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Discharge amplified photo-emission from ultra-thin films applied to tuning work function of transparent electrodes in organic opto-electronic devices

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ABSTRACT

A novel photoemission technique utilising localised discharge amplification of photo-yield is reported. It enables fast, accurate measurement of work function and ionisation potential for ultra-thin buffer layers vacuum deposited onto single and multilayer transparent conducting electrodes for organic solar cells and OLED's. Work function in most traditional transparent electrodes has to be raised to maximise charge transfer while high transmittance and high conductance must be retained. Results are presented for a range of metal oxide buffers, which achieve this goal. This compact photo-yield spectroscopy tool with its fast turn-around has been a valuable development aid since ionisation potential can vary significantly as deposition conditions change slightly, and as ultra-thin films grow. It has also been useful in tracking the impact of different post deposition cleaning treatments along with some storage and transport protocols, which can adversely reduce ionisation potential and hence subsequent device performance.

1. Introduction

Techniques for measurement of work function (WF) and ionisation potential (IP) continue to be of interest and have evolved recently to deal with nanostructures using vibrating AFM tips and STM probes [1]. However photoemission (PE) remains the most widely used technique. The method presented represents an advance in photo-yield spectroscopy (PYS) utilising discharge amplification of photo-yield induced by a low energy UV source. Its operational principles parallel those of the gaseous secondary electron detector (GSED) as used in environmental scanning electron microscopes. These detectors enable quality imaging in various atmospheres.

The work function of conducting contacts are needed for traditional junction devices, in particular the differences between WF value of the electrode and that of the semiconductors used. The latter's replacement with organic [2] and organometallic conductors, and their use in various optoelectronic systems has driven new demands on both work function or ionisation potential values and their measurement. Depending on just how contacts are made, and whether they are anode or cathode, work function or ionisation potential may be involved. IP is relevant for many oxide electrode buffer layers as they are semiconductors not conductors. That is in their ground state they are insulators and their filled levels do not traverse the Fermi level so that electron or hole conduction occurs via thermal activation. Several PE examples given in this paper are for such oxides. They are very thin and used to facilitate charge transfer between the transparent conducting electrode and the active organic system. Our PYS device can measure both WF for conductors and IP for semiconductors. For buffer oxides confusion has arisen in the literature with some authors using the term "IP", but many use "WF". Traditionally IP has referred to transitions from the top of the valence band in semiconductors to the vacuum. In sub-stoichiometric transition metal oxides however the highest occupied states arise from defect states that form within the pure oxide band gap. Thus traditional photo-excitation from the valence band and from gap states are both present. As long as the oxide is a semiconductor two classes of ionisation potential thus exist, the traditional one and that resulting from the presence of gap states. It is important to know when IP and when WF are given by PE spectra. Given the misunderstandings that exist we introduce here new nomenclature and acronyms: IPV and IPD to define respectively, ionisation potential from valence states, and ionisation potential due to defect or gap states, with IP used when a combination occurs. Both contribute to our data.

For many organic opto-electronic devices maintenance of high ionisation potential is essential for the anode. For organic solar cells (OPV) and OLEDS at least one contact needs to combine three

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or more attributes. High conductivity, high transmittance over a bandwidth dictated by the active material, and a narrow range of IPD are the prime concerns, but other features such as flexibility and stability against changes in IPD induced by atmospheric conditions, or cleaning either chemically or with discharge ions, may also be needed. Highly flexible electrodes are of interest for OPV and they also enable roll-to-roll production of complete OPV systems. Good flexibility usually demands much thinner layers than are used to achieve the desired conductance in traditional transparent conducting oxide (TCO) films such as indium tin oxide (ITO) and aluminium doped zinc oxide (AZO). Multilayers involving anti-reflected very thin silver are one approach to achieving desired electrical and optical responses in flexible sub-100 nm total thicknesses. While high ionisation potential oxides can be used to achieve anti-reflectance of the silver their conductivity is not as high as one would like. An alternative is to anti-reflect with a TCO material and buffer this with a high IP layer only a few nm thick. An example emission spectrum and IP result on such a four-layer electrode using our PYS technique are presented later.

The aim in the multilayer is thus to optimise surface ionisation potential while retaining high conductivity and high transmittance. A sufficiently thin transparent outer buffer layer can do this even if its material is only a moderate conductor. Buffer layer materials of interest include MoO_x, ZnO, WO_3, TiO_2 and V_2O_5 [3]. It is thus important to know the IP of such thin, vacuum deposited layers, which should remain around 5 nm or less in thickness. Very thin films of these oxides when sputtered or evaporated may have different structures, stoichiometry and defect content to the outer layers of their thicker counterparts. Such changes modify work function, and also carrier densities and mobilities. Any surface modifications must also not induce any other additional barriers for charge transfer as these can degrade I–V characteristics and hence performance.

Traditional approaches to photoemission such as Ultraviolet Photoelectron Spectroscopy (UPS) require relatively thick films of sufficient conductivity to minimise probing of the substrate and charging. An attraction of the PYS technique is that it is performed in an atmosphere in the 1–5 Torr range so charging of the sample becomes significantly less of a problem. The sample set up described later also helps eliminate charging as an issue. Thus the need for expensive UHV equipment is avoided. It utilises a scanned low energy mono-chromatic UV source at 4–7 eV, [4,5] rather than a high energy 22.1 eV source as used in UPS. As a verification of the lack of charging effects photo-emission spectra on standard insulators, semiconductors and strong conductors were all found to be as expected and in agreement with accepted values. It exploits the same processes which helps make the environmental scanning electron microscope viable as a high resolution imaging system.

2. Materials and methods

This approach to PYS utilises the gas cascade, which occurs when an electron is emitted from the sample surface, allowing us to measure the positive ion current as the nearest path to ground is through the pico-ammeter [5,6]. The layout must be carefully designed to ensure the discharge occurs through to the desired electrode rather than to other grounded areas of the chamber. To assist in this Teflon sheeting is used for electrical isolation to cover any other grounded surfaces near the probe and sample stage.

A wide variety of materials are of interest for use in flexible transparent conducting electrodes including mixed oxides and nano-composites, while different deposition conditions and surface treatments are also used in the search of optimised electrodes. This means that in development of transparent conducting electrodes there is a need for rapid and accurate analysis. This compact instrument enables many samples to be measured and analysed in a short period.

Our system, as depicted in Fig. 1, consists of a StelaNet SL3 Deuterium Lamp and JobinYvon HR 250 monochromator with stepper motor to control the wavelength of the incident light. The output of the monochromator is focused downwards using a parabolic mirror tilted at 45° after the output slit. The vacuum chamber has a quartz window to allow exposure of the test sample to the UV light. Our overall design aims to optimise signal amplification, rather than it simply being a side effect of measuring in a gaseous environment. The positive electrode consists of a copper wire directed towards the sample stage at a spacing of 3–5 mm with a high voltage feed through, connected to a variable high voltage power supply set in the range of 500–600 V. The sample stage is a sheet of stainless steel embedded in a polycarbonate frame such that it is electrically isolated from the rest of the chamber. This feature plus the sharp probe, its placement, the gas flow, the voltages used and insulation of chamber walls, ensure that the ionisation of the gas is controlled so that fields and hence ionisation is localised and occupies a small fraction of the view from any point on the wall. Breakdown is prevented and stray signal resulting from secondary emission off the walls is also prevented by the higher than normal pressures and weak or absent field strength near the walls. No visible discharge is apparent but the voltage drop developed at the high gas pressures and gas flow regime used is enough to cause some ionisation and cascading, hence amplification, but not enough to induce breakdown. If pressure was reduced by a moderate amount, applied voltage raised too much above the set range, or gas flow cut-off, the instrument would no longer function as intended. Thus the overall spatial design, plus operational settings and their control, are each important. Results on a variety of oxide, semiconductor and metal layers including some standards, confirm that ion impact damage is as expected, not a problem.

The chamber is evacuated using a rotary pump. An air inlet valve positioned such that the gas flow flushes past the electrode and stage, is used to set the desired pressure (1–5 Torr) to maximise amplification [7]. Currently our set-up is used for testing samples in an air atmosphere, though testing in other atmospheres is a trivial matter of attaching the desired carrier gas to the inlet valve. We have continued to use air as it gives a good indication of surface contaminants that may get onto samples when processed into devices. It is essential to monitor the pressure of the chamber and ensure that it is stable, as variations in pressure will affect the gain of the gas-cascade amplification.

Upon illumination with the UV light electrons are emitted from the sample surface. As each of these electrons, accelerated by the local applied electric field, strike molecules in the atmosphere the gas molecules are ionised thereby liberating further electrons to continue the cascade process towards the positive electrode. As noted above this method is much the same as that used to produce the secondary electron signal in environmental scanning electron microscopes [6]. The amplified photoemission current can then be measured by grounding the sample stage through a precision ammeter, in our case a Keithley 617 Electrometer. Measuring the grounded stage rather than the typical method of measuring the current on the high voltage side was done for two reason, firstly the protection of the electrometer from high voltage input and secondly to further eliminate signal from any stray UV light not incident on the sample surface.

As many of our samples are produced on insulating substrates we have found that utilising a strip of copper tape from the rear surface that contacts the stainless steel stage to the front side of the sample is a simple method to eliminate substrate related charging issues. In order to optimise the measurement conditions for each sample type it is convenient to set the monochromator to 200 nm which is where the peak signal of our samples is acquired. As with