Photoemission study of In$_2$O$_3$ thin films on NiIn(0001): valence bands and indium 4d levels of a model for ITO

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Abstract

Ultraviolet photoemission has been used to study the growth of ultrathin films of In$_2$O$_3$ on NiIn(0001), a model material for technologically important indium–tin–oxide (ITO). He II excited In 4d spectra are shown to be an excellent monitor of the indium oxidation, which allows an interface layer to be discerned between the alloy and In$_2$O$_3$ film. The growth of the second layer begins before the completion of this layer. Valence band spectra show that the electronic structure of the films is consistent with photoemission data from bulk In$_2$O$_3$ and In$_2$O$_3$ grown on Si(111), and with published density of states calculations. From a comparison of He I and He II excited valence band spectra we suggest that the valence band contains a finite contribution from In 4d antibonding states, as seen in the published calculations. With the exception of oxygen plasma treated ITO, which also shows significant differences to the calculations, the In$_2$O$_3$/NiIn(0001) valence band spectra are in good agreement with spectra from differently treated ITO samples. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In a recent paper [1] we showed that ultrathin films of stochiometric In$_2$O$_3$ could be grown by the oxidation of NiIn(0001). Although no long range order is present, these films are flat and of the order 10 Å thick [1]. Such films can be readily studied using electron spectroscopy, unlike bulk In$_2$O$_3$ which is known to be a surface insulator [2], and can be reproducibly grown in ultrahigh vacuum (UHV). This makes them a good experimental model for surface studies of tin doped indium oxide, known as ITO (from indium–tin–oxide). ITO is the industrial standard transparent conductor, and is commonly used as the substrate for devices based on electroactive organic materials. Commercial ITO is not particularly suited to reproducible surface studies, as its properties vary wildly depending on the exact manufacturing process used [3], and also on the method of in situ surface preparation [4–7]. However, a number of photoemission studies of adsorbates on ITO are beginning to appear [4–9]. Surprisingly, given the technological importance of ITO, there have been very few studies of indium oxide itself, with photoemission studies being limited to an X-ray photoemission spectroscopy (XPS) study, using a flood gun to overcome charging problems, of bulk In$_2$O$_3$ [3], and UV photoemission spectroscopy (UPS) studies of films of In$_2$O$_3$ on Si(111) [10,11]. In addition, the complexity of the In$_2$O$_3$ unit cell

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makes full bandstructure calculations difficult, and as a result the only high-quality ab initio electronic structure calculations for \( \text{In}_2\text{O}_3 \) in the literature are the cluster calculations of Tanaka et al. [12].

In our previous paper [1] we reported that XPS could not be used to study the valence band electronic structure of the \( \text{In}_2\text{O}_3 \) films, as the signal was dominated by the Ni 3d band of the alloy substrate. There are two reasons for this. Firstly, the mean free path of valence electrons in XPS is relatively high, increasing the substrate signal, and secondly the photoionization cross-sections [13] heavily favour the Ni 3d over the O 2p level, which is the dominant contribution to the oxide valence band [12], as can be seen in Table 1. As a result the XPS valence band spectra are dominated by the substrate Ni d bands, with in fact no change detectable between the clean and fully oxidised sample [1]. For UPS the situation is quite different, as the technique is intrinsically much more surface sensitive than valence band XPS. In addition, as Table 1 shows, the photoionization cross-sections are much more favourable. Consequently, we have studied the growth of the oxide film on NiIn(0001) using angle resolved UPS (ARUPS), for comparison with results from ITO [4–6] and with those from \( \text{In}_2\text{O}_3 \) films on Si(111) [10,11], and the calculations of Tanaka et al. [12].

The In 4d levels in NiIn are at a binding energy of \( \sim 17 \text{ eV} \) [14], and are relatively narrow, with their linewidth in XPS being resolution limited [14]. These factors, combined with their relatively high cross-section (see Table 1), mean they can be studied using unmonochromated He II radiation. As can be seen in Fig. 1, their kinetic energy when excited by He II is greater than that of the Fermi edge excited by He I, and they are rather intense. We have therefore also studied the film growth using In 4d core level photoemission, with higher resolution than the XPS data reported earlier [1].

2. Experimental

The data were taken with a Vacuum Generators ADES 400 angle-resolving spectrometer, with a base pressure of \( 10^{-10} \text{ mbar} \). He I (h\( v = 21.2 \text{ eV} \)) or He II (40.8 eV) radiation from a discharge lamp were used, giving an overall energy resolution of 100 and 350 meV respectively, as determined from measurements of an Al Fermi edge. The NiIn(0001) sample was cleaned by cycles of Ar\( ^+ \) bombardment (2 kV, 0.7 Am\(^-2\) ) and annealing to 700 K. Full details of the preparation of the NiIn crystal are given elsewhere [14]. Oxygen was dosed by background exposure at room temperature, and all dosages are derived from uncorrected ion gauge readings.

3. Results and discussion

3.1. Indium 4d levels

Normal emission ARUPS spectra of the In 4d levels as a function of oxygen exposure are shown in Fig. 2, together with the results of a curve fitting procedure. The lineshapes used were Voigt func-

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Table 1

Selected photoionization cross-sections (Mb) [13]

<table>
<thead>
<tr>
<th>Level</th>
<th>He I (21.2 eV)</th>
<th>He II (40.8 eV)</th>
<th>He III (48.4 eV)</th>
<th>Mg K(\alpha) (1253.6 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In 4d</td>
<td>(&lt; 5\times 10^{-2})</td>
<td>(2.7\times 10^{-2})</td>
<td>(4.9\times 10^{-2})</td>
<td>(&lt; 5\times 10^{-2})</td>
</tr>
<tr>
<td>Ni 3d</td>
<td>4.0</td>
<td>8.4</td>
<td>–</td>
<td>(1\times 10^{-2})</td>
</tr>
<tr>
<td>O 2p</td>
<td>10.7</td>
<td>6.8</td>
<td>–</td>
<td>(5\times 10^{-2})</td>
</tr>
</tbody>
</table>

* Estimated from data in Ref. [13].
branching ratio. The unit cell of NiIn contains two distinct indium sites [14], but there is no indication of anything more than a single spin-orbit split doublet in the data for clean NiIn in Fig 2. The width of the 4d\(_{5/2}\) component was found to be 0.46 eV, compared to 0.36 eV for indium metal [15], and so it is possible that there are two unresolved contributions. A good fit would, of course, also be obtained if a further doublet were introduced. However, it seems unreasonable to add another doublet when one cannot be resolved, even as a shoulder. The parameters thus obtained were kept fixed when fitting the data for the oxygen-dosed surfaces.

Simple visual inspection shows that two additional doublets are required to fit the data for doses of 20 L and higher – a high binding energy component which dominates at high doses, and a lower binding energy component which causes the apparent asymmetry of the metallic peaks at low doses. The lineshape of the two oxygen-induced doublets were obtained from the fit of the 10 000 L dosed surface, constrained to have the correct branching ratio, and the same spin-orbit splitting (0.89 eV) as the metallic indium doublet. The oxygen induced peaks were not constrained to be symmetric, but in practice the asymmetries came out to be zero, or very close to zero. The spectra for doses between 20 and 1000 L were fitted using the lineshapes of the three doublets as already obtained, with the only variable parameters being their relative intensities, and that of the background. As can be seen from Fig. 2, this produced very good fits in all cases.

The binding energies and widths of the 4d\(_{5/2}\) contributions to the lineshapes of Fig. 2 are given in Table 2. The binding energy shift from the alloy component to the peak labelled oxide I, the dominant peak at high exposure, is

![Fig. 2. Normal emission ARUPS spectra (hν=40.8 eV), with curve fits, of the In 4d levels of NiIn(0001) as a function of oxygen exposure.](image)

<table>
<thead>
<tr>
<th>Component</th>
<th>Binding energy (eV)</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic</td>
<td>16.7</td>
<td>0.47</td>
</tr>
<tr>
<td>Oxide II</td>
<td>17.0</td>
<td>0.82</td>
</tr>
<tr>
<td>Oxide I</td>
<td>17.8</td>
<td>1.3</td>
</tr>
</tbody>
</table>
1.1 eV. This is the same value as the difference between XPS 3d binding energies of In$_2$O$_3$[3] and NiIn [14], indicating that the oxide I species is stoichiometric In$_2$O$_3$. The second oxide component, oxide II, is significant at low exposures, with binding energy intermediate to those of the alloy and the full oxide. Such a feature has also been observed for Al 2p spectra of Al$_2$O$_3$/NiAl(110) [16] and Ti 2p spectra of TiO$_2$/Ni$_{54}$Ti$_{46}$(110) [17].

In the former case it was attributed to an interfacial layer between the alloy and the oxide, while in the latter it was attributed to the presence of suboxides, TiO$_{1.5}$. As Table 2 shows, the width of the oxide II component for In$_2$O$_3$/NiIn(0001) is relatively narrow, being less than that of the In$_2$O$_3$ component. This suggests that it is due to a well defined species, rather than the presence of multiple suboxides. It would appear that the oxide II species is therefore due to an interface, that is, first oxygen-containing, layer, which may well be of indium monoxide.

The relative proportions of the three species, that is, metal, oxide and interface, determined from the curve fits of Fig. 2, are shown in Fig. 3. The proportion of interface, that is, oxide II, has a maximum at an exposure of 100 L, after which its proportion relative to the metallic contribution remains essentially constant, while both interface and metallic contributions decrease relative to the oxide I signal. This suggests that the interface layer is complete after 100 L exposure, after which further growth consists of the full oxide. This is consistent with the oxygen uptake curve obtained using Auger electron spectroscopy (AES) [1], which shows power law behaviour up to ~100 L, and exponential thereafter. A finite contribution from the full oxide, oxide I, is also required to fit the spectra from exposures from 20 to 100 L, before the completion of the interface layer. This implies that growth of the full oxide, the second layer and above, occurs before the completion of the first, interface, layer.

### 3.2. Valence band

Valence band ARUPS spectra as a function of oxygen dose are shown in Fig. 4. The spectrum of clean NiIn(0001) shows the double peak in the Ni 3d band characteristic of this alloy [18,19]. As the oxygen dose is increased the intensity of the Ni 3d band diminishes, but the lineshape remains unchanged, with the double peak clearly visible even in the spectrum of the fully oxidised (10 000 L dose) sample. This is further evidence, along with the unchanged Ni 2p XPS and MVV AES line-shapes upon oxidation [1], that the oxide film consists entirely of indium oxide. The visibility of the Ni 3d band in the spectrum of the oxidised sample also serves to demonstrate the ultrathin
nature of the oxide film, but unfortunately obscures any possible defect induced states between the valence band edge and the Fermi level. The spectra show a finite Fermi edge step at all exposures, but this is of course due to the underlying metallic substrate.

The O 2p derived band at ca. 4 eV binding energy is prominent in the spectra even after doses as low as 20 L, which represents a coverage of \( \sim 0.2 \) monolayers, assuming 100 L as the completion of the first, interface, layer. This occurs since the O 2p photoionization cross-section [13] for He I radiation (Table 1) is more than twice that of the Ni 3d, and Ni, of course, makes up only half the composition of the alloy.

Spectra of the In\(_2\)O\(_3\) film, taken using He I and He II radiation, are shown in Fig. 5. The shaded area in the He II spectrum corresponds to the In 4d levels excited by the He II \( \beta \) (48.8 eV) satellite line, which has a non-negligible intensity (\( \sim 10\% \)) compared to that of the main He II line. Table 1 shows that the photoionization cross-section for the O 2p in He II is 6.8 Mb, compared to 40 Mb for the In 4d using He II, so that taking into account the expected ratio of He II/He I\( \beta\) the cross-sections are very similar.

The full extent of the oxide valence band is not particularly apparent in the He I spectrum, which consists largely of an asymmetric peak at a binding energy of 4 eV. Using He II the full bandwidth becomes apparent. The valence band edge occurs at 3.2 eV, with the full bandwidth being \( \sim 6 \) eV, although this is difficult to determine accurately.
Table 3  Work function (eV) of the In$_2$O$_3$/NiIn(0001) films and those of various differently treated ITO samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Work fn.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$O$_3$/NiIn(0001)</td>
<td>4.54</td>
<td>this work</td>
</tr>
<tr>
<td>ITO solvents</td>
<td>4.5</td>
<td>[4]</td>
</tr>
<tr>
<td>ITO Ar$^+$</td>
<td>4.3</td>
<td>[4]</td>
</tr>
<tr>
<td>ITO Ar$^+$ + H$_2$O</td>
<td>4.2</td>
<td>[6]</td>
</tr>
<tr>
<td>ITO O plasma</td>
<td>4.4</td>
<td>[7]</td>
</tr>
<tr>
<td>ITO O plasma</td>
<td>4.7</td>
<td>[6]</td>
</tr>
<tr>
<td>ITO O plasma</td>
<td>4.96</td>
<td>[5]</td>
</tr>
<tr>
<td>ITO UV-ozone</td>
<td>4.58</td>
<td>[5]</td>
</tr>
<tr>
<td>ITO UV-ozone</td>
<td>4.75</td>
<td>[4]</td>
</tr>
</tbody>
</table>

Ar$^+$ bombarded material, on the other hand, do resemble the spectra of Fig. 5. Ar$^+$ bombardment is generally regarded as reducing In$_2$O$_3$ [2], but in this case [6] the authors report that the O:In ratio, as measured by XPS, was not affected by this treatment.

4. Conclusions

The In 4d level in He II excited UPS has been shown be an excellent monitor of oxide growth on NiIn(0001), as the resolution obtained was superior to that available in conventional XPS studies [1]. Oxide growth has been confirmed to proceed in two distinct regimes, with an interface layer, possibly of indium monoxide, formed between the alloy and the In$_2$O$_3$ film.

The valence band electronic structure of the resulting film is consistent with photoemission studies of both bulk In$_2$O$_3$ [2], and In$_2$O$_3$ films grown on Si(111) [10,11]. In addition, excellent agreement with the cluster calculations of Tanaka et al. [12] is obtained, with evidence found for the presence of In 4d states at the lower edge of the valence band as predicted theoretically [12]. The valence band spectra were found to be significantly different from those of oxygen plasma treated ITO, which are dominated by a peak at ~8 eV binding energy. This peak has no counterpart in our spectra, and none in the calculations [12], indicating that it is not characteristic of indium oxide, but due to the presence of an additional surface species. However, both the valence band lineshape, and the In 4d binding energies, of the In$_2$O$_3$/NiIn(0001) films are very similar to that of UV-ozone treated ITO, suggesting that the films are a good model for ITO surfaces after such treatment.

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References