Work function of indium tin oxide transparent conductor measured by photoelectron spectroscopy

Y. Park,[a) V. Choong, and Y. Gao
Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627

B. R. Hsieh
Xerox Co., Wilson Center for Research and Technology, 14-39D, Webster, New York 14580

C. W. Tang
Imaging Research and Advanced Development, Eastman Kodak Co., Rochester, New York 14650

We used ultraviolet and x-ray photoelectron spectroscopy (XPS) and (UPS) techniques to directly measure absolute values of vacuum work function of indium tin oxide (ITO) thin films. We obtained a work function of 4.4–4.5 eV which is lower than the commonly cited value. These values do not change substantially by heating and Ar ion sputtering. The atomic concentrations of each element in ITO, measured with XPS, are also quite stable under heat treatment and ion sputtering. © *1996 American Institute of Physics.* [S0003-6951(96)04219-2]

Indium tin oxide (ITO) film exhibits excellent light transmission characteristics in the visible region of spectrum while maintaining high electrical conductivity. Because of this unique combination of properties ITO is widely used in optoelectronics applications such as solar cells and liquid crystal flat panel display devices. It is also used as a hole-injecting electrode in organic electroluminescent devices[1] that may hold great promise in flat panel display technology. In many such applications, the work function of ITO has a critical importance in device performance because it affects the energy barrier height at the heterojunction interface. The published values of ITO work function ranges from 5.53 eV (Ref. 2) down to 4.1 eV,[3] although a recent estimate seems to converge into the range 4.6–4.7 eV.[4,5] However, all these values were either deduced from the tunneling characteristic of ITO/semiconductor heterojunctions that might introduce uncertainties due to interfacial layers,[3–5] or measured in air with respect to a reference electrode.[2]

In this letter, we present absolute and direct measurements of ITO work function in ultrahigh vacuum (UHV) using an inelastic secondary electron cutoff of ultraviolet photoelectron spectroscopy (UPS) energy distribution curve (EDC). This method[6,7] does not depend on any experimental parameters except for the photon energy of UV source (in our case He I discharge at $h\nu = 21.22$ eV) which is known very accurately. Also, the measurement is performed in UHV that excludes any possibility of altering surface properties due to contamination. We obtained an ITO work function of 4.4–4.5 eV depending on the surface treatment, which is lower than the commonly cited value of about 4.7 eV. We have also found that that the value is very stable under heating up to 3 h at 300 °C and Ar ion sputtering for 1 h at 2 keV beam energy.

The ITO sample was a 300 Å film coated on a borosilicate glass, obtained from Donnelly Applied Films. The sample was first cleaned by scrubbing in a detergent, then thoroughly rinsed in deionized water. After rinsing it was spin dried with heating from a radiant source. Finally the sample was subjected to an O_2 plasma cleaning for 5 min. After these treatments, the sample was stored in a vacuum desiccator and exposed only briefly to the air before introduced into an UHV chamber[8] equipped with an angle-resolved electron energy analyzer, He discharge lamp for UPS, Mg $K\alpha$ x-ray source, and heating and sputter-cleaning facilities. The base pressure of the chamber was 2×10^{-10} Torr which rose to 5×10^{-6} Torr during Ar ion sputtering due to Ar gas backfilling. During UPS measurement the pressure went to high 10^{-9} Torr range mainly due to the He. For UPS, He I discharge at 21.22 eV was used and the energy resolution was 0.1 or 0.2 eV depending on the choice of electron energy analyzer pass energy. The Mg $K\alpha$ line at 1253.6 eV was used in XPS and the energy resolution was about 1.2 eV.

Figure 1(a) shows a typical He I UPS spectrum for ITO in kinetic energy scale. The spectrum was taken for −3.000 V sample bias so that the sample inelastic cutoff could be distinguished from that due to the spectrometer[7] which is observable in Fig. 1(a) as a small peak near 2 eV. This figure also illustrates the relation between the width of the spectrum, and sample work function ϕ and photon energy $h\nu$.[7] The spectrum width is determined from the distance between the sample inelastic cutoff and the Fermi edge as illustrated in Figs. 1(b) and 1(c), respectively. Ideally, these edges should be infinitely abrupt but due to the limited spectrometer resolution and thermal effects, they are broadened. The actual positions are determined as the center of the slopes as indicated with vertical lines. The estimated error in energy position was less than 0.02 eV. The determination of the position of inelastic cutoff was unambiguous for all samples while the Fermi edge did not readily show up for some samples. However, this did not pose a problem because the Fermi edge is the reference point of energy scale in photoelectron spectroscopy and should not change from sample to sample as long as they are grounded. Nevertheless, we checked the position of the Fermi edge using Au films electrically connected and positioned next to the ITO sample. We also checked any systematic error in the procedure when
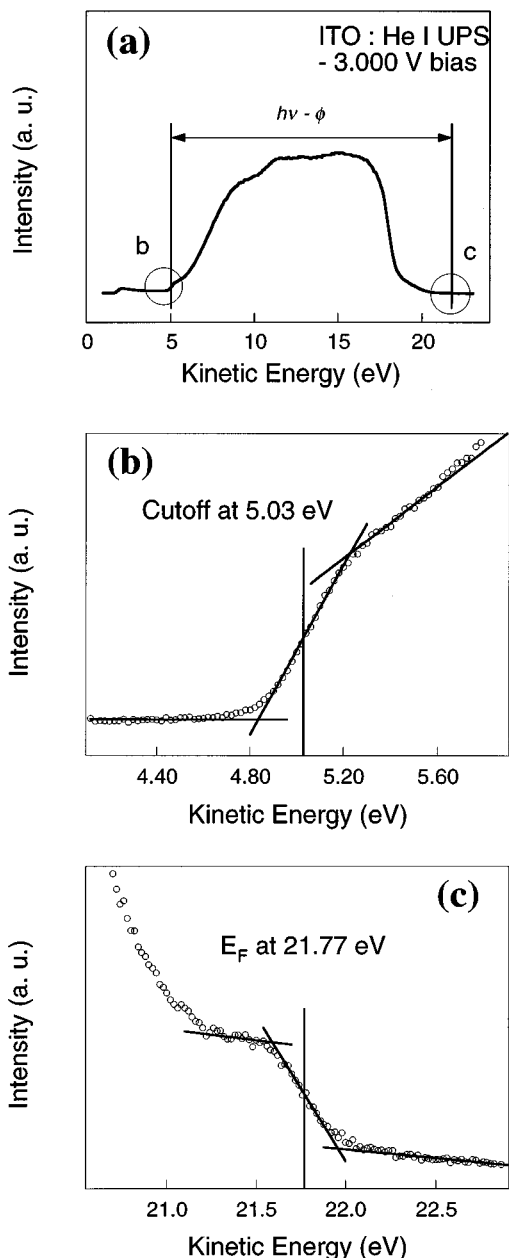
[a)]Electronic mail: park@alfalfa.pas.rochester.edu

FIG. 1. (a) Shows a typical He I ($h\nu$=21.22 eV) UPS spectrum of ITO taken with -3.000 V bias applied to the sample. Also shown is inelastic cutoff (circle b) and Fermi edge (circle c). The relation between spectrum width $h\nu$, and work function ϕ is illustrated. (b) Shows a detailed spectrum of inelastic cutoff region. It also shows the cutoff energy with a vertical bar; (c) is similar to (b), but shows Fermi edge region.

used with our spectrometer by measuring the work functions of clean Au and Ca films, which yielded 5.17 and 2.78 eV, respectively, in good agreement with the published values.[9]

The values of the ITO work function thus determined are summarized in the second column of Table I for several ITO samples with different treatment. Note first that the work function is remarkably insensitive to the treatment. This is in contrast with the results reported earlier[2] where postdeposition heat treatment in air or in hydrogen gas greatly alters the work function of electron-beam-evaporated ITO films. In our case heating in UHV or Ar sputtering causes less than a 0.1 eV change in work function. The change caused by various

TABLE I. Changes in work function and atomic concentrations, $C_X(X=\text{In,Sn,O})$, for ITO treated in various ways. The heating was done in UHV environment and the sputtering was performed in 5×10^{-6} Torr Ar pressure.

Treatment	ϕ (eV)	C_{In} (%)	C_{Sn} (%)	C_O (%)
As is	4.40	34.7	5.6	59.7
Heating 3 h ~200 °C	4.47	34.8	5.6	59.6
Heating 3 h ~300 °C	4.48	36.4	5.8	57.8
Sputtering 1 min ~500 eV	4.48	36.4	5.9	57.7
Sputtering 10 min ~2 keV	4.44	41.0	4.9	54.1
Sputtering 60 min ~2 keV	4.42	40.8	4.2	55.0

degrees of sputtering with Ar ion is also less than 0.1 eV. Also shown in Table I are the atomic concentrations of In, Sn, and O determined from the XPS peak intensities after taking into account the electron spectrometer characteristics and relative atomic cross sections.[10] The atomic concentration determined in this way typically has a few percent of errors.[10] The concentration of In suddenly increases after 10 min of sputtering at 2 keV while it does not show any substantial change during the heat treatments. The concentration of O and Sn decreases in commensurate with the increase in In concentration. However, the change in work function (<0.1 eV) is too small to be attributed to these concentration changes. The concentration is determined by the intensity of XPS with a probing depth of about 30–40 Å while the work function is determined by a thinner layer at the surface;[6] therefore the change in concentration may not be reflected by the change in work function. The work function obtained here is consistently lower than commonly cited value of about 4.7 eV. This may have some important consequences in correlating a certain device performance with respect to the work function of electrode. For example, organic based light-emitting devices that employ ITO as hole injection electrode[1,4] and low work function metals as electron injection electrodes. In those cases the work function of ITO determines hole injection barrier height, which in turn has a crucial effect on the device efficiency.

In summary, we were able to measure absolute values of the ITO work function without relying on any other materials parameter by UPS. We obtained values of 4.4–4.5 eV which are consistently lower than the one commonly cited. At the same time they do not change upon heating to 300 °C in UHV or sputtering at 2 keV for an extended period of time although the atomic concentration determined by XPS showed slight changes. This significantly lower work function might be responsible for the low efficiencies observed for certain organic based light-emitting devices.

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