

# Characterization Study of Oxidized Polycrystalline Tin Oxide Surfaces before and after Reduction in H<sub>2</sub>

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An oxidized polycrystalline tin oxide film has been examined using electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (AES), ion-scattering spectroscopy (ISS), and electron energy loss spectroscopy (ELS) before and after reduction in 40 Torr of H<sub>2</sub> for 1 h at 200 °C. The data indicate that the oxidized tin oxide surface is fairly inert to this strongly reductive treatment. The ISS spectra show that the oxygen concentration in the outermost atomic layer does not change significantly during the reduction but that the reduced surface is more electrically conductive. This is due to the loss of oxygen in the subsurface region which is detected by ESCA. The ELS data were taken using primary beam energies of 200, 400, and 600 eV in order to vary depth sensitivity. Over the depths examined, the ELS data indicate that the predominant component of the reduced, oxidized, and reoxidized surfaces is a transitional oxide phase which has a composition between that of SnO and SnO<sub>2</sub>. Both the ESCA and ELS data indicate that a small portion of this transitional oxide phase is reduced to SnO during the reduction. The reduced surface was then reoxidized in 40 Torr of O<sub>2</sub> for 1 h at 200 °C. The ISS spectrum obtained from this surface indicates a large increase in the amount of oxygen contained in the outermost atomic layer, and the ESCA and ELS data indicate that most of the SnO produced during the reduction is reoxidized to SnO<sub>2</sub>.

## Introduction

Tin oxides are important components in various types of heterogeneous catalysts,<sup>1-12</sup> gas sensor materials,<sup>13-16</sup> and transparent conductive films.<sup>17-20</sup> The chemical and physical properties of these materials are determined by the chemical states of the Sn present as well as the structure and distribution of these species, which are all strongly dependent upon the history and method of preparation of the sample. Thus, tin oxide surfaces are quite complex since numerous types of tin oxide phases exist<sup>7,21-25</sup> and tin oxide always contains hydrogen in several forms<sup>26-28</sup>

with higher concentrations near the surface. Many characterization studies have been carried out on various tin oxide surfaces, and the assumption has usually been made that SnO and SnO<sub>2</sub> are the only stable types of tin oxide which need to be considered. However, Cox and Hoflund<sup>21</sup> found evidence for the presence of an oxide other than SnO or SnO<sub>2</sub> in tin oxide films which they called a transitional oxide because it seemed to be intermediate in composition between SnO and SnO<sub>2</sub> and more prominent during the oxidation of SnO or reduction of SnO<sub>2</sub>. This same transitional oxide was also identified by Hoflund and Corallo<sup>25</sup> in a study of the oxidation of polycrystalline tin. Thus, the assumption that SnO and SnO<sub>2</sub> are the only forms of oxide present in tin oxide appears to be incorrect.

The purpose of this study is to determine the Sn chemical state distribution in the near-surface region of a tin oxide film after oxidation in 40 Torr of O<sub>2</sub> at 200 °C for 1 h, then after reduction in 40 Torr of H<sub>2</sub> at 200 °C for 1 h, and then again after reoxidation in 40 Torr of O<sub>2</sub> at 200 °C for 1 h. These conditions are typical of those used to pretreat low-temperature CO oxidation catalysts.<sup>1,3,4,6</sup> This study is part of a larger study in which the reduction of platinumized tin oxide catalysts is being examined. By considering the reduction of tin oxide with and without Pt present, the role of the Pt during the reduction can be understood. In the previous part of this study,<sup>29</sup> the effects of reduction of polycrystalline tin oxide thin films in 40 Torr of CO at 100 and 175 °C for 1 h were investigated using electron

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spectroscopy for chemical analysis (ESCA or XPS), Auger electron spectroscopy (AES), ion-scattering spectroscopy (ISS), and electron-stimulated desorption (ESD). Although the changes in the surface composition and chemical states of the surface species are small for the reductive conditions used according to the XPS, AES, and ISS data, significant changes do occur with regard to the amounts and the chemical forms of the hydrogen-containing species remaining after the reduction according to the ESD data. The techniques used in this present study were ISS, AES, ESCA, and electron energy loss spectroscopy (ELS). ESCA is relatively insensitive for distinguishing between the various forms of tin oxides. This fact has hindered efforts to characterize tin oxide films. However, Powell<sup>24</sup> has shown that ELS is capable of distinguishing between SnO and SnO<sub>2</sub> as well as Sn metal. This fact has been used in several studies of tin oxide and oxygen-exposed tin surfaces<sup>24,25,30-33</sup> to determine the Sn oxidation state. The ELS results obtained after the various treatments are compared with results obtained using ISS, AES, and ESCA in order to gain a more complete understanding of tin oxide surfaces. This combination of techniques also provides a nondestructive depth profile of the near-surface region because they probe different depths beneath the surface. Additionally, the depth sensitivity of ELS has been varied by changing the primary electron beam energy. As in the previous part of this study,<sup>29</sup> the changes due to the reductive and oxidative treatments are subtle, but these spectral changes are reproducible and meaningful.

### Experimental Section

Thin polycrystalline tin oxide films supported on titania foil were prepared using a high-temperature spray hydrolysis method described previously.<sup>34</sup> An as-prepared film was inserted into a sample preparation chamber where it was annealed at 200 °C in 40 Torr of O<sub>2</sub> for 1 h using a heater system<sup>35</sup> which does not dissociate the background gas. The sample was moved into the UHV analysis chambers (10<sup>-10</sup>–10<sup>-11</sup> Torr) without exposure to air where it was analyzed using ELS, ISS, ESCA, and AES. Then the sample was moved back into the preparation chamber where it was reduced in 40 Torr of H<sub>2</sub> at 200 °C for 1 h. After examination of the reduced surface with the characterization techniques, the sample was reoxidized in 40 Torr of O<sub>2</sub> at 200 °C for 1 h and examined again with the four techniques. This whole procedure was carried out on a second tin oxide sample, and the second set of spectra accurately reproduce the first set even though the second sample was prepared and analyzed several months after the first sample.

AES, ISS, ESCA, and ELS were performed using a double-pass cylindrical mirror analyzer (CMA; Perkin-Elmer PHI Model 25-270AR) as the charged-particle energy analyzer. AES was performed using the internal, coaxial gun with a primary beam energy of 3 keV, spot size of about 0.5 mm, and primary beam current of about 10 μA. The CMA was operated in the nonretarding mode using analog phase-sensitive detection with a 10-kHz oscillating voltage of 0.5 V<sub>pp</sub> applied to the outer cylinder. ISS was also performed in the nonretarding mode using pulse

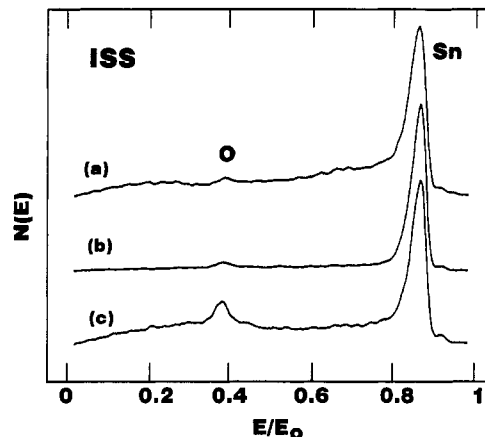


Figure 1. ISS spectra obtained from the (a) oxidized, (b) reduced, and (c) reoxidized polycrystalline tin oxide surfaces.

counting detection.<sup>36</sup> A 1-keV <sup>4</sup>He<sup>+</sup> primary ion beam (100 nA defocused over a spot size of about 1 cm in diameter) was used to collect a spectrum in 90 s. Exposure to the primary beams in ISS, AES, and ELS was minimized in order to reduce beam-induced damage. ESCA was performed using Mg K $\alpha$  excitation and by operating the CMA in the retarding mode with a 50-eV pass energy for collection of survey spectra and a 25-eV pass energy for collection of high-resolution spectra. ELS was performed by operating the CMA in the retarding mode with a pass energy of 25 eV using pulse counting detection. A primary electron beam current of 100 nA over a spot size approximately 0.5 mm in diameter was used. The primary beam from the CMA electron gun was normal to the sample, and electrons leaving the sample at an angle of 42.3  $\pm$  6° with respect to the sample normal were collected. Three primary beam energies of 200, 400, and 600 eV were used in order to vary depth sensitivity.

### Results and Discussion

ISS spectra obtained from the oxidized, reduced, and reoxidized surfaces are shown in Figure 1, parts a, b, and c, respectively. Peaks due only to O and Sn are present as expected. The ISS scattering cross section is an increasing function of atomic weight.<sup>37</sup> A cross-section calibration has been carried out recently on O-exposed Ag surfaces,<sup>38</sup> and the O/Ag cross section ratio has been found to be about 0.045 for the same experimental parameters used in the present study. Since the atomic weight of Sn is only about 10% greater than that of Ag, the O/Sn ratio may be similar to the O/Ag ratio. On the basis of O and Sn peak heights in Figure 1a, the outermost atomic layer contains about 50 atomic % O. The background consisting of He ions which have scattered more than once is quite large, indicating that these ions are not efficiently neutralized at this surface.

The ISS spectrum obtained from the reduced surface and shown in Figure 1b contains O and Sn peaks which are similar in size to those obtained from the oxidized surface. However, the background is very small compared to the spectrum shown in Figure 1a. This characteristic has been observed in many previous studies.<sup>4,38-42</sup> As a metallic surface is oxidized, the ISS background increases,

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and it decreases when the near-surface O concentration is lowered by a reductive treatment. An explanation for this observation is that the neutralization efficiency of a surface is significantly influenced by the electrical properties of a surface. The conductivity of a surface is the product of the conduction electron density and the electron mobility. Generally, these are both lowered as a metallic surface is oxidized so the ion neutralization efficiency is lowered, resulting in an increased ISS background. The reduction of a bulk oxide can be more complex due to the interplay between the subsurface region and the outermost atomic layer and the fact that electrical properties are dependent upon many complex factors. Although systematic studies of the relationships between these parameters have not been carried out, these simplistic arguments are consistent with a large amount of ISS data. As discussed in previous studies,<sup>43,44</sup> reduction of tin oxide films produces O vacancies which can increase the electrical conductivity by as much as several orders of magnitude. The fact that the O and Sn peak heights are similar in the ISS spectra obtained from the oxidized and reduced surfaces suggests that the O vacancies are located primarily beneath the outermost atomic layer. A reductive treatment of an oxide can actually increase the O content of the near-subsurface region. During reduction, subsurface O migrates toward the surface under a chemical driving potential. Surface O reacts, leaves the surface, and is replaced by more O migrating to the surface. Thus, the O content at the surface remains high while the O content of the subsurface region is decreased. This behavior has been observed for the reduction of TiO<sub>2</sub>(001).<sup>45</sup>

The ISS spectrum obtained from the reoxidized surface (Figure 1c) contains a large O peak. On the basis of the O and Sn peak heights, the outermost atomic layer of this surface contains about 80 atomic % of oxygen. This O content is greater than that of a Sn surface exposed to air at room temperature for 1 h.<sup>46</sup> Yamazoe et al.<sup>47</sup> have performed temperature-programmed desorption (TPD), electron spin resonance (ESR), and electrical conductivity measurements on oxygen-exposed tin oxide surfaces and have proposed that oxygen chemisorbs on tin oxide surfaces in a number of different forms including O<sub>2</sub>, O<sub>2</sub><sup>-</sup>, O<sup>-</sup>, and O<sup>2-</sup>. Several or all of these species may have chemisorbed on this reduced tin oxide surface. The fact that more O is present on the reoxidized surface than on an air-exposed surface must result from carrying out the reoxidation at elevated temperature, suggesting that chemisorption of O<sub>2</sub> on a reduced tin oxide surface may be an activated process. The background in Figure 1c is significantly increased compared to that obtained from the reduced surface, indicating that the neutralization probability decreases by reoxidation. However, the background from the reoxidized surface is not as large as that obtained from the oxidized surface even though the outermost atomic

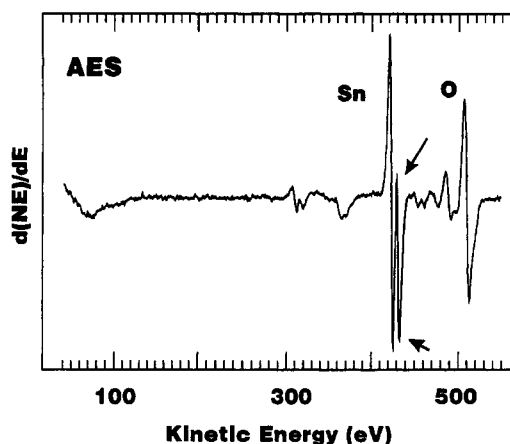


Figure 2. Auger spectrum taken from the oxidized tin oxide surface.

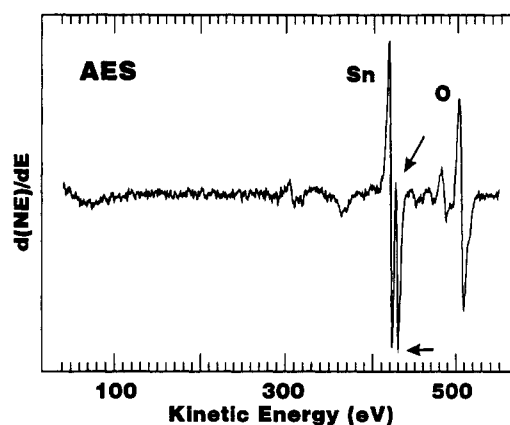


Figure 3. Auger spectrum taken from the reduced tin oxide surface.

layer of the oxidized surface contains much less O than the outermost atomic layer of the reoxidized surface. This fact is readily apparent by overlaying the normalized spectra, but this is difficult to see in Figure 1. It indicates that the reoxidized surface is quite different from the oxidized surface probably because subsurface O vacancies exist on the reoxidized sample. Therefore, the history of a tin oxide surface is very important in determining its properties; i.e., exposing two different tin oxide surfaces to a given environment does not necessarily produce two identical surfaces. This point is illustrated further by the fact that O chemisorbs differently on an as-prepared surface than on a reduced surface as seen by comparing Figure 1, parts a and c.

Auger spectra obtained from the oxidized, reduced, and reoxidized surfaces are shown in Figures 2–4, respectively. These spectra show that the tin oxide surface is very clean in that peaks due to Sn and O are apparent, but no peaks due to contaminants such as C or Cl are present. The differences between these three spectra are subtle but meaningful and due to compositional changes. Comparing peak-height ratios from the three surfaces is reasonable in this case because the peak-shape changes are very small, so the trends are believed to be meaningful. The peak-shape changes are very small for two reasons. First, as shown by Powell,<sup>24</sup> there is no significant difference in Auger peak positions for SnO and SnO<sub>2</sub> and their Sn peak shapes are nearly identical. Second, the chemical state changes are subtle for the reductive treatments used as described in the ELS discussion below. Therefore,

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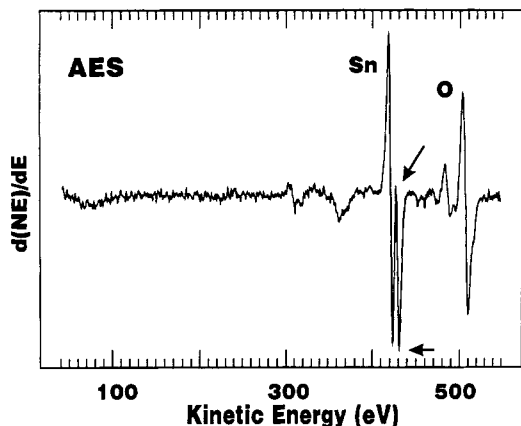


Figure 4. Auger spectrum taken from the reoxidized tin oxide surface.

comparing Auger peak-height ratios and ascribing the variations to compositional changes is reasonable. The O/Sn peak-height ratio is slightly larger for the reduced surface (0.69) than for the oxidized surface (0.65). This fact is consistent with the statements made above that during reduction O migrates to the near-surface region under a chemical driving potential resulting in an increased O concentration in the near-surface region sampled in AES. Thus, the O vacancies responsible for the increased conductivity of the reduced surface seem to lie beneath the outermost few atomic layers. The O/Sn peak-height ratio obtained from the reoxidized surface (0.71) is slightly increased over that obtained from the reduced surface. This is due to oxidation of SnO in the near-surface region as discussed below and to chemisorption of oxygen species in the outermost atomic layer as observed in the ISS data. In addition to the small peak-height changes, subtle peak-shape changes also occur. With increasing surface O content, the height of the splitting between the Sn peaks decreases and the bottom portion of the predominant Sn peaks changes in a manner which correlates with the O content in that the higher kinetic energy peak increases in size with respect to the lower kinetic energy peak. Apparently, these small changes have not been observed by other researchers, and they may be due to the slight changes in the Sn 3d levels described below. Subtle changes in the three O AES peak shapes are also apparent, but these depend upon the relative amounts of the different chemical states of O present and are difficult to interpret.

An ESCA survey spectrum obtained from the reoxidized surface and shown in Figure 5 exhibits peaks due only to Sn and O. The ESCA survey spectra obtained from the oxidized and reduced surfaces are nearly identical to this spectrum, so they are not shown. Even in narrow-range, detailed spectra no C peak is present, but small Cl and Na peaks just barely above the noise level are present. A very small Cl peak usually is present in Auger spectra obtained from these tin oxide films because HCl was used in the sample preparation. In this study some of the Cl probably was desorbed during the initial oxidation, and the rest may have desorbed by electron stimulated desorption during collection of the Auger spectrum as observed previously.<sup>34</sup> This explains why a small Cl peak appears in the ESCA spectra but not the Auger spectra. These points again emphasize that these surfaces are very clean. The Sn/O ESCA peak-area ratios obtained from detailed ESCA Sn 3d<sub>5/2</sub> and O 1s peaks are given in Table 1 for the oxidized, reduced, and reoxidized tin oxide surfaces. A

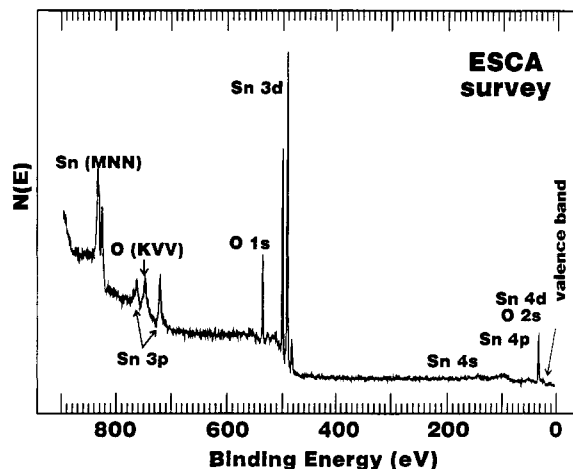


Figure 5. ESCA survey spectrum obtained from the reoxidized tin oxide surface.

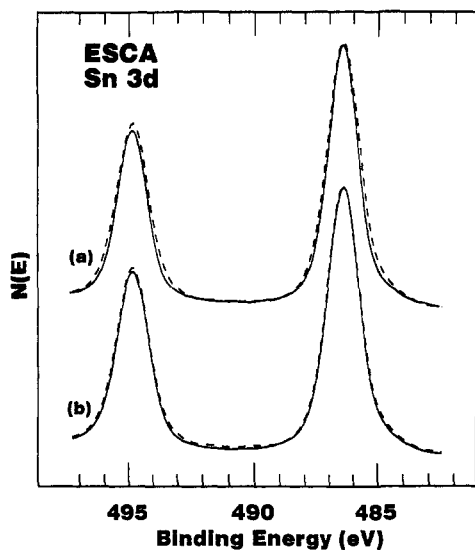
Table 1. ESCA Sn/O Peak Area Ratios

	Sn/O
reduced <sup>a</sup>	3.91
oxidized	3.50
reduced	3.88
reoxidized	3.66

<sup>a</sup> Reduced in 40 Torr of CO for 1 h at 100 °C.<sup>29</sup>

value is also provided for a tin oxide surface which was reduced in 40 Torr of CO for 1 h at 100 °C.<sup>29</sup> The Sn/O ratio obtained from the oxidized surface is 3.50. This is the smallest ratio obtained from all of the surfaces examined indicating that this surface contains the most O in the region sampled by ESCA. Reduction in H<sub>2</sub> increases this ratio to 3.88 which is nearly equal to the 3.91 value obtained by reduction in CO. The AES and ESCA data appear to be contradictory in that AES indicates an increased O content whereas ESCA indicates a decreased O content for the reduced surface. This is due to the fact that ESCA probes more deeply than AES because the Sn 3d and O 1s photoelectrons have larger kinetic energies and, hence, longer mean-free paths than the Sn and O Auger electrons. Therefore, the combined use of ISS, AES, and ESCA essentially provides a nondestructive profile of the near-surface region. The AES data coupled with the ESCA data indicate that the near-surface region becomes enriched in O during reduction while the region further beneath the surface becomes depleted in O, and the ISS data show that the O content of the outermost atomic layer remains unchanged. According to ESCA, the O content of the reoxidized surface is increased but not to that of the oxidized surface. The O vacancies remaining on the oxidized surface lie beneath the surface. This interpretation is consistent with the information obtained from the ISS data in that there seems to be a direct correspondence between the neutralization efficiency of multiply scattered ions and the ESCA Sn/O ratios.

High-resolution ESCA Sn 3d spectra obtained from the oxidized, reduced, and reoxidized surfaces are shown in Figure 6. To accentuate the subtle differences, the spectrum obtained from the reduced surface (dashed line) is plotted over that obtained from the oxidized surface in Figure 6a and over that obtained from the reoxidized surface in Figure 6b. The differences between these spectra are small, but they have been reproduced many times. In Figure 6a the Sn 3d peaks obtained from the

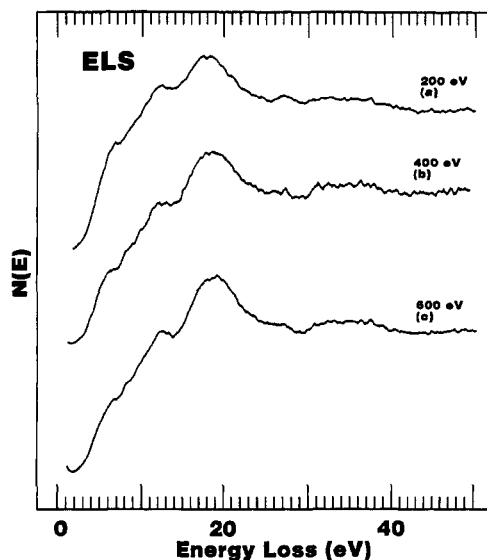


**Figure 6.** ESCA Sn 3d spectra taken from the (a) oxidized and reduced tin oxide surfaces and (b) reduced and reoxidized tin oxide surfaces. The spectrum obtained from the reduced surface is the dashed curve in both (a) and (b).

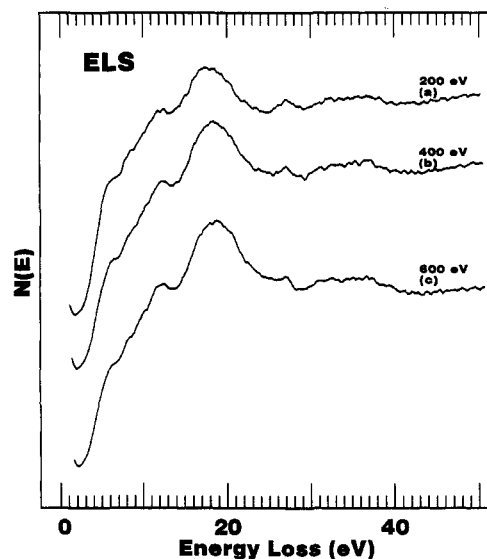
reduced surface are slightly broader than those obtained from the oxidized surface. It is relatively easy to distinguish metallic Sn from Sn oxide because the Sn 3d peaks are shifted about 1.8 eV in binding energy. The situation is quite different for distinguishing between SnO and SnO<sub>2</sub> which have nearly identical binding energies. Paparazzo et al.<sup>48</sup> have determined using monochromatized X-rays that the binding energy shift between SnO and SnO<sub>2</sub> is 0.18 eV. This value appears to be consistent with the magnitude of the broadening observed in Figure 6a and therefore suggests that a portion of the transitional oxide discussed below is partially reduced to SnO during the reduction. The peaks obtained from the reduced surface also exhibit a broadening on the low binding energy side. This point is discussed below.

The Sn 3d peaks obtained from the reoxidized surface (Figure 6b) are slightly narrower than the Sn 3d peaks obtained from the reduced surface indicating that the reduced Sn becomes more oxidized. However, they are not as narrow as those obtained from the oxidized surface. This indicates that the extent of oxidation is not complete enough to fully reoxidize the surface, which is consistent with the data in Table 1. This set of Sn 3d spectra are also consistent with the ion neutralization efficiency information obtained from the ISS data. High-resolution ESCA O 1s peaks were obtained from these surfaces, but they are not shown because they do not exhibit any significant shape differences.

ELS spectra taken using primary beam energies of 200, 400, and 600 eV were obtained from the oxidized, reduced and reoxidized surfaces and are shown in Figures 7–9, respectively. On the basis of mean-free path calculations made in the previous study,<sup>25</sup> the 200-, 400-, and 600-eV primary beam energies sample 1.9, 2.6, and 3.2 nm beneath the surface, respectively. The ELS spectra are all fairly similar exhibiting only subtle changes after the reductive and oxidative treatments. Many studies<sup>21,24,25,30–33,49</sup> have presented detailed discussions on the assignment of ELS



**Figure 7.** ELS spectra taken from the oxidized tin oxide surface using primary beam energies of (a) 200 eV, (b) 400 eV, and (c) 600 eV.



**Figure 8.** ELS spectra taken from the reduced tin oxide surface using primary beam energies of (a) 200 eV, (b) 400 eV, and (c) 600 eV.

features obtained from metallic tin and tin oxides, and these studies form the basis of the discussion presented here. The peaks which are used in the analysis presented below are the 13- and 27-eV peaks due to SnO, the 20-eV peak (shoulder in this study) due to SnO<sub>2</sub>, and the 18-eV peak due to a transitional oxide phase which has an O content between that of SnO and SnO<sub>2</sub>. An important fact which has been discussed very carefully in the previous ELS studies<sup>21,24,25</sup> is that SnO is the only tin oxide species which yields a 27-eV feature in this study. Metallic Sn does yield a 28-eV feature which is due to a loss process involving excitation of two bulk plasmons and can yield features in this region due to excitation of the Sn 4d electrons to unfilled levels. Generally, the plasmon loss feature is more prominent, but the interband-transition feature can be brought out by increasing the surface sensitivity and collecting data in the derivative mode as discussed by Bevolo et al.<sup>32</sup> SnO<sub>2</sub> does not yield a peak in this region. The SnO peak and the Sn metal features have different shapes.<sup>25</sup> The shapes of the 27-eV peaks

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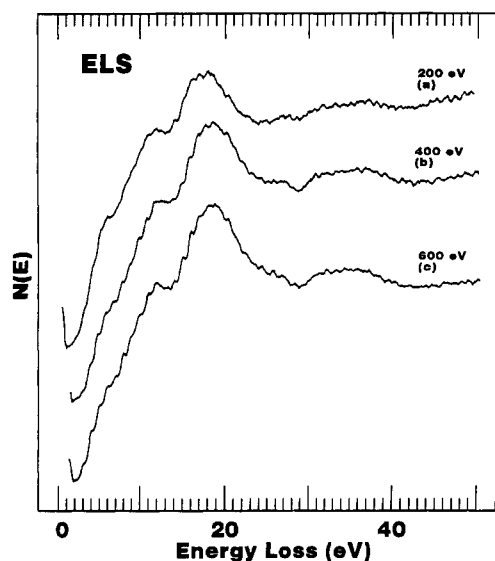


Figure 9. ELS spectra taken from the reoxidized tin oxide surface using primary beam energies of (a) 200 eV, (b) 400 eV, and (c) 600 eV.

in Figure 7–9 correspond to that of SnO. Furthermore, the absence of metallic plasmon features at 10 and 14 eV indicates that Sn metal is not present, so it cannot contribute to the 27 eV feature.

All of the features listed above appear in each of the ELS spectra in Figures 7–9, but the relative strengths vary with both pretreatment and depth. A most interesting fact is that the largest feature in all of these spectra is the 18-eV peak. This indicates that the near-surface regions of these tin oxide films consist predominantly of this transitional oxide phase. This is also the case in the previous ELS study of tin oxide (see the 200-eV spectrum shown in Figure 3 of ref 21), but it was not recognized at that time. In the ELS spectra obtained from that sample after annealing in vacuum at 750 °C, the energy loss moves from about 18 to 20 eV as the primary beam energy increases from 200 to 1500 eV. Also the ELS spectrum taken with a primary beam energy of 50 eV exhibits a predominant feature at 13 eV and a large peak at 27 eV. These data then indicate that the outermost atomic layers consist mostly of SnO, the region below this consists of the transitional oxide phase, and SnO<sub>2</sub> lies beneath the transitional oxide phase. The ELS data shown in Figures 7–9 are believed to indicate the presence of this same type of layered structure. However, the use of primary beam energies ranging from 200 to 600 eV limits the depths probed in this study primarily to the region consisting of the transitional oxide phase.

Neither the composition nor the structure of the transitional oxide phase is known. The ELS data obtained in previous studies<sup>21,25</sup> indicate that SnO<sub>2</sub> can decompose to SnO and that SnO can be oxidized to SnO<sub>2</sub> by passing through the transitional phase. Also, ESCA O-to-Sn atomic ratios of about 1.4 are usually obtained from tin oxide surfaces by assuming that the near-surface regions are homogeneous and using published sensitivity factors.<sup>50</sup> In this study they range from 1.37 to 1.45. This fact has not been understood previously and is consistent with the observation based on the ELS data that the near-surface

regions of tin oxide films consist primarily of this transitional oxide phase with a composition intermediate to that of SnO and SnO<sub>2</sub>. Handy et al.<sup>51</sup> have presented evidence for the presence of such a phase using electron diffraction to study alumina-supported tin. After treating in oxygen at 770 K, their diffraction patterns indicated the presence of both SnO<sub>2</sub> and SnO and another phase which they refer to as an intermediate tin oxidation state.

The ELS spectra obtained from the oxidized surface vary with increasing primary beam energy and, therefore, with increasing depth. The spectrum obtained using a 200-eV primary beam energy indicates the presence of the largest amount of SnO based on the relative signal strengths of the 13- and 18-eV features. Furthermore, it indicates that less SnO<sub>2</sub> is present in the near-surface region than further beneath the surface. These observations are consistent with the results obtained in previous studies.<sup>21,25</sup>

In Figure 8 the 27-eV feature is increased in spectra b and c with respect to the comparable spectra shown in Figure 7. This indicates that reduction of some of the transitional phase to SnO occurs beneath the surface during the reduction but not in the outermost surface region. Although subtle, it seems that the predominant feature may be slightly broadened at about 20 eV in the spectrum obtained using a 200-eV primary beam. This suggests that the SnO<sub>2</sub> concentration is increased in the very near surface region on the reduced surface. As discussed above in conjunction with the Auger data, the O enrichment at the surface is induced by the reductive chemical driving potential. With increasing depth the SnO<sub>2</sub> concentration increases as expected.

The ELS spectra obtained from the reoxidized surface and shown in Figure 9 exhibit very small 27-eV peaks, indicating that most of the SnO produced during reduction is oxidized to the transitional oxide. On the basis of the sizes of the 27-eV peaks, it seems that the ELS spectrum obtained using a 400-eV primary beam energy exhibits a larger SnO concentration. This implies that O does not penetrate deeply enough beneath the surface to oxidize the SnO at this depth. It also appears that transitional oxide is not oxidized to SnO<sub>2</sub> during the reoxidation. These facts yield insight as to why the surface O content of this surface is increased by only a small amount during the reoxidation according to AES.

The question of whether a metallic Sn overlayer exists at the outermost surface of tin oxide films has been considered in many studies. On the basis of the large inelastic background in the ISS spectra obtained from the oxidized and reoxidized surfaces, metallic Sn most likely is not present at these surfaces. However, the situation may be different for the reduced tin oxide surface. This surface has a high ion neutralization efficiency in ISS which is characteristic of a conductive surface. Furthermore, the ESCA Sn 3d spectrum obtained from the reduced surface (Figure 6a) exhibits a slight shoulder on the low binding energy side which may be due to metallic Sn. However, the ELS spectra obtained from this surface do not exhibit bulk- or surface-plasmon features characteristic of metallic Sn. Thus, the spectra obtained in this study yield inconclusive evidence regarding the formation of metallic Sn during the reduction of an oxidized tin oxide surface.

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### Summary

A polycrystalline tin oxide surface produced by spray hydrolysis was examined using AES, ISS, ESCA, and ELS after an oxidative treatment in 40 Torr of O<sub>2</sub> at 200 °C for 1 h, after a reductive treatment in 40 Torr of H<sub>2</sub> at 200 °C for 1 h and after another oxidative treatment in 40 Torr of O<sub>2</sub> at 200 °C for 1 h. The ELS data indicate that the region examined using primary beam energies between 200 and 600 eV consists predominantly of the transitional oxide phase and smaller amounts of SnO and SnO<sub>2</sub> regardless of the pretreatment.

Subtle but complex changes occur during the reductive and oxidative treatments. The techniques used probe different depths beneath the surface, and the various types of data demonstrate that the processes occur to varying extents at different depths. During the reduction, the ISS ion neutralization efficiency of the outermost atomic layer increases, indicating that the electrical conductivity of the surface increases. The Auger spectra also indicate a small increase in the O/Sn ratio after reduction. This is due to an increase in the subsurface O concentration under the influence of the reductive chemical driving potential. The ELS data indicate that a small amount of transitional oxide is converted to SnO which is consistent

with the small decrease in the O/Sn peak-area ratio exhibited by ESCA. Subtle peak-shape changes also occur in both the ESCA and AES data which are characteristic of the Sn chemical state changes.

The reoxidation causes significant changes in the ion neutralization efficiency and composition of the outermost atomic layer. The ISS background increases, and a large amount of O adsorbs. This O and reoxidized SnO result in an increased O/Sn AES signal. The ESCA O/Sn ratio also increases. The ELS data indicate that most of the SnO is reoxidized to transitional oxide, and this observation is consistent with ESCA Sn 3d peak-shape changes. The data obtained in this study provide a correlation between the electrical properties and O content of the near-surface region. Furthermore, the O profile and distribution of O-containing species in the near-surface region are very complex and depend upon the history of the particular tin oxide surface.

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