffusion parallel to the surface). As another proof of the oxygen diffusion phenomena, we have also checked that the absolute intensity of the O 2s emission increases during annealing, while the Sn 4d absolute intensity remains the same.



n°1 : Ar- ion Bombardment (122 a.u.)
 n°2 : Annealing 1000K
 n°3 : Annealing 1050K
 n°4 : Ar- ion Bombardment (65 a.u.)
 n°5 : Ar -ion Bombardment (185 a.u.)
 n°6 : Annealing 1000K
 n°7 : Ar-ion and annealing 1100K

Fig.3: $I(\text{Sn } 4d) / I(\text{O } 2s)$ area ratio measured at the Cooper minimum for seven successive treatments of a freshly-introduced SnO_2 single crystal exposing its (110) face. The arbitrary units indexing each ion bombardment are the product of the incident current times the duration of the ion beam exposure. An evolution towards low $[\text{Sn}]/[\text{O}]$ ratios is visible.

In conclusion, we want to emphasize the distinction between the oxide composition based on the relative concentrations of cations in formal valence state Sn^{4+} or Sn^{2+} , determined through lineshape analysis of the Sn 4d levels, and oxide composition based on the $[\text{Sn}]/[\text{O}]$ ratio obtained through the $I(\text{Sn } 4d) / I(\text{O } 2s)$ area ratio measured at the Cooper minimum. Although the relative concentrations of Sn^{4+} (dominant species) and Sn^{2+} cations take reproducible values characteristic of sputtering or annealing [3], Fig.3 reveals a two-fold variation of the $I(\text{Sn } 4d) / I(\text{O } 2s)$ intensity ratio after some cleaning cycles. Such large differences could explain why former Auger studies [14] mainly based on $[\text{Sn}]/[\text{O}]$ ratios often showed large variations or irreversible changes with sample history. It is thus clear that the relative "stability" of UPS spectra which are usually exploited through their "chemical bonding" or valence state informations rather than through the atomic concentrations point-of-view could well keep important phenomena hidden. The determination of these atomic concentrations requires the availability of an oxygen core level with an area comparable with the chosen metal core line. We have shown that for tin oxides, O 2s levels are ideal candidates for that purpose. O 2s spectroscopy using SR-induced photoemission is thus useful to study diffusion processes in tin oxides and can bring valuable information to the study of oxygen/tin systems.

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