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Work function measurements on indium tin oxide films

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Abstract

We determined the work function of indium tin oxide (ITO) films on glass substrates using photoemission spectroscopy (PES). The ITO coated glass substrates were chemically cleaned ex-situ, oxygen plasma treated ex-situ, or sputtered in-situ. Our results suggest that the performance of ultraviolet photoemission spectroscopy (UPS) measurements can induce a significant work function reduction on the order of 0.4–0.5 eV, on ex-situ chemically and oxygen-plasma treated ITO samples. This was demonstrated by the use of low intensity X-ray photoemission spectroscopy (XPS) work function measurements before and after the UPS measurements were carried out. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Work function; Ultraviolet photoemission spectroscopy (UPS); X-ray photoemission spectroscopy (XPS); Organic light emitting diodes (OLED)

1. Introduction

Recent commercialization of organic light-emitting diodes has sparked significant interest in the electronic structure of the interfaces between organic and electrode materials. Indium tin oxide (ITO) is usually used as a high work function electrode since it combines good conductivity and transparency in the visible range. High work function electrodes are used to inject holes into the organic materials, hence as high as possible work function values are desirable. A number of recent studies have been focusing on determining the work function of commercially

available and surface modified ITO substrates by using ultraviolet photoemission spectroscopy (UPS) [1–6] and Kelvin probe (KP) [7]. Our experiments focus on the methodology of work function measurements using photoelectron spectroscopy (PES) and demonstrate that it is possible to induce significant work function reduction by exposing ITO to the UV light used in UPS measurements. These results potentially explain the differences seen between UPS and KP work function measurements [7].

2. Experimental

The photoemission experiments were performed in a commercially available Omicron XP ultrahigh vacuum (UHV) apparatus. The analysis chamber was equipped with an Omicron HIS13 high current UV lamp, a SPECS RQ20/38 retractable X-ray gun and

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a VSW EA 125 electron energy analyzer. The base pressure of the analysis chamber was $\sim 5 \times 10^{-11}$ mbar. Electrical contact to the ITO surfaces was established by a small dot of silver paste at one side of the sample. The 15-mm diameter samples were checked for good Ohmic contact along the fringes. Sample sputtering was carried out using a SPECS PU-IQE 11 sputter gun. The work function measurements were carried out using UPS (He I, 1-mm circular entrance slit, 5-eV pass energy) and X-ray photoemission spectroscopy (XPS) (Mg K α , 12 kV/5 mA). The XPS spectra were measured at the same analyzer settings used for the UPS measurements. The XPS spectra were measured with the X-ray gun in 'stand by mode' and retracted by 50 mm from the regular measurement position in order to reduce the photon flux and minimize the presence of stray-electrons photoemitted from the Al bremsstrahlung filter window and Cu nozzle of the gun. A -5 -V bias was applied to the sample during the measurements in order to distinguish between the analyzer and the sample cut-offs. The spectrometer was calibrated to yield the standard values [8] of 75.13 eV for the Cu3p and 932.66 eV for the Cu2p(3/2) binding energy positions on an Ar⁺ sputtered Cu substrate. All spectra are shown in original kinetic energies corrected for the applied bias and analyzer work function. This allowed determination of the work function values directly from the spectra by fitting straight lines into their low kinetic energy cut-off and determining the intersect with the base line of the spectra [9]. To account for the analyzer broadening (± 0.1 eV [10]) 0.1 eV was added to the work function values. All data evaluation was carried out using Igor Pro software (Wavemetrics).

The ITO coated glass substrates were obtained from Planar America. One sample was sonicated in deionized water, acetone, iso-propanol and finally in boiling iso-propanol (labeled 'plain ITO' in the figures below). The second sample (labeled 'ashed ITO') was cleaned by hand rubbing using a detergent solution. It was then sonicated (5 min each) in deionized water, acetone and in iso-propanol, dried in iso-propanol vapor and treated in a microwave generated oxygen plasma (4 mbar, 5 min). The third sample (labeled 'sputtered ITO') was sputtered in-situ for 10 min. The sputtering conditions were 2 kV, 10^{-5} mbar Ar pressure, and 13- μ A emission current. The gun to sample distance was ~ 10 cm.

3. Results

Fig. 1 shows the low kinetic energy cut-off measured on the 'plain ITO' and 'ashed ITO' samples by XPS and UPS. The spectra were normalized, which is necessary since the UP spectra have an ~ 2000 times higher intensity than the XP spectra. It should be noted that the cut-off feature is formed by inelastically scattered photoelectrons, i.e. the excitation energy has no significant influence on the cut-off position. Therefore, the location of the cut-off is only determined by the sample work function, allowing its measurement at the same location with any photon energy exceeding the sample work function.

The XPS measurements were initially conducted prior to the UPS measurements and are shown as the bottom spectra in Fig. 1. The weak feature at the low kinetic energy side of the cut-offs is most likely a result from stray electrons coming from the Al window and Cu nozzle of the X-ray gun, which have a lower work function than the ITO coated glass substrate. The UPS spectra are depicted in the middle of Fig. 1 and indicate a strong shift to lower kinetic energy, corresponding to a reduction of the work function. The work function change during UPS measurements occurred immediately and no gradual change could be observed by reducing the exposure time to the possible minimum (1 min was the shortest possible exposure time required for a measurement by quickly positioning the lamp spot on the sample and running a scan across the low kinetic energy cut-off spectral region). The XPS spectra, taken after the UPS measurements and shown at the top of Fig. 1, confirm the UPS kinetic energy positions. Table 1 lists the work function values as derived from the spectra shown in Fig. 1 by the fitting procedure. The values given were corrected for the analyzer broadening. The lines fitted to the cut-offs shown in Fig. 1 reflect this procedure.

Fig. 2 shows the same set of spectra measured on an in-situ sputtered ITO sample. The insert shows the full UP spectrum (on the binding energy scale) corresponding to the UPS cut-off. The deep valley between the cut-off and the valence band emissions indicates a carbon-free sample surface. This was confirmed by XPS measurements where the C 1s emission region only showed a flat background

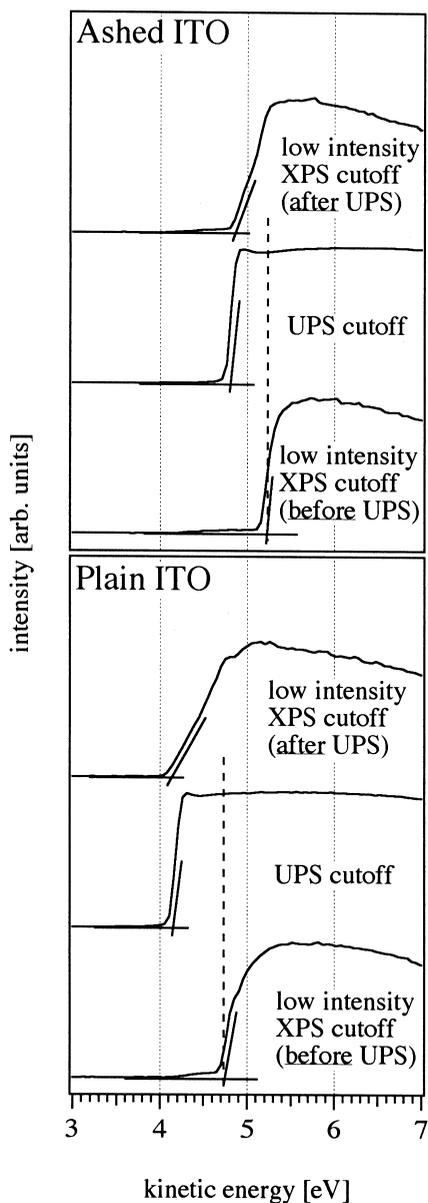


Fig. 1. Normalized low kinetic energy cut-off of XP- and UPS-spectra measured on ITO coated glass substrates. Graph on top corresponds to data obtained on an oxygen plasma treated ex-situ sample ('ashed ITO') while the bottom graph shows data obtained on a solvent cleaned ex-situ ITO surface ('plain ITO'). The bottom spectra in each graph were measured using low intensity XPS after introduction of the samples to the vacuum chamber before carrying out the UPS measurements. The spectra in the middle were taken by UPS. A strong shift to low kinetic energy is evident corresponding to a UV-induced work function reduction of the ITO surfaces. Top spectra were measured again with low intensity XPS confirming the UPS values.

signal, indicating that carbon related contamination was reduced below detection limit. Table 1 shows the corresponding work function values obtained on this sample by XPS and UPS, which are neither sensitive to the type of measurement nor to the order in which the measurement was taken.

Fig. 3 shows the results of a control experiment carried out on a Pt foil that was sputtered in-situ. The XPS cut-offs are at the same positions before and after the UPS measurement. The calculated average work function value of 5.53 ± 0.1 eV is in good agreement with previously published values [11]. The shoulders towards low kinetic energy are probably again caused by the emissions from X-ray source. They appear stronger relative to the smaller features seen in the ITO spectra, since the absolute intensities of the Pt cut-offs were considerably lower. These data demonstrate that low intensity XPS measurements are capable of yielding work function values of similar accuracy as those determined from UPS.

4. Discussion

It is evident from the results shown in Fig. 1 that the use of UPS for work function measurements on an ex-situ treated ITO sample can modify the surface of ITO and lead to a lower work function, which would not reflect that of the ITO sample before measurement. This is important especially for the evaluation of the performance of optoelectronic and electro-optic devices such as photovoltaic and electroluminescent devices. A comparison of the results on the ex-situ cleaned samples shown in Fig. 1 with the in-situ sputtered sample (Fig. 2) allows the conclusion that species adsorbed on the ITO samples which were treated in ambient atmosphere play a crucial part in the work function reduction observed upon exposure to the UV radiation provided by the UPS measurements. Once the UPS induced change occurs on the ex-situ cleaned ITO samples, it is permanent. The samples were kept in the vacuum chamber for ~ 10 h and no further significant changes in the work function values were detected after the initial change had been induced by the UPS measurements.

The measured UPS work function values given in Table 1 are in reasonable agreement with those

Table 1
Work function values (eV) derived from the cut-off spectra shown in Figs. 1–3

Method of measurement	Plain ITO (cleaned chemically) ^a	Ashed ITO (oxygen plasma) ^a	Sputtered ITO ^b	Sputtered Pt foil ^b
XPS prior to UPS (eV)	4.78	5.24	4.26	5.52
UPS (eV)	4.20	4.85	4.25	5.52
XPS after UPS (eV)	4.17	4.89	4.28	5.54

^a Treated ex-situ.

^b Treated in-situ.

previously published for similarly prepared ITO samples and determined by UPS. In the following comparison one needs to keep in mind, however, that even small differences in the surface preparation can have a significant impact on the work function. Therefore, a comparison between the various published results is difficult and should be taken only as tentative. In Ref. [2] Sugiyama et al. report a work function of 4.5 ± 0.1 eV on Balzers ITO cleaned in acetone/propanol vapor which is equivalent to the treatment the ‘plain ITO’ sample received. The same ITO type treated in a UV generated ozone environment yielded a higher work function of 4.75 ± 0.1 eV. This treatment is somewhat different from our method which uses a radio frequency (RF) generated O₂ plasma. Park et al. [3] and Le et al. [12] state a work function of 4.40 eV on an ITO sample cleaned by O₂ plasma. Kugler et al. [4] report a work function value of 4.40 ± 0.1 eV on a sample treated in a similar fashion like our ‘plain’ sample.

Ding et al. [1] also state 4.40 ± 0.1 eV on an ex-situ O₂ plasma treated sample. It is interesting to note that the same ITO material yielded a much higher work function of 5.2 eV after it was plasma cleaned in-situ. It appears, supported by the defined valence bands shape and the well-developed valley between the high binding energy cut-off and the valence bands in Fig. 1 of Ref. [1], that the in-situ plasma cleaning procedure probably largely removed the ambient contamination. This supports our conclusions that UV radiation can cause the observed work function reduction only in presence of environmental contaminants (water, CO, CO₂, hydrocarbons). The reason for the work function change might be a chemical modification of the surface induced by the UV radiation resulting in a surface dipole. However, our core level data do not permit well-founded

conclusions about the mechanisms due to the limited resolution of our XPS measurements using non-monochromatic X-rays. High-resolution XPS measurements before and after UV exposure would likely yield more conclusive insight into these phenomena.

The large absolute difference between the work function of the in-situ sputtered ITO samples (our value of 4.26 ± 0.1 eV is in good agreement with the value of $4.3 \text{ eV} \pm 0.1$ stated by Sugiyama et al. [2]) and the in-situ oxygen plasma cleaned ITO points to the fact that sputtering does more to the surface of ITO than removal of adsorbed species. Sputtering can cause modifications of the surface morphology and preferential sputtering effects can alter the surface stoichiometry. A comparison of the present data with recent results presented by Kim et al. [7] where KP measurements on various ITO samples were compared with UPS work function data, also supports our findings. In this paper it is stated that KP measurements generally yield higher work function values than obtained with UPS on the same sample types. Exposure of the samples to UV radiation in ambient atmosphere during the KP measurements leads to a work function decrease similar to the observed effect on our samples. However, the same reference states that, once the UV source had been switched off, the ITO work function values partially recovered their original higher values. This phenomenon might be related to the fact that the KP experiments in Ref. [7] were carried out in ambient atmosphere. Therefore, UV induced desorption in combination with post-UV readsorption of environmental contaminants on the probe itself might have caused additional changes of its work function. KP measurements in UHV would be needed to draw final conclusions about these effects.

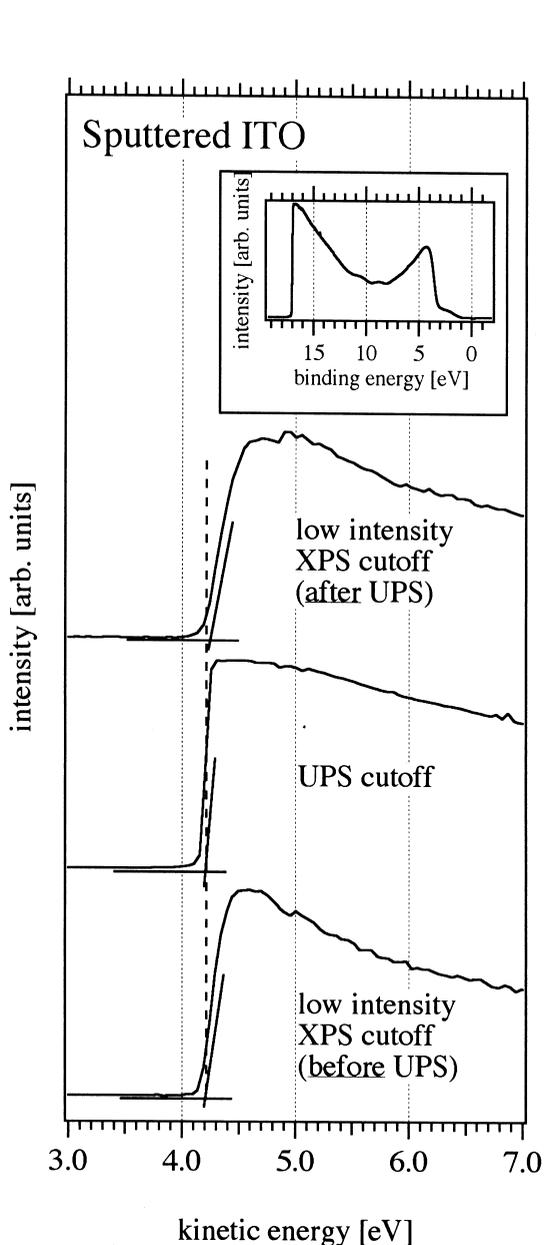


Fig. 2. Normalized low kinetic energy cut-off of XP- and UP-spectra measured on an in-situ sputtered ITO coated glass substrate. The bottom spectrum was measured using low intensity XPS after sputtering the sample. The second spectrum was measured by UPS and the third one again by low intensity XPS. In contrast to the ex-situ prepared samples no shift occurs after the UPS measurement, supporting the conclusion that ambient contamination plays a key role in the UPS induced work function changes. The inset shows the full He I spectrum. The well defined valence bands emissions indicate a clean sample surface.

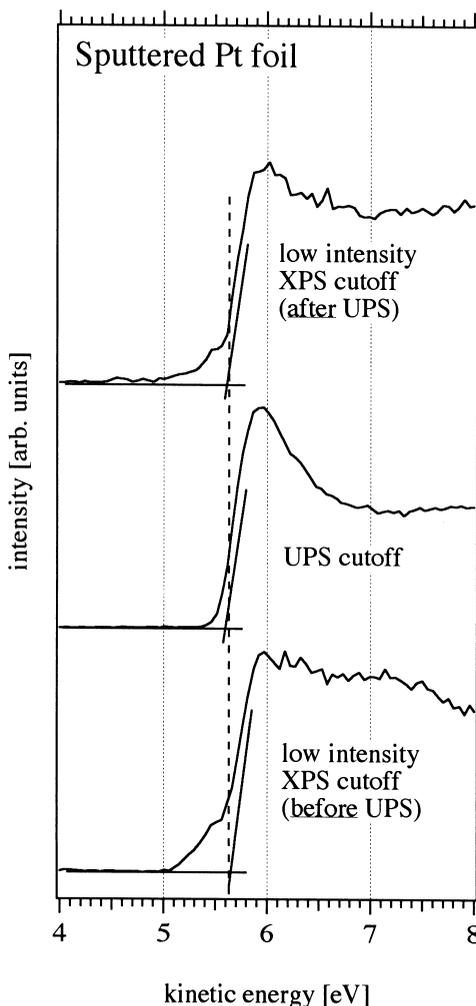


Fig. 3. Control measurements performed on an in-situ sputtered Pt foil. The low kinetic energy cut-offs measured by XPS before (bottom) and after (top) UPS measurements closely agree with the UPS cut-off shown in the middle. This demonstrates that work function values can be reliably measured by low intensity XPS and that these values closely agree with the UPS values if no UPS induced surface modification occurs.

5. Conclusion

Our results demonstrate that UPS work function measurements on ex-situ ITO electrodes may result in a measurement induced work function reduction of the samples during the measurement. This was demonstrated by using low intensity XPS work function measurements prior to and after the UPS

measurements. Additional experiments on sputter cleaned samples suggest that environmental contaminants play a key role in this effect. A comparison of our results with KP work function measurements supports these conclusions as KP typically yields higher work function values than measured by UPS.

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