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Band offset of the In_2S_3/indium tin oxide interface measured by X-ray photoelectron spectroscopy

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ABSTRACT

In_2S_3 thin films have been grown on Indium Tin Oxide (ITO) by Chemical Spray Pyrolysis. The structural and physical–chemical properties of the films have been investigated by means of X-ray Diffraction and X-ray Photoelectron spectroscopy (XPS). The valence band discontinuity at the In_2S_3/ITO interface has been determined by XPS resulting in a value of 1.9 ± 0.2 eV. Consequently, the conduction band offset has been estimated to be 1.0 ± 0.4 eV.

1. Introduction

Research on organic polymer-based photovoltaics is continuously attracting an increasing interest because cells can be manufactured at low temperatures on flexible substrates by simple fabrication processes like coating, spraying and printing techniques [1–3].

In their common configuration, polymer solar cells have a Transparent Conducting Oxide (TCO) electrode acting as the high work function anode for hole collection and a low work function metallic cathode acting as the electron collector. However, the use of a highly oxidizing low work function metal requires additional steps in cell manufacturing and is a source of performance degradation. In order to avoid the use of an air-unstable highly reactive low work function metal as the electron collector, an inverted scheme has been proposed which allows the use of a TCO film as the cathode and a low reactive, non-oxidizing high work function metal anode [4].

In an inverted structure polymer solar cell, the electrons generated in the active layer are collected by the transparent conducting front electrode, usually Indium Tin Oxide (ITO), whereas the holes are collected by the top metal electrode. The performance of these devices (both in common and in reverse configuration) can be improved by using a semiconductor as the electron selective layer (ESL) [5,6]. The ESL is introduced between the active layer and ITO whereas an electron blocking layer is inserted between the metallic electrode and the active layer. The purpose of this layer is to ensure the smooth collection of either charge carriers at the two electrodes by minimizing recombination at these electrodes. Recently, the application of In_2S_3 as the ESL in a reverse cell architecture has been reported. In this scheme, In_2S_3 is the hole blocking layer in contact with the electron collecting ITO layer [7]. In_2S_3 has gained increasing interest in solar cell technology because it has been identified as a suitable alternative to cadmium sulfide (CdS) buffer layer in thin film solar cells. Copper indium gallium (di)selenide (CIGS) solar cells with In_2S_3 buffer layers co-evaporated from In and S powder have shown efficiencies of up to 12.4% [8]. In_2S_3 is a wide band gap, high electron affinity n-type semiconductor and can be prepared with low-cost techniques such as Chemical Spray Pyrolysis (CSP) [9,10].

As a result of more than three decades of research on semiconductor devices, the understanding of the interface properties and the control of the interface formation is crucial for device tailoring [11]. Being layered devices, thin-film solar cells performance is strongly affected by the interface properties as well, and the basic parameters characterizing the interface are the band discontinuities at the heterojunctions between the layers constituting the cell stack.

Photoemission spectroscopy has been found to be an effective tool in interface analysis. In the past decades a great amount of work has been devoted to the study of semiconductor interfaces by this method [12–14]. More recently, many papers (see for example [15–19]) have reported the use of this technique for determining the band offsets at various interfaces in thin film solar cells and photonic devices.

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In this work, we have investigated the band discontinuities at the interface between ITO and an In_2S_3 layer deposited by CSP by means of X-ray Photoelectron Spectroscopy (XPS). The band discontinuity at the valence band has been evaluated by a direct method involving the measurement of the valence band at a suitable thickness that allows the simultaneous detection of the band edges of both layers [13,15,16] and also by an indirect method requiring the acquisition of the binding energy of selected core levels [12,14,18,19]. The valence band discontinuity at the In_2S_3/ITO interface obtained by means of the two methods resulted to be 1.9 eV.

2. Experimental details

In_2S_3 thin films were deposited on ITO coated glass substrates (2000 Å thickness, 10 Ω/cm^2 sheet resistance) by using the CSP technique. The technique involves spraying aqueous solution containing indium chloride and thiourea at a rate of 2 ml/min onto the heated substrate kept at 350 ± 5 °C. A home-developed automated spray pyrolysis unit was used for the deposition process. All the deposition parameters such as spray rate, substrate temperature, pressure of carrier gas, distance between spray head and substrate, can be controlled in this unit. More details related to automated spray unit and CSP technique have been described elsewhere [20,21]. For the present work, we prepared In_2S_3 thin films with In/S ratios of 1.2/8 and 2.5/3 in the spray solution. This was achieved by varying the molarity of the precursors keeping the volume of solution fixed. A total volume of 20 ml was sprayed in both the cases. Thickness of the films was measured using a Stylus Profilometer (Dektak-6 M) and was found to be about 200 nm and 350 nm for 1.2/8 and 2.5/3 ratios, respectively. For the sake of clarity, the samples with 1.2/8 ratio shall be referred as to sample A, whereas samples with 2.5/3 ratio shall be referred to as sample B.

X-ray Diffraction (XRD) data were acquired by a Rigaku Geigerflex powder diffractometer in Bragg-Brentano geometry equipped with a Cu K_α long fine focus X-ray tube and with graphite curved monochromator on the diffracted beam. XPS data were acquired in an ultra-high vacuum system operating at 4×10^{-8} Pa base pressure and equipped with a VG Al K_α monochromatized X-ray source and a CLAM2 hemispherical analyzer working at constant pass energy mode. The binding energy is referred to the C1s peak position measured on the "as inserted" sample and set to 285 eV. In order to reach the In_2S_3/ITO interface the samples have been Ar sputtered with energies ranging from 500 eV to 1600 eV. A careful investigation of the behavior of the XPS In/S intensity ratios as a function of sputtering time and ion energy has allowed to exclude any preferential sputtering effects in this energy range. No change in the In3$d_{5/2}$ and S2p core-level lineshapes, relative intensities and binding energy (BE) positions has been detected by XPS after sputtering cycles on the In_2S_3 layer indicating that Ar bombardment did not induce any observable surface modifications.

3. Results and discussion

Fig. 1 shows the XRD pattern of samples A and B, respectively. Both samples show the characteristic β-In_2S_3 diffraction peaks [10,22–24] together with the features related to a In_2O_3 phase that can be ascribed to the underlying ITO layer as their positions coincide with the powder reference data. In_2S_3 peak width in sample A (In/S = 1.2/8) is narrower than the width of peaks in sample B (In/S = 2.5/3) and peak positions in both spectra are at higher values compared to the β-In_2S_3 powder reference data (JCPDS 25-0390; dashed lines in Fig. 1), with the broader peaks of sample B being shifted more to higher values. By applying the Scherrer formula for estimating the grain sizes, sample B shows In_2S_3 grain dimensions of the order of 11 nm while in sample A the In_2S_3 grain size is estimated to be greater than 25 nm. The shift in the 2θ positions of the In_2S_3 phase in the deposited films reflects a change in the lattice parameters with respect to the pure β-In2S3 tetragonal phase:

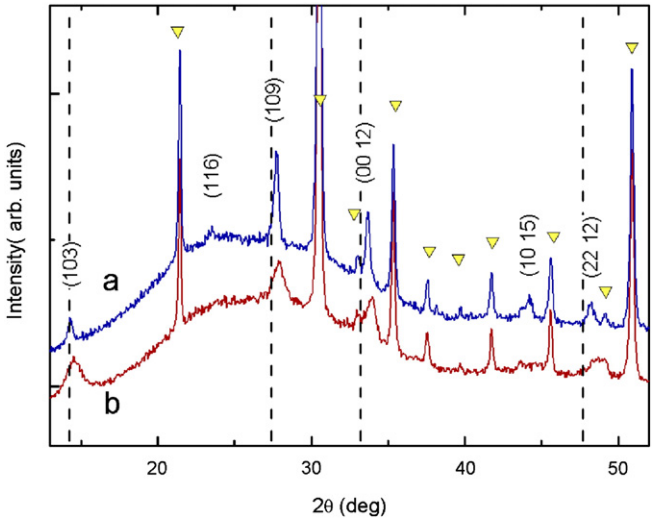

Fig. 1. XRD pattern of sample A (curve a; blue online) and sample B (curve b; red online). The dashed lines show the peak positions of the powder reference (JCPDS 25-0390) β-In2S3 phase. The triangles (yellow online) indicate ITO peaks. For better clarity, the intense ITO (222) reflexes at about 30.5° have been truncated.

a = b = 7.619 Å and c = 32.329 Å (JCPDS 25-0390). As the indices are known from reference data, the lattice parameters a (a = b) and c were calculated from the most intense reflections (0 0 12) and (1 0 9) located at 33.67° and 27.72° in spectrum A and at 33.87° and 27.86° in spectrum B, respectively. The variation for lattice parameter 'a' is estimated to be within the experimental error, whereas the 'c' parameter shows a contraction by 1.3% in sample A and by 1.9% in sample B. The smaller lattice parameters have been associated [10] to a higher content of oxygen in the sample. From XPS data (see below) the estimated oxygen content for samples A and B was about 8 ± 1 at.% and 10 ± 1 at.%, respectively thus indicatively agreeing with the XRD results. Barreau et al. [25] have shown that oxygen can substitute sulfur in the β-In_2S_3 lattice forming $In_2S_{3-3x}O_{3x}$ and inducing a widening of the bandgap. By considering that the measured optical bandgap for our samples is 2.8 ± 0.1 eV [7], it is reasonable assuming the presence of a similar phase in our In_2S_3 films.

Fig. 2 shows selected XPS survey sequences taken on sample A (In/S = 1.2/8) on two binding energy ranges of interest. The XPS data are plotted for different cumulative sputtering times starting at t = 0 from the "as inserted" sample, which shows a C and O contaminated In_2S_3 surface. The survey spectra show the expected In4d, In4p, In4s, S2p and S2s photoemission peaks with the additional presence of Sn3d and O1s (see right panel) and a small amount of Cl2p. Cl was found only in the In_2S_3 layer and is due to the $InCl_3$ precursor used in spray pyrolysis [7] and shows an intensity estimated to be less than 3 at.%. Oxygen is a contamination probably due to the synthesis method as it is found to have a constant amount of 8 ± 1 at.% within the In_2S_3 layer. Determination of the atomic quantities from XPS core-level intensities was obtained by using Scofield's factors [26] and correcting for the transmission function of the electron analyzer [27]. XRD results have shown the possible presence of an $In_2S_{3-3x}O_{3x}$ phase in the In_2S_3 layer and that is further supported by the binding energy values measured for S and O. With the C1s peak set as reference at 285 eV, the binding energies were measured 161.0 ± 0.1 eV for S2$p_{3/2}$ and 530.8 ± 0.1 eV for O1s indicating that the bonds have a metallic character [25] and supporting the XRD results. After 9' sputtering, S2p core level intensity is observed to decrease, while at the same time an increase of the O1s intensity is registered and the Sn3d spectral intensity at about 487 eV BE becomes detectable. This indicates that the interface region has been reached and the simultaneous contributions from