Synchrotron radiation photoelectron spectroscopy study of ITO surface

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Abstract

Synchrotron radiation photoelectron spectroscopy (SRPES) has been applied to surface analysis of indium tin oxide (ITO) thin films. Several different components of In and Sn were observed at the clean ITO surface. By comparing the chemical compositions of the film before and after vacuum annealing, the contents of In_2O_{3-x} and Sn_3O_4 were found to be the major factors influencing the electrical conductivity and optical transparency of the film. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Because of its high conductivity and transparency, indium tin oxide (ITO) is widely used in many kinds of optoelectronic devices, including organic light-emitting devices (OLEDs) [1,2], solar cells [3,4], and panel liquid-crystal displays. Due to its efficient hole-injection capability, ITO is often used as the anode contact in OLEDs. Particular treatments of the substrates, which modify the surface potential and reduce the potential barrier at the interface, might affect the luminance and lifetime of the devices. Degradation studies and failure analyses of OLEDs have revealed that the operational instability of the devices is mainly caused by damage of ITO/organic-film interface, which results partly from the Joule effect [5,6]. It has also been found that after some kinds of treatment to the ITO surface, device performance can be enhanced, but how the ITO surface properties affect device performance has yet to be fully understood [7–14]. The surface compositions and the chemical shifts related to the In and Sn oxides are important parameters in governing device performance. However, it is difficult to accurately distinguish the different chemical states of various In and Sn oxides using conventional X-ray photoelectron spectroscopy (XPS) [15,16] and Auger electron spectroscopy (AES) [9,17] due to the small chemical shifts that occur. In contrast, synchrotron radiation photoelectron spectroscopy (SRPES) can

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provide high surface sensitivity and energy resolution and should be a better method for studying the chemical states of the ITO surface. To the best of our knowledge, there has been no SRPES analysis in the literature concerning the chemical states of the ITO surfaces thus far.

In this work, we have analyzed the chemical states of In and Sn at the ITO surface and found the existence of three chemical states for In and Sn each. The samples were annealed in a vacuum at 450°C, after which In was found to be further oxidized and more Sn_3O_4 appeared. Accompanying the changes of the components, the resistance and transparency of ITO were also changed after annealing, indicating that the contents of In_2O_{3-x} and Sn_3O_4 were the major factors affecting the ITO surface properties.

2. Experiments

The samples used in the experiment were commercially available ITO/glass substrates. The thickness and sheet resistance of the ITO layer were about 1 μm and 200 $\Omega/\square$, respectively. The samples were ultrasonically cleaned by sequential rinses in acetone, ethanol and de-ionized water (DIW) for 10 min each, followed by drying in flowing nitrogen. Then they were loaded into the ultra-high vacuum system of SRPES.

The SRPES measurements were performed at the National Synchrotron Radiation Laboratory, Hefei. Base pressure of the analysis chamber was lower than 5×10^{-8} Pa. Photon energy of 90 eV was used, highly efficient and surface sensitive for In 4d and Sn 4d measurements. In order to monitor the variation in oxygen content, which was not available at the utilized beam line, conventional XPS spectra were also measured. Al Kα-line with a photon energy of 1486.6 eV was used as X-ray source in the XPS study. In addition, resistivity and transparency were measured, too, before and after annealing of the samples.

3. Results and discussion

SRPES spectra of In 4d and Sn 4d core levels for the as treated and annealed ITO surfaces are shown

in Figs. 1 and 2, respectively. All peaks are curve-fitted with fixed spin-orbit splitting shifts and $d_{5/2}/d_{3/2}$ branching ratios. They are, respectively, 0.85 eV and 1.5 for In 4d, 1.00 eV and 1.5 for Sn 4d [18]. The binding energies referred to below are the values of the $d_{5/2}$ levels with respect to the valence-band maximum of the clean ITO surface.

In 4d spectra of the samples as treated, post-annealed at 450°C and 560°C for 10 min each are shown in Fig. 1a, b and c, respectively. The peaks in Fig. 1a and b can be fitted by three overlapped components at the binding energies of 17.7, 18.2 and 18.8 eV, respectively. In addition to the three overlapped components, there is a new component with a binding energy of 16.9 eV in Fig. 1c. This new component is surely related to the metallic In state, resulting from decomposition of In oxides upon annealing above 500°C. Despite that, the oxide states still existed at the annealed surface and a mirror-like surface could also be observed by naked eyes. With
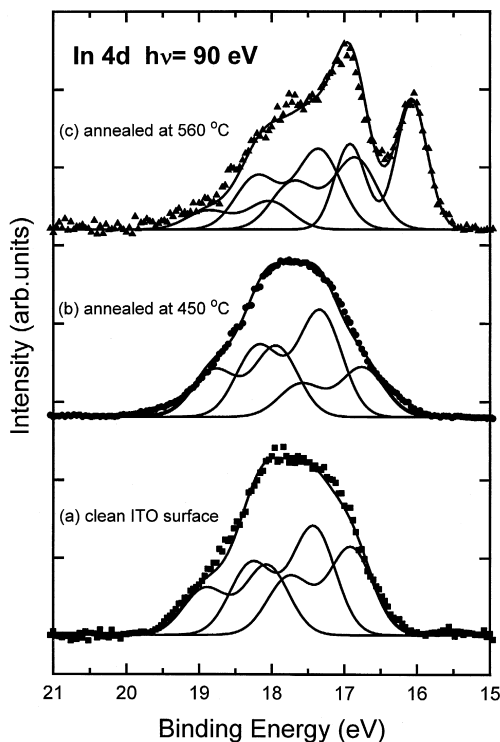

Fig. 1. SRPES spectra for In 4d of as treated and post-annealed (in UHV) ITO surfaces.

Sn 4d hν=90 eV

(b) annealed at 450 °C

(a) clean ITO surface

Intensity (arb.units)
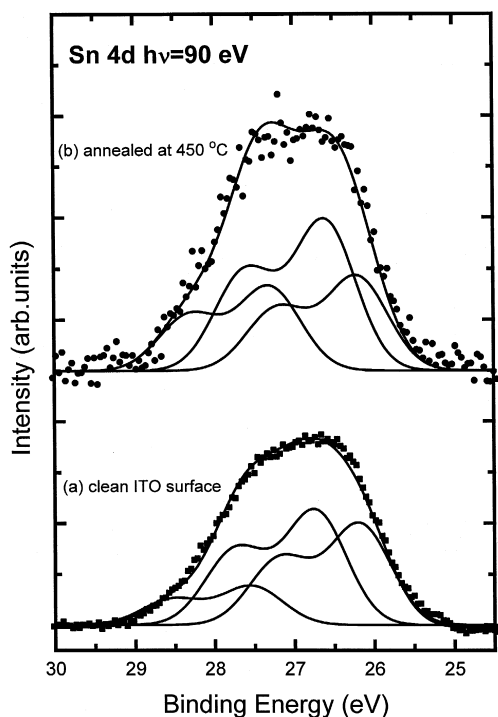
Binding Energy (eV)

Fig. 2. SRPES spectra for Sn 4d of as treated and post-annealed (in UHV) ITO surfaces.

respect to the metallic In state, the other three components have the chemical shifts of 0.8, 1.3 and 1.9 eV, respectively. Since it has been found that In 4d core levels for In_2O_3 and In–S bond states have the same chemical shift with respect to that of the In–P bond state [19], the 1.3 eV-shifted (binding energy of 18.2 eV) component found in the present experiment can be assigned to the In_2O_3 state. The same shift was found to be present for In–S bond states. This assignment on In_2O_3 is consistent with the fact that the main component in ITO is In_2O_3. The component with the chemical shift of 1.9 eV (binding energy of 18.8 eV) might relate to the In peroxide state formed during the growth of ITO. In_2O_3 crystal has a structure of cubic bixbyite, where O^{2-} ions occupy the interstices of a face-centered cubic In^{3+} ion array. In ITO, however, since the O^{2-} ions are not orderly arrayed in totality, there might be some oxygen vacancies, which leads to the presence of In_2O_{3-x}. We cannot accurately give value x yet

with the present data. Here, the lowest shift of 0.8 eV (binding energy of 17.7 eV) can be assigned to In_2O_{3-x}. Comparing Fig. 1a with Fig. 1b, one may find that the relative intensity of In_2O_{3-x} is reduced after the samples have been annealed at 450°C, while the intensities of In_2O_3 and peroxide do not change much.

Fig. 2a and b show the Sn 4d spectra of the as treated ITO sample and the sample annealed at 450°C in the vacuum chamber, respectively. Three peaks are present in each spectrum, with binding energies at 26.1, 26.6 and 27.3 eV, respectively. The main peak with the binding energy of 26.6 eV is obviously related to SnO_2, the main state of Sn in ITO. Now, the question is what the other two peaks are. Similar to other Group IV elements Pb and Ge, Sn has the character of semi-metal which may not follow the normal chemical-shift rule for metals that the higher the valence state, the higher the binding energy. Early analyses using normal XPS gave different results [15,16,20]. With a monochromatic XPS, Ashley Talor et al. [16] recently found that the binding energy of Sn $3d_{5/2}$ in SnO_2 was 0.5 eV higher than in SnO, whereas Fan and Goodenough [15] reported opposite assignments of the two in an earlier study. Here, we follow the former and suggest that the peak, with the binding energy of 26.1 eV, is related to SnO, another Sn-containing component conventionally existing in ITO. Fan and Goodenough [15] also found that, besides SnO and SnO_2, there was a third state of Sn oxide, Sn_3O_4, whose content could influence the transparency of ITO significantly. Such a species is often formed during the deposition of Sn oxides in vacuum [21]. We tentatively attribute the lowest peak with the binding energy of 27.3 eV to Sn_3O_4. One can clearly see in Fig. 2 that the intensity of this peak was increased after annealing. Meanwhile, the transparency of the sample was reduced, confirming that our assignment of the peak is consistent with what was found previously.

From the XPS intensity measurements, we found that the content of oxygen was slightly reduced after annealing, while the component ratio of In to Sn did not change significantly. That means there should exist oxygen transfer from Sn oxides to In oxides during the annealing process, as higher In oxide forms became dominant after annealing. This is confirmed by the evolution of the peak intensities shown

in Fig. 2: accompanying the increase in the intensity ratio of In_2O_3 to In_2O_{3-x} from 1.2:1 to 2.2:1, the ratio of SnO_2 to Sn_3O_4 decreases from 3.0:1 to 1.7:1. In other words, the reduction of SnO_2 to Sn_3O_4 provides the oxygen needed for the oxidation of In_2O_{3-x} to In_2O_3.

It has also been observed that the resistivity of ITO increased after annealing. For 450°C annealing, the resistivity increased from 13.3 to 41.0 Ω cm. Since the resistivity measured is essentially a bulk-like property of the film whereas the chemical composition acquired by photoelectron spectroscopy is surface sensitive, it is of interest to examine if one can link them properly. It is concluded that there is such a link in two aspects. First, the decrease in the content of In_2O_{3-x}, i.e., the decrease in the content of oxygen vacancies, can cause the increase of resistance. In In_2O_{3-x}, the In^{3+}-5s around each O vacancy lacks one covalent bond, which would form a shallow donor state that can trap two electrons. High O vacancies (i.e., large x) can even produce a degenerate semiconductor [15]. After the annealing, along with further oxidation of In, less O vacancies are present, which can increase the resistance. Second, the decrease in the amount of SnO_2, which also contributes to the conductivity of ITO, will also increase the resistance. Actually, the fact that no extra oxygen source is needed for the further oxidation of In_2O_{3-x} hints that the aforementioned oxidation–reduction process may occur not only at the surface but also in the bulk of the ITO film.

4. Conclusion

The study of chemical states of ITO surfaces by SRPES shows that the forms of the In and Sn oxides in an ITO film will complementarily change after vacuum annealing. The increase of ITO resistivity results mainly from further oxidation of In_2O_{3-x} and reduction SnO_2. The appearance of more Sn_3O_4 after annealing at 450°C can cause lower transparency of the ITO film.

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