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Journal of Electron Spectroscopy and Related Phenomena 152 (2006) 12–17

JOURNAL OF  
ELECTRON SPECTROSCOPY  
and Related Phenomena[www.elsevier.com/locate/elspec](http://www.elsevier.com/locate/elspec)

# Direct comparison of photoemission spectroscopy and in situ Kelvin probe work function measurements on indium tin oxide films

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Received 3 July 2005; received in revised form 31 January 2006; accepted 1 February 2006

## Abstract

The work function of commercially available indium tin oxide (ITO) films on glass substrates was measured using photoemission spectroscopy (PES) and ultra-high vacuum (UHV) Kelvin probe in direct comparison. Absolute Kelvin probe work function values were determined via calibration of the measured contact potential difference (CPD) using an in situ sputtered Au reference sample. The Kelvin probe data confirmed that ultraviolet photoemission spectroscopy (UPS) measurements change the work function of ITO surfaces previously exposed to ambient environment, when measured without in situ surface cleaning procedures. The results also demonstrate that both Kelvin probe and PES yield virtually identical work function values, as long as the Kelvin probe data are calibrated against a known standard. As a consequence, previously reported higher work function values determined with Kelvin probe as compared to values obtained with UPS on similar samples are likely related to a photochemically generated surface dipole during UPS measurements. Comparison between Kelvin probe and low intensity X-ray photoemission spectroscopy (LIXPS) work function measurements demonstrated that accurate work function measurements on ITO previously exposed to the ambient are possible with PES.

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*Keywords:* Work function; Photoemission spectroscopy; Kelvin probe; ITO

## 1. Introduction

Indium tin oxide (ITO) is widely used as a high work function electrode for optoelectronic applications, such as solar cells or light emitting and sensing devices, since it combines good electrical conductivity with optical transparency in the visible range. Its relatively high work function makes ITO particularly suitable as a hole injection electrode for organic materials [1,2], or as front contact for thin-film solar cells [3,4]. In order to determine the electronic structure of the interface between the ITO electrode and active device layer, exact knowledge of the work function of ITO is necessary. A number of recent studies have been focusing on determining the work function of commercially available and surface modified ITO substrates using ultraviolet photoemission spectroscopy (UPS) [5–11] and Kelvin

probe [12–15]. Significant differences were found between the work function values obtained by UPS in an ultra-high vacuum (UHV) environment, and Kelvin probe measured in air or nitrogen atmosphere. Recent experiments using low intensity X-ray photoemission spectroscopy (LIXPS) suggest that the UV light used in UPS measurements may result in a lowering of the work function of the ITO surface during the measurement procedure itself [16]. These experiments showed that LIXPS work function measurements prior to standard UPS measurements yielded larger work function values, indicating a way to perform accurate work function measurement, as long as the photon flux is low enough to prevent significant photochemical changes of the ITO surface during the duration of the measurement. These experiments, however, left one significant question unanswered: is the initially measured LIXPS already affected by a photon induced reduction or not?

The experiments discussed in this paper address this issue through a direct comparison of work function values measured with PES and in situ Kelvin probe (which does not expose the sample to ionizing radiation) on the same sample without breaking the vacuum. The results confirm that UPS indeed lowers

*Abbreviations:* ITO, indium tin oxide

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the work function of ITO previously exposed to the ambient, that Kelvin probe and PES yield identical work function values within measurement accuracy, and that LIXPS measurements can result in accurate work function values on ITO. Examination of X-ray photoemission spectroscopy (XPS) core level line positions before and after UV exposure allowed the conclusion that the effect is caused by the formation of a surface dipole, and that no significant band bending is involved.

## 2. Experimental

The experiments were carried out in a commercially available integrated surface analysis system (SPECS, Berlin, Germany) consisting of a fast entry load-lock, a preparation chamber, and an analysis chamber equipped with monochromated and standard XPS, UPS and a UHV-compatible Kelvin probe (UHV-KP; KP Technology Ltd., Thurso, Scotland, UK). The system is pumped by turbomolecular/rotary vane pumps in combination with ion getter pumps. The base pressure of the system is  $2 \times 10^{-10}$  Torr. The PES system consists of a SPECS UVS 10/35 high current UV Source, a SPECS XR 50 retractable X-ray gun, SPECS XR 50 M X-ray source with FOCUS 500 ellipsoidal crystal monochromator, and a SPECS Phoibos 100 hemispherical electron energy analyzer with HSA 3500 electronics. Sputter cleaning of the AU-sample was carried out with a SPECS IQE 11/35 ion source attached to the preparation chamber. The sputtering conditions were 2 kV,  $7 \times 10^{-6}$  Torr Ar pressure, and 10 mA emission current with a sample to gun distance of about 20 cm.

ITO coated glass substrates (15 mm  $\times$  15 mm) were obtained from Thin Film Devices, Inc. (thickness: 1500 Å, conductivity: 20  $\Omega$ /square). Electrical contact to the films was established via a small stripe of silver epoxy applied to the coated side of the samples. Good Ohmic contact between ITO layer and sample holder was ensured prior to loading into the vacuum system to minimize charging artifacts.

All presented XPS core level spectra were measured using monochromatized Al K $\alpha$  radiation. The PES work function measurements were carried out using He I (21.21 eV) and non-monochromatized Mg K $\alpha$  excitation. The analyzer settings were identical for both X-ray and He I work function measurements (3 mm entrance slit and 1 eV pass energy). It should be noted that the excitation energy has no influence on the work function measurements, since the spectral low kinetic energy cutoff (or “secondary edge”) feature is formed by inelastically scattered photoelectrons (secondary electrons), which have completely “forgotten” their initial energy. While UPS work function values were determined directly from standard UP-spectra, the LIXPS values were determined from secondary cutoff spectra measured with the X-ray gun in stand-by mode, and retracted by about 30 mm from the standard measurement position. This procedure yielded a reduced photon flux of about 1.2% of the flux under normal operation conditions (20 mA emission current, 240 W), as determined from a comparison of core level peak intensities. It also minimized the presence of stray electrons photoemitted from the Al bremsstrahlung filter window and Cu nozzle of the gun, which can result in superimposed spectral features at the

secondary cutoff. A  $-5$  V bias was applied to the sample during the work function measurements to distinguish between the analyzer and the sample cutoff, and to collect emitted electrons more efficiently into the analyzer.

All cutoff spectra in this paper are shown on the kinetic energy scale corrected for the applied bias and analyzer work function. This allowed the direct determination of the work function from the spectra by fitting straight lines into their low kinetic energy cutoff, and determining the intersect with the base line of the spectra [17]. To account for analyzer broadening ( $\pm 0.1$  eV [18]), 0.1 eV was added to the work function values thus obtained.

All data evaluation was carried out using Igor Pro software (WaveMetrics, Inc.). The spectrometer was calibrated to yield the standard Cu 2p $^{3/2}$  line at 932.66 eV and the Au 4f $^{7/2}$  line at 84.00 eV [19]. Kelvin probe contact potential difference (CPD) values were transformed into absolute work function numbers by using the CPD of a clean, previously UPS characterized Au surface as reference. This calibration routine was performed before and after the measurement series. The Kelvin probe measurements were performed before and after all PES measurements, allowing direct comparison of the work function values measured with both methods, and to observe possible PES related work function changes.

## 3. Results

Fig. 1 shows the low kinetic energy cutoff measured on an ITO sample directly after insertion into the UHV chamber by LIXPS and UPS. The spectra are shown normalized, since the UP spectra have a several magnitudes higher intensity than the XP spectra due to the much lower photon flux during LIXPS measurements. The spectra are presented in the order in which they were measured, starting at the bottom. The initial measurement with LIXPS yielded a cutoff position corresponding to a work function of 4.55 eV. The subsequently measured UP-spectrum shows a significant shift of the cutoff to lower kinetic energy, corresponding to a 3.90 eV work function. The LIXP-spectrum measured after the UPS measurement shows a cutoff at essentially the same position (3.91 eV), indicating a permanent change of the work function caused by the UPS measurement. The corresponding Kelvin probe work function values are summarized in Table 1. The values measured before (4.56 eV) and after (4.51 eV) the initial LIXPS measurement are very similar to the LIXPS value itself. This confirms that LIXPS has a sufficiently low photon flux which does not appear to change the work function significantly during the typical time span necessary for the LIXPS measurement ( $\sim 3$ – $5$  min). This suggests that LIXPS offers a reliable way to measure accurate work function values on ITO samples with an ambient contamination layer. The insert shown in Fig. 1 shows the full UP-spectrum of the sample (note the binding energy scale). The broad structure between 4 and 12 eV is typical for the presence of ambient contaminants (hydrocarbons, water) on the surface.

Fig. 2 shows the UP cutoff spectra measured on the Au calibration sample for reference. The work function determined from the spectrum of 5.26 eV is in good agreement with

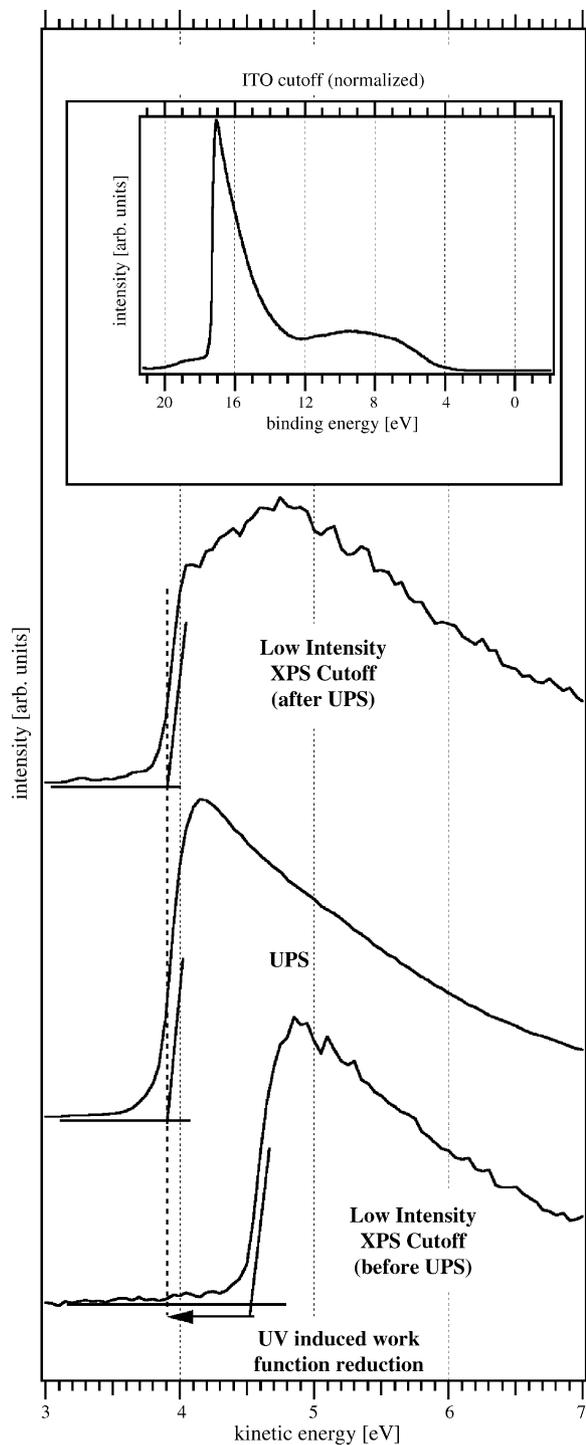


Fig. 1. Low kinetic energy cutoffs (“secondary edge”) measured directly after introduction of the ITO sample into vacuum with low intensity X-ray photoemission spectroscopy (LIXPS, bottom), with ultraviolet photoemission spectroscopy (UPS, middle), and again with LIXPS after the UPS measurement (top). A clear shift to low kinetic energy of the feature is observed after the UPS measurement, which is related to the formation of a surface dipole by means of a photochemical reaction between ITO surface and components of the ambient contamination layer. *Insert*: Full UP-spectrum, indicating the presence of contamination.

Table 1

Work function values determined on the ITO and Au samples

Sample/experimental step	PES work function (eV)	Kelvin probe work function (eV)
(1) As-introduced ITO		
Before PES measurements		4.56
1st LIXPS measurement	4.55	4.51 (measured after LIXPS)
UPS measurement	3.90	3.85 (measured after UPS)
2nd LIXPS measurement	3.91	3.92 (measured after LIXPS)
(2) Sputter-cleaned Au film		
UPS measurement	5.26	:=5.26 (calibration)

Work function values determined from photoemission spectroscopic low kinetic energy cutoff features are given in the second column. The third column contains the corresponding values obtained by in situ Kelvin probe measurements. Kelvin probe contact potential difference (CPD) values were calibrated to absolute work function using the CPD against a sputtered Au substrate, which yielded a work function of 5.26 eV as determined by UPS.

previously published values [20]. All presented Kelvin probe CPD measurements were calibrated using this value to yield absolute work function values.

In order to elucidate the origin of the observed work function changes, core level spectra were measured before and after an ITO sample was exposed to UV exposure corresponding to a UPS measurement. Fig. 3 shows the O 1s and In 3d<sup>5/2</sup> core levels before and after exposure. The O 1s line is composed of at least two components. The low binding energy peak at 530.8 eV corresponds to O atoms bonded in ITO [21], while the peak at 532.5 eV is related to O-based contaminants (this was determined by sputtering an ITO sample, which caused this peak to completely vanish). Examination of the O 1s spectra indicates a slight reduction in the intensity of this contamination related peak before and after UPS measurement. The In 3d<sup>5/2</sup> line, on the other hand, remains unchanged by the UV exposure. The C 1s line was also measured (not shown), indicating the presence of surface contamination. No significant changes were observed before and after UV exposure.

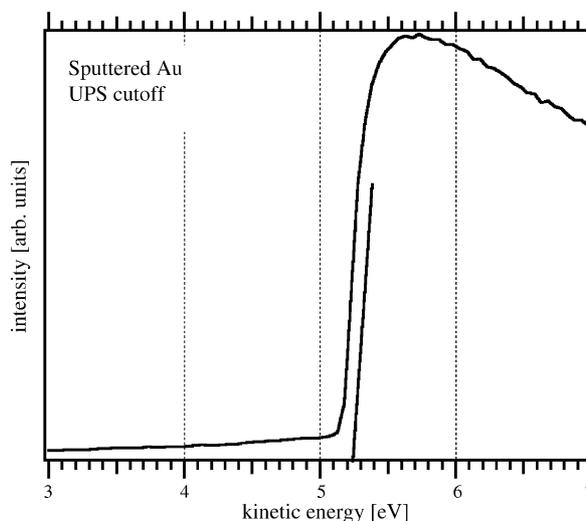


Fig. 2. Low kinetic energy cutoff of the sputtered Au sample used for calibration of the Kelvin probe contact potential difference (CPD) values.

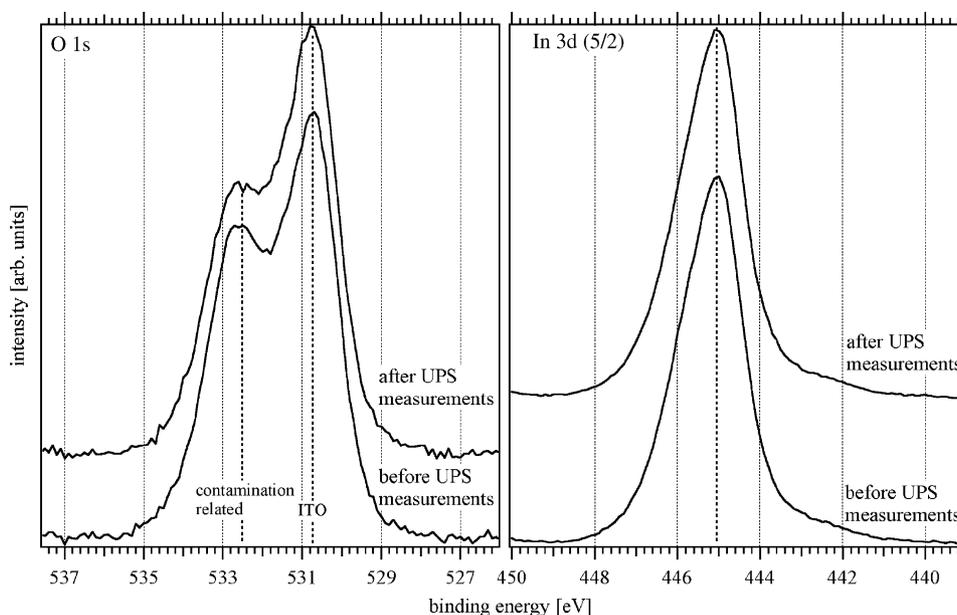


Fig. 3. O 1s and In 3d<sup>5/2</sup> core level spectra measured before and after UV exposure. The O 1s emission is composed of at least two lines corresponding to ITO substrate and contamination layer. No significant changes were observed except a small reduction of the O 1s contamination peak due to UV induced desorption. The unchanged binding energies of the ITO related peaks indicate that no significant band bending is induced by the UV exposure.

#### 4. Discussion

The low kinetic energy cutoff spectra sequence shown in Fig. 1 essentially reproduces the data obtained in our earlier experiments [16], i.e. confirms the work function lowering impact of UV exposure levels typical for UPS measurements. However, the extracted work function values before and after UPS measurements are about 0.2–0.3 eV smaller than measured in our previous experiments. This is probably related to the fact that the ITO material used in Ref. [16] came from a different source. Small changes in composition and surface morphology can easily result in noticeable work function variations on ITO. The UPS induced work function reduction, however, is close to the one reported in Ref. [16].

The Kelvin probe work function values listed in Table 1 closely match those obtained from PES measurements. The Kelvin probe values measured before and after the initial LIXPS measurement can be regarded as identical within measurement accuracy. This clearly indicates that the X-ray exposure during LIXPS does not affect the work function, i.e. LIXPS can be used confidently for work function measurements. It should be pointed out that the effect can already be observed after less than 1 s UV exposure, i.e. lowering the UV exposure time in UPS measurements usually does not have any impact. Perhaps the use of a less intense UV source might be a possible alternative if LIXPS is not feasible. The Kelvin probe work function values measured after UPS and second LIXPS measurements also closely match the PES values. This indicates that the observed work function reduction is indeed a permanent change and not, as could be suspected, a charging artifact. These results also demonstrate that absolute work function values determined by Kelvin probe measurements can be as accurate as PES measurements, provided that a well-defined standard such as a sputtered

Au sample is used for calibration. In the authors' experience, Kelvin probe CPD values are prone to drift over time, even if the vacuum in the analysis chamber is not compromised, i.e. calibrations needs to be performed in regular intervals to ensure accurate absolute work function values. Another consequence of these results is that comparison between Kelvin probe measurements in air and UPS measurements in vacuum are intrinsically difficult due to the UV induced work function reduction artifact. Furthermore, the determination of absolute work function values using Kelvin probe under ambient conditions needs to be approached with caution, since it is difficult to obtain an accurate calibration due to the poor definition and reproducibility of surfaces under ambient conditions. One way to attempt calibration of in-air measurements is by using a highly oriented pyrolytic graphite (HOPG) crystal as reference [15,22]. It has been shown that HOPG does not develop significant interface dipoles with organic materials in contact [23–25] (in contrast to noble metals, where contamination usually results in a significant work function reduction). This implies that a contamination layer is likely to not change the work function of HOPG significantly, resulting in a fairly constant work function of about  $4.6 \pm 0.1$  eV.

With regard to the origin of the UV induced work function reduction, the XPS core levels shown in Fig. 3 clearly indicate that the development of band bending at the surface can be excluded as a significant contributor to the phenomenon. Since band bending causes the position of the Fermi level to shift within the band gap, the work function changes by an amount corresponding to the magnitude of the occurring band bending. However, in the presented results the ITO related peaks remain stable at the same positions indicating that the Fermi level resides at the same position within the band gap after UV exposure. This leaves the formation of a surface dipole due to a UV induced chemical reaction between ITO and a surface contaminant as

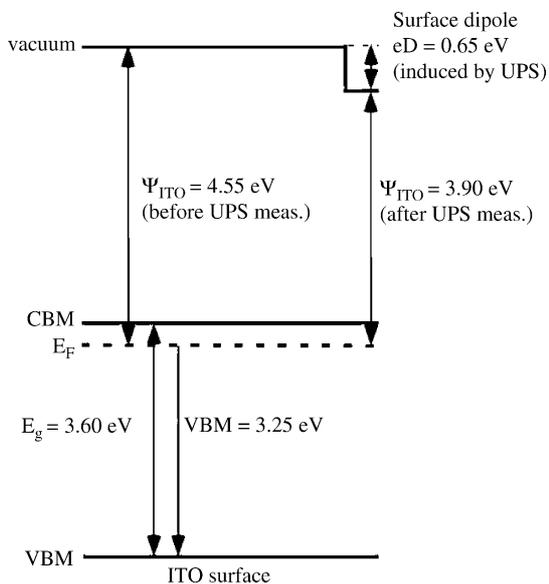


Fig. 4. Schematic of the electronic structure of the ITO surface after UV exposure: while the Fermi level position remains constant in the band gap, the work function of the surface is reduced by formation of a surface dipole.

most likely mechanism for the work function reduction. Fig. 4 shows the electronic structure at the surface of the ITO after UV exposure according to this model. The valence bands maximum (VBM) position relative to the Fermi level was determined using the In  $3d^{5/2}$  peak position (445.05 eV), since the VBM position could not be determined from the UP-spectra due to superimposed emissions from the contamination layer (compare insert in Fig. 1). Using the energetic difference between In  $3d^{5/2}$  line and VBM of 441.8 eV [21], a VBM binding energy of 3.25 eV was determined. The conduction band minimum (CBM) position of 0.35 eV above the Fermi level was estimated using the optical gap of ITO (3.6 eV) [21]. The surface dipole of  $eD = 0.65$  eV was determined using the work function difference between LIXPS measurements before UV exposure, and the value determined from the actual UPS measurement.

Regarding the origin of  $eD$  it can only be speculated at this point, since the core level spectra only yield an inconclusive picture. The only significant change after UV exposure is the slight reduction of the contamination related O 1s component by about 20% intensity. This indicates that part of the contamination layer is being desorbed by the incident UV light. However, it is unlikely that this is the reason for the work function reduction, since most of the contamination layer obviously remains after the UV exposure, and the presence of a single monolayer or even less is typically sufficient to cause significant work function change. This leaves the formation of a chemical bond between a contamination component and the ITO surface. One can speculate that  $H_2O$  and  $OH^-$  present on the surface may passivate O vacancies, which are usually present in ITO and responsible for the high n-type doping of ITO layers. However, if this would be the case, the Fermi level position should have changed somewhat due to the change in the defect related surface charge, i.e. core level peak shifts should have been detected. Since this was not the case, it has to be concluded that the UV induced process

has no bearing on the doping level, i.e. a pure surface dipole is being formed due to a localized chemically driven charge transfer from adsorbate to ITO. Further insight in this phenomenon would need more experiments, specifically adsorption experiments, where isolated components of ambient contamination layers could be adsorbed to the surface, and the impact of subsequent UV exposure on the work function be observed.

## 5. Conclusions

The presented results confirm that UV exposure in doses typical for UPS measurements results in a significant work function reduction of ITO samples prepared ex situ. Kelvin probe work function measurements in situ confirmed this artifact, and also demonstrated that low intensity X-ray photoemission (LIXPS) work function measurements do not result in a work function reduction, i.e. can be used to characterize ITO surfaces. Additional core level spectroscopic characterization before and after UV exposure conclusively shows that the Fermi level position at the surface remains unchanged by the UV exposure, i.e. the induction of band bending through surface passivation or similar effects can be excluded leaving the formation of a surface dipole as only mechanism for the observed work function reduction.

## Acknowledgements

Financial support by the National Science Foundation (grant DMR 0205577), and the Petroleum Research Fund (grant 38584-AC7) is gratefully acknowledged. A.J.C. acknowledges partial funding through an Engineering Undergraduate Research Fellowship provided by the USF College of Engineering Research Experience for Undergraduates program.

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