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Effects of Oxygen Plasma Treatments on the Work Function of Indium Tin Oxide Studied by *in-situ* Photoelectron Spectroscopy

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Using UV and X-ray photoelectron spectroscopy (UPS & XPS), we have studied the work function (WF) evolution and chemical changes of an indium-tin-oxide (ITO) surface after a series of *in-situ* oxygen plasma treatments (OPTs). We took special care not to damage the sample's surface with OPT by employing the weakest possible plasma conditions. Even after such gentle OPT the WF of ITO dramatically increased up to 6.6 eV after about 300 s of OPT. The carbon contamination at the surface was completely removed after only 40 s of the gentle OPT. However, in contrast to similar studies, the compositions and the chemical states of In, Sn, and O at the ITO surface showed only minimal changes as confirmed by XPS core-level peak analyses.

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I. INTRODUCTION

Indium tin oxide (ITO) is the most widely used transparent conducting material. It has been used from the early days of organic light-emitting diodes (OLEDs) [1], organic photovoltaic (OPV) cells [2], and other flat-panel [3] and liquid-crystal displays. Despite much effort to develop alternative materials, ITO will most likely continue to be popular for years to come. A recent review article is a good guide to an understanding of the properties and the issues involving this class of materials [4]. While the optical transmittance and the electrical resistance are important performance metrics of ITO, the work function (WF) is also an extremely critical parameter [5] that determines the performance of many optoelectronic devices such as OLEDs and OPV cells, where the energy level alignment between the Fermi level of ITO and the molecular orbitals of the organic semiconductors is a key to efficient charge-carrier injection and extraction.

When it is used as a hole injection electrode in OLEDs, performance enhancements were reported when UV-ozone treatment or O_2 plasma treatment (OPT) was performed on the ITO surfaces [1,6–8]. Other treatments, such as insertion of a thin transition-metal-oxide layer of high WF [9] or UV radiation treatment in dichlorobenzene, also resulted in an increased ITO WF and concomitant improvements in OLED performances [10,11].

In general, carbon and other contaminats accumulate on the surfaces when ITO substrates are stored in ambient conditions. These contaminats tend to reduce the surface WF, therefore, OPT or UV-ozone treatment increases the WF by removing them. An additional WF increase upon further plasma treatment was reported and attributed variously to increased oxygen contents [12,13] or to reduced surface segregation of Sn [7,14]. Once the WF had been increased after the OPT, numerous reports were published on WF reduction when the sample surface was exposed to various ambient conditions [15] or UV irradiations [16]. Most investigations on the WF variation of ITO were performed *ex situ*, meaning that the samples were exposed to air between the OPT and the WF measurements, during which varying degrees of contamination might accumulate again on the surface and affect the measured WF values. In addition, most OPT studies did not pay much attention to the plasma damage that might have been caused by intense or prolonged plasma treatments.

Here, we have investigated the influence of OPT on ITO surfaces by using ultraviolet electron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). Unlike most previous investigations, we performed all the experiments *in-situ*. Samples were never exposed to ambient conditions between the OPT and the UPS/XPS measurements. We also paid close attention to preventing possible plasma-induced damage. The samples were moved into a plasma region only after the power of the plasma had been adjusted to the minimum sustainable level. Under these gentle OPT conditions, we found that the ITO WF could be increased to a value as high as 6.6 eV after just 300 s. The gentle OPT was found to cause minimal change in the chemical states of ITO. The

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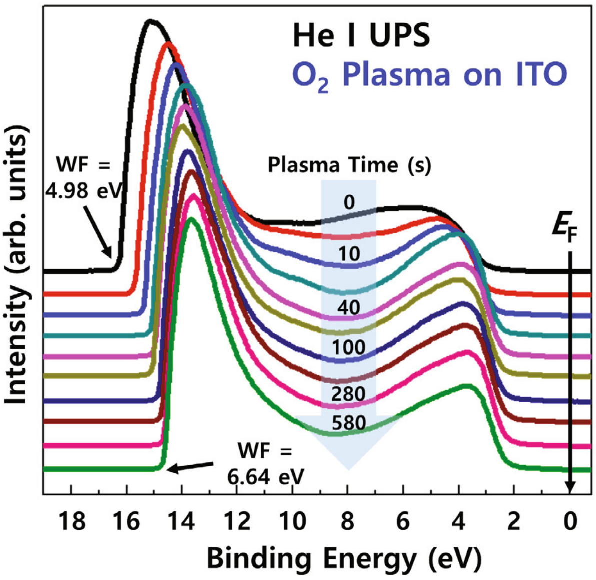

Fig. 1. (Color online) UPS spectral evolution of the ITO surface after a series of OPTs. The work function increase from 4.98 to 6.64 eV after an 880-s gentle OPT, as indicated. A shift in the spectral weight from a binding energy region of 6 - 8 eV to 2 - 4 eV is also observed.

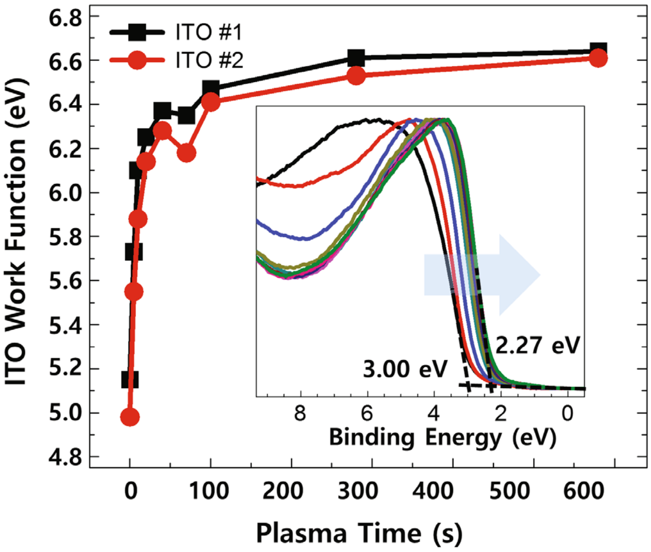

Fig. 2. (Color online) Work function evolution of typical ITO surfaces as a function OPT time. Most of the WF change happened during the first 100 s. The inset shows enlarged and normalized UPS spectra emphasizing the shifts of the valence band edges from 3.00 eV for as-received ITO to 2.27 eV for plasma-treated ITOs, as indicated by the dashed lines.

relative compositions of the three elements (In, Sn, and O) were almost unchanged before and after the OPT if we disregarded the presence of carbon contamination. We believe the high WF and the minimal chemical disturbance of ITO after our OPT are direct results of the gentle nature of the treatment, which effectively removed the surface contamination while causing no further damage to or alteration in the surface species.

II. EXPERIMENTS

About 100-nm-thick ITO films coated on 1.0 × 1.0 cm^2 glass substrates were used for the experiments. Typical surface resistances of the ITO film were 20 - 30 Ω/□. UPS and XPS measurements were carried out in an ultra-high-vacuum analysis chamber with base pressure of 1×10^{-9} Torr. Photoelectron spectra were recorded using a modified KRATOS AXIS165 system with a He I (21.2 eV) source for UPS and a Mg K_α (1253.6 eV) source for XPS. A sample bias of −10 V was applied when the UPS spectra were recorded to clearly distinguish the secondary electron cut-off positions. Energy resolutions were approximately 0.1 eV and 1.0 eV for UPS and XPS, respectively. No sample temperature control was attempted during the experiments.

All the OPTs were performed in a separate preparation chamber. We used a minimum sustainable plasma rf power of typically less than 1.0 W at 13.6 MHz into 41-mm-diameter circular electrodes, resulting in a power density below 0.1 W/cm^2. The O_2 pressure during the OPT was 8.0×10^{-2} Torr, and the DC bias was approximately −50 V. Special care was taken to minimize possible plasma ignition shock. The plasma was initially turned on without the ITO sample on the electrode, and the rf power was adjusted to the lowest level for a sustained plasma. The ignition power level was typically much higher than the minimum steady-state power level. The grounded ITO sample was introduced to the plasma region only after the plasma was stabilized at the minimum power level. We believe possible surface damage due to the energetic particles at the time of plasma ignition could be avoided in this way. The OPT preparation chamber was connected to the analysis chamber for UPS and XPS so that samples could be transfered between the two chambers without breaking the vacuum. This feature enabled us to focus on the effects of OPT and to exclude other factors that might otherwise affect the ITO surface.

III. RESULTS AND DISCUSSION

Figure 1 shows the evolution of valence band spectra as a function of the OPT time obtained by using UPS, and Fig. 2 shows the variation in the WF value with increasing OPT time for a couple of typical ITO samples. As indicated in Fig. 1, the WF values were determined by the secondary electron cut-off positions in the UPS spectra [5]. Starting from the top spectrum for as-received ITO, the OPT time was gradually increased up to 880 s in Fig. 1. The blue semitransparent arrow indicates the direction of increasing OPT time, which also applies to all subsequent spectral figures. The overall shape of the UPS spectrum did not show a dramatic change although a clear spectral weight shift from the binding energy (BE) region of $6 - 8$ eV to $2 - 4$ eV was seen. Figure 2 clearly shows that most of the work function increase happened within the first 100 s although the increasing trend continued slowly afterwards, reaching 6.64 eV after 580 s of OPT. This rapid initial increase of the WF suggests that it is mainly due to the removal of carbon contamination by the OPT, as seen in Fig. 3(d), where the C 1s XPS peak intensity becomes negligible after just 40 s of OPT. The spectral weight shift and the detailed change near the valence-band region shown in the inset of Fig. 2 correlate well with the WF increase in Fig. 2. The amount of valence band edge shift was 0.72 eV (from 3.00 eV for as-received ITO to 2.27 eV for OPT ITO), and most of the change happened within 100 s, which is again correlated with the removal of surface carbon contamination.

ITO is generally considered as an n-type degenerate semiconductor where the Fermi level is at or above the conduction-band edge [17]. The observed shift of the valence-band edge in the inset of Fig. 2 during the OPT might be due to a compensation of n-type doping at the surface [18]. The WF increase has been suggested to be due to this movement of the Fermi level inside the band gap according to the doping [17, 19]. However, the valence band edge shift is about 0.72 eV, which is far less than the observed WF increase. In addition, the shift observed here is not consistent with the measured XPS peak shifts, which will be discussed later. Furthermore, the initial shift of the valence-band edge is dominated by the spectral weight shift caused by carbon removal, which obscured the effect of possible surface doping compensation.

The WF increase of more than 1.6 eV by OPT alone is quite significant. Our by-no-means comprehensive literature search revealed only a single paper reporting a WF increase larger than ours, which is also a result of *in-situ* OPT and a UPS study [13]. Most previous studies seem to agree that the removal of carbon contamination from the surface is largely responsible for the WF increase. However, these studies also show that some residual carbon contamination remains on the ITO surface even after the OPT either because the contamination was not completely removed in the OPT process or the surface was re-contaminated by exposure to air during the transfer process. Therefore, *in-situ* studies like ours are essential to assure a complete removal of contamination and to unambiguously discern the effect of it on the WF and the surface chemistry.

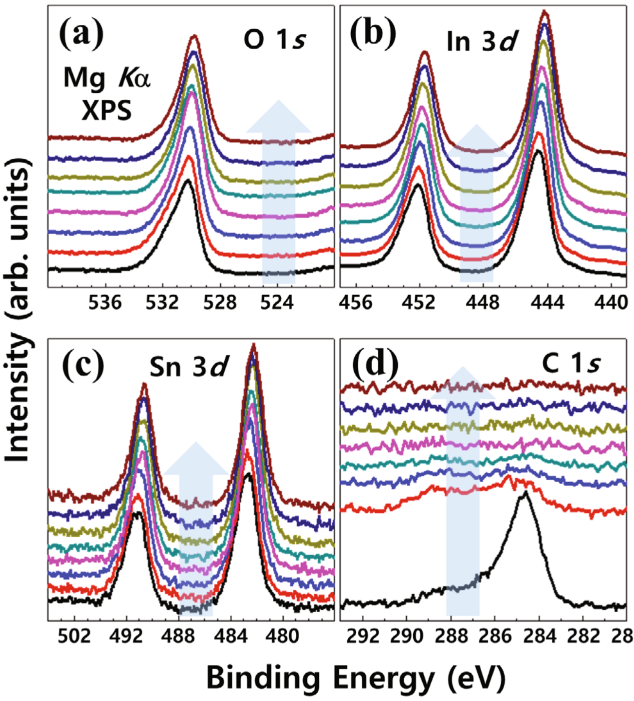

Fig. 3. (Color online) Evolution of core-level XPS peaks during the OPT. The semitransparent blue arrows indicate increasing OPT time. The spectra corresponds to 0-, 5-, 10-, 20-, 40-, 100-, 280-, and 580-s OPTs. While the C 1s peak in (d) has almost completely disappeared after 40 s, the other peaks in (a)-(c) show no dramatic changes, except for a rigid peak shift of about 0.4 eV toward the low-BE direction.

Figure 3 shows the evolution of the core level XPS peaks during the OPT. The semitransparent blue arrows again indicate the direction of increasing OPT time. From bottom to top, each spectrum corresponds to 0, 5, 10, 20, 40, 100, 280, and 580 s, respectively. A dramatic change was observed only in C 1s peak in Fig. 3(d) where the peak disappeared almost completely after 40 s as the carbon mostly exists as contaminations on the surface of the as-received samples. As pointed out earlier, this removal of carbons from the ITO surface correlates well with the WF change. For other XPS peaks, no dramatic peak shape or position change caused by the OPT was observed. Only small BE shifts of about 0.4 eV toward the low BE direction were observed for all the peaks in Figs. 3(a)-(c). This uniform shift of XPS peaks suggests that it is mainly due to the shift of the Fermi level caused by changes in surface doping, as mentioned earlier. The contribution of OPT-driven doping compensation to the WF shift is about 0.4 eV, which is much less than the apparent valence-band edge shift of 0.72 eV seen in the inset of Fig. 2 [19].

We calculated the surface concentrations of each element from XPS the peak intensities. The results are summarized in Table 1. The surface of the as-received ITO sample contained about 16 at.% of carbon, which decreased rapidly with increasing OPT time and became negligible after 40 s. Nominal oxygen-saturated ITO has concentrations of 18, 74, and 8% in weight of O, In, and Sn, which correspond to 61.2, 35.1, and 3.67 at.%, respectively. This is equivalent to a mixture of 90% In_2O_3 and 10% SnO_2 or 9.5% Sn doping of pure In_2O_3. Comparing these nominal values with the ones in Table 1 after carbon was removed, we found they were surpris-

Table 1. Evolution of the atomic concentrations of the surface species of ITO as a function of the OPT time. The removal of carbon contamination is complete after 40 s, and no significant change was observed after that.

Times (s)	O (%)	In (%)	Sn (%)	C (%)
0	51.6	29.2	3.03	16.16
5	56.1	30.9	3.25	9.72
10	57.9	34.0	3.45	4.53
20	59.0	34.8	3.64	2.54
40	64.0	32.5	3.44	0.00
100	60.7	35.5	3.81	0.00
280	60.9	35.4	3.68	0.00
580	60.7	35.5	3.77	0.00

ingly close. The gentle nature of our OPT procedure seems to have left the ITO surface almost intact while effectively removing the contamination that reduces the WF. Furthermore, even before the surface carbon was removed, the concentrations of the other three elements were nearly the same as those after its removal. For example, if one ignores the carbon, as-received ITO showed concentrations of 61.6, 34.8, and 3.61% for O, In, and Sn, respectively, while they were 60.6, 35.7, and 3.74% after 20 s. These values are not greatly different from the nominal ones or those obtained after the carbon removal, which is clearly an indication that our gentle OPT did not alter the original concentrations of ITO. More than 100 s of OPT did not change the concentration of any element significantly.

Another *in-situ* OPT study [13] showed that the carbon contamination was completely removed after 25 s of the plasma treatment, in agreement with our results. However, their concentration estimates for the other elements showed that the amount of oxygen increased by about 4 at.% after the OPT and that of indium decreased by a similar amount. The authors concluded that the WF increase was facilitated first by the removal of carbon and was then augmented by the filling of oxygen vacancies by OPT. However, our analysis showed that the concentrations of oxygen and indium changed by less than 0.4% during the course of a more than 1.6-eV WF increase. Certainly, the gentle nature of our OPT played a role here, but this also suggests that the increase in the total oxygen concentration may not be the main cause of the WF increase.

To further investigate the effects of the OPT on the chemical state of species at the ITO surfaces, we performed least-squares peak deconvolution procedures for all the XPS peaks at the various stages of OPT. We employed full Voigt functions for synthetic peaks for the fitting after Shirley background subtraction had been applied. The Gaussian width of the Voigt functions was fixed at 1.0 eV, which is the estimated energy resolution of our XPS instruments. The Lorentzian widths were varied from 0.61 to 0.84 eV for the O 1s peaks and from 0.77 to 0.94 eV for the In 3$d_{5/2}$ peak components. Figure 4 shows an example of such a peak fitting for the O 1s and the In 3$d_{5/2}$ peaks. To see the maximum difference caused by the OPT, we compared peaks for the as-received ITO with those after 580 s of OPT.

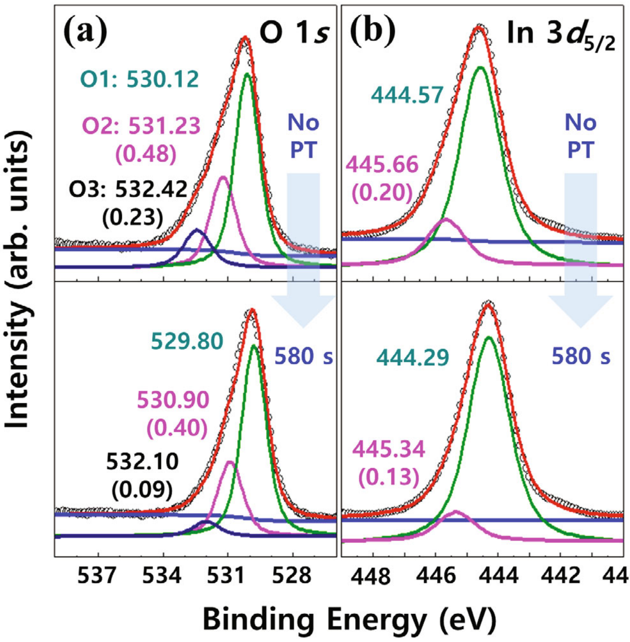

Fig. 4. (Color online) Least-squares fitting decompositions for the (a) O 1s and the (b) In 3$d_{5/2}$ core level peaks. The top panels show the fitting results for the as-received ITO sample, and the bottom panels are those after a 580-s OPT. The peak component labeled as O1 in (a) was initially at 530.12 eV and shifted to 529.80 eV after the OPT. Similarly, O2 shifted from 531.23 to 530.90 eV and O3 from 532.42 to 532.10 eV. For In 3$d_{5/2}$ peaks in (b), the In1 component shifted from 444.57 to 444.29 eV and the In2 component from 445.66 to 445.34 eV. In addition, the intensity ratios of the peak components are shown in the parentheses. $I_{O2}/I_{O1} = 0.48$ and $I_{O3}/I_{O1} = 0.23$ for the as-received sample and changed to 0.40 and 0.09 after the OPT, respectively. Similarly, I_{In2}/I_{In1} changed from 0.20 to 0.13.

For both the O 1s and the In 3$d_{5/2}$ peaks in Fig. 4, the intensities of higher BE components are seen to be generally diminished after the OPT. The positions of the three O 1s peak components O1, O2, and O3 are 530.12, 531.23, and 532.42 eV, respectively before the OPT and were shifted to 529.80, 530.90, and 532.10 eV after the OPT. The positions of the two In 3$d_{5/2}$ peak components In1 and In2 are 444.57 and 445.66 eV, respectively before the OPT and are shifted to 444.29 and 445.34 eV after the OPT. For all the peaks shown in Fig. 4, the peak shifts were toward the low BE direction by 0.3 - 0.4 eV after the OPT. The relative intensity of O3 component decreased from 23% to 9% after the OPT, indicating that it is mainly associated with loosely-bound carbon contamination. The O2 component decreased only slightly from 48% to 40%. This has two origins, namely, oxygens from C-O contamination and oxygens bonded to In and Sn at the surface [20]. This assignment is consistent with the slight decrease in this component with the OPT, which may have removed the C-O contamination.

The In2 component in In $3d_{5/2}$ peak at 445.66 eV is associated with the many-body screening effect of core holes in the process of photoionization. The separation of this satellite peak from the In1 main peak is about 1.1 eV, which is consistent with a calculation based on 10% Sn doping. However, the intensity ratio between 0.14 and 0.2 is more consistent for In_2O_3 with no Sn doping [17]. A higher doping concentration reduces the relative intensity of the O2 component, which was observed in Fig. 4(b). However, the amount of Sn increased only slightly when compared with the concentration before carbon removal. These inconsistent results call for further detailed study of the interplay between the doping concentration and the associated satellite features in ITO.

Regardless of the various spectral features observed, our data indicate that the WF increase is primarily due to the removal of carbon and related contamination from the ITO surface. Furthermore, the concentrations of atoms near the surface did not change meaningfully after the dramatic WF increase. We believe these results suggest that the increased oxygen at the surface, which is usually presented as either evidence for oxygen vacancy filling [13] or for the formation fragile O-O bonds [15] and is associated dipoles reported in the literature, is not an essential requirement for a large WF increase. Rather, the complete removal of surface contamination by our gentle OPT and the resulting restoration of In-O bonding and associated dipoles are sufficient for achieving the very high WF we demonstrated.

IV. CONCLUSIONS

We used UPS & XPS to study the WF evolution and chemical changes of an ITO surface after a series of *in-situ* oxygen plasma treatments. When a very gentle plasma treatment was applied, the surface concentrations of the elements were preserved while the carbon contamination was completely removed. This resulted in a dramatic WF increase up to 6.6 eV after only a 300-s OPT. We conclude that the observed WF increase is primarily due to the restoration of a clean ITO surface without any excess oxygen or to the reduced tin concentration caused by the plasma treatments.

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