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Photoemission studies on undoped SnO₂ buffer layers for CdTe thin film solar cells

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Abstract

Intermediate highly resistive layers of transparent undoped oxide materials are known to improve the characteristics of thin film solar cells, as observed for SnO₂ used in CdTe solar cells with reduced CdS layer thickness. Comparative photoemission spectroscopy studies were carried out on commercial undoped and fluorine doped SnO₂ prepared by spray-pyrolysis, revealing that the Fermi level positions of the surfaces of both commercial samples are identical and degenerate. The commercial SnO₂ was compared to SnO₂ prepared by RF magnetron sputtering under different oxidation conditions. The sputtered samples were only weakly n-doped. Additionally, the influence of different sample treatments was investigated.

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1. Introduction

Intermediate highly resistive layers of transparent undoped oxide materials have recently attracted great interest for solar cell applications [1]. The use of different highly resistive so called buffer layers like SnO₂, In₂O₃, and Zn₂SnO₄ have led to increased values of open circuit voltage V_{OC} and fill factor FF

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in CdTe thin film solar cells when CdS films with thicknesses below 100 nm are applied [2, 3]. The decrease in CdS film thickness is preferable as it leads to higher values of the short circuit current J_{SC} ; yet for thin CdS, local shunts between CdTe and the front contact TCO material are more likely to be formed affecting V_{OC} and FF . Theoretical calculations support these observations: In contrast to a homogeneous device, an inhomogeneous device modeled by a parallel connection of solar cells with a distribution of diode parameters can benefit from an additional series resistance [4–6].

Glass manufacturers offering TCO coated glasses for solar cell applications have reacted to the demand for resistive buffer layers by offering combinations of a TCO ($\text{SnO}_2\text{:F}$) and the corresponding undoped oxide (SnO_2) on request. Although these products have been available for some time, little is known regarding the nature of these films. In the case of the $\text{SnO}_2\text{:F}/\text{SnO}_2$ layers investigated here, the TCO and presumably also the undoped oxide are prepared by a patented pyrolytic spray process [7]. The specifications of the TCO layer sequence concern conductivity, roughness, and haze. Li et al. [8] have investigated the optical, structural, and compositional properties of the $\text{SnO}_2\text{:F}$ films. In order to gain knowledge on the electronic properties, we have applied X-ray photoelectron spectroscopy (XPS) to investigate the $\text{SnO}_2\text{:F}$ TCO samples with and without undoped buffer layer (SnO_2) in comparison with two types of RF magnetron sputtered SnO_2 samples prepared in our lab.

2. Experimental

The experiments were carried out in the Darmstadt Integrated System for Solar Cell Research “DAISY-Sol”, allowing for in situ investigations without leaving vacuum conditions [9].

Two types of Pilkington samples were investigated. The first type consists of soda lime glass covered with $\text{SnO}_2\text{:F}$ (Pilkington Tec15, subsequently “Tec15”). The second type is a Pilkington Tec15 substrate with an additional undoped SnO_2 layer on top, also purchased from Pilkington (subsequently “Tec15B”). Before characterisation by XPS, both types of samples were cleaned in a multi step process: 15 min ultrasonic bath in a soap solution, rinsing with water, 15 min ultrasonic bath in isopropanole, rinsing with de-ionised water, 15 min ultrasonic bath in de-ionised water, drying with a nitrogen fan.

Two types of undoped SnO_2 films were deposited onto Tec15 substrates by RF magnetron sputter deposition using an undoped SnO_2 target, a deposition pressure of approximately $5 \cdot 10^{-3}$ mbar, a substrate temperature of 435 °C and a sputtering power of 25 W. One type of sample was deposited using pure Argon as sputtering gas, the other type using a mixture of oxygen and Argon (12 % O_2). The thus deposited SnO_2 layers were characterised in situ by XPS measurements.

In order to enable a comparison between the in situ sputtered SnO_2 layers and the commercial substrates, a series of sample treatments and subsequent measurement steps was carried out. A SnO_2 sample sputtered in pure Argon atmosphere was exposed to air, annealed in situ in vacuum, cleaned in the same multi step process as the Tec15 and Tec15B samples, and again annealed in situ in vacuum. After each step, XP spectra were recorded. The commercial substrates were exposed to the same annealing step before they were in turn characterised by XPS. The annealing step in vacuum was carried out in the setup used for close space sublimation (CSS) deposition of CdS in the DAISY-Sol [9] and corresponds to the temperature profile the TCO substrates experience during the CdS deposition as applied in CdTe solar cells. During this profile, the samples were heated up to 450 °C in 7.5 min and subsequently to 520 °C in another 7.5 min. This temperature of was held for 9 min and the samples were then allowed to cool down. The XPS measurements were carried out in a VG-Escalab-250 Photoelectron Spectrometer. The spectra were obtained in constant analyser energy mode using a pass energy of 10 eV. For excitation, monochromatised Al K_α radiation was used. The Fermi level position was aligned to a binding energy $E_{\text{bin}} = 0$ eV using clean metallic samples (Au, Ag, Cu).

3. Results and discussion

3.1. Spectral features of commercial and in situ sputtered SnO₂

Figure 1a shows the valence band (VB) spectra of all four types of samples. Figure 1b shows the corresponding Sn 3d core level spectra. It is pointed out that the spectra of the samples Tec15 and Tec15B were recorded after storage in air and cleaning whereas the sputtered samples were characterised in situ. The Sn 3d core level peak positions and the valence band maximum (VBM) positions E_{VBM} with respect to E_{F} are displayed in figure 1. Assuming a value of approximately 3.6 eV for the energy band gap of SnO₂ [10, 11], both types of sputtered SnO₂ can be regarded as weakly n-doped as their Fermi level positions correspond well with low conductivity undoped SnO₂ films deposited on glass substrates [12]. The film sputtered in a mixed atmosphere exhibits the smallest $E_{\text{F}}-E_{\text{VBM}}$ of 2.8 eV. No dependence on the use of the substrate (Tec15 or Tec15B) or the thickness of the sputter deposited films was observed.

The two Pilkington samples Tec15 and Tec15B have values of $E_{\text{F}}-E_{\text{VBM}}$ corresponding to a degenerate n⁺-doped TCO layer with E_{F} situated in the conduction band (CB). Their VB spectra look essentially identical. The small density of states just below the Fermi level can be assigned to the presence of occupied states in the CB and is an indication for a degenerate material [13].

In the shape of the VB onset of the sample sputtered in Argon atmosphere, a tail of states can be seen, exceeding up to about 1.8 eV below E_{F} . These states can be assigned to a reduced Sn²⁺ surface species as the films were deposited under reducing conditions (Argon) which gives rise to a surface reconstruction exhibiting Sn⁴⁺ and Sn²⁺ sites [14]. For the sample sputtered in a mixed Ar/O₂ atmosphere (oxidising conditions), the Sn²⁺ species is no longer visible. A different surface reconstruction results in leaving all Sn atoms in the 4+ oxidation state. Accordingly, the samples Tec15 and Tec15B, which were exposed to air before measurement, do not show this density of states either.

Regarding the difference between core level emission line positions and VBM of the different samples, a general semiconductor behaviour can be observed [15]: For intrinsic semiconductors, the difference in binding energies of the spectral features is a fingerprint of a certain material. The values taken from figure 1 (difference: 483.5 eV for the sputter deposited films and 483.1 eV for the commercial samples) show that this is not the case anymore when the Fermi level exceeds the CB minimum. The position of core levels is therefore deceptive, and we will focus on the VB spectra for the following discussion.

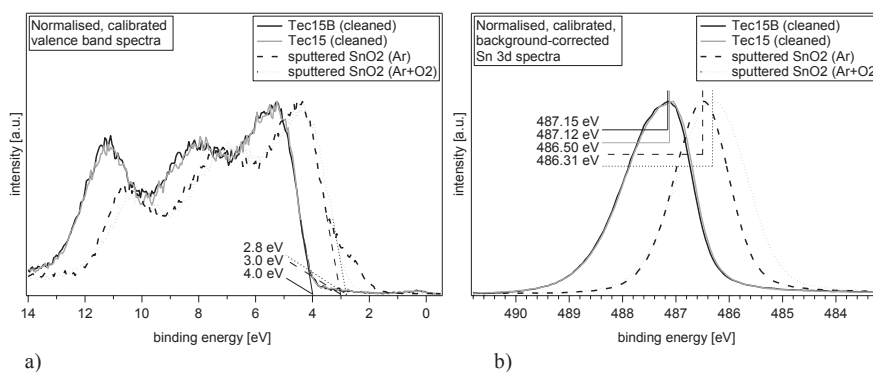


Fig. 1. Comparison of VBM position and Sn3d core level position of different SnO₂ samples. The samples Tec15B and Tec15 were cleaned before measurement, the sputtered SnO₂ samples were characterised in situ as deposited. One sample was sputtered in pure Argon atmosphere, one in a mixture of Argon and oxygen. (a) normalised and calibrated VB spectra; (b) normalised, calibrated, and background-corrected Sn 3d core level spectra.

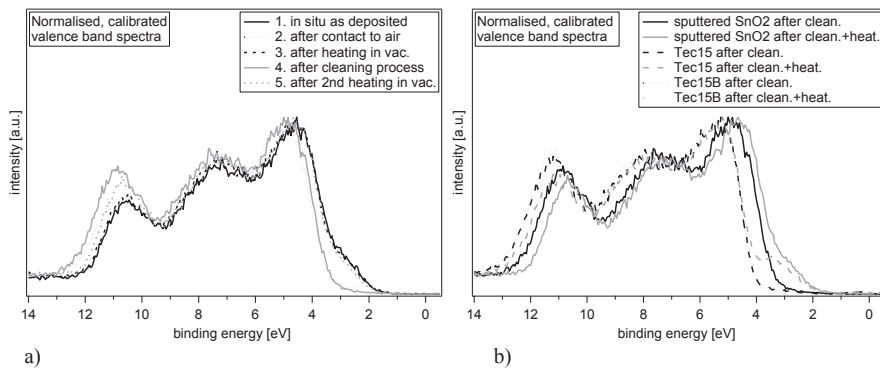


Fig. 2. Normalised and calibrated VB XP spectra of different SnO_2 samples: (a) spectra recorded from a SnO_2 sample sputtered in pure Argon atmosphere, which underwent a series of consecutive treatments (legend 1.-5.); (b) comparison of Ar sputtered SnO_2 , Tec15, and Tec15B samples after a cleaning process in air and after a subsequent heating step in vacuum. Details about the cleaning and heating processes are given in the Experimental section.

3.2. Influence of surface treatments

The difference in the VBM position of the commercial samples and the in situ sputter deposited SnO_2 may partly be due to the different pre-treatments of the samples. Figure 2a shows the influence of different subsequent sample treatments on a sputtered SnO_2 sample (Argon atmosphere). After exposing the sample to air and after cleaning the sputtered film in the same way as the commercial samples, the spectra show a slightly higher value of $E_F - E_{\text{VBM}}$ (3.4 eV) as compared to the in situ recorded spectrum (3.0 eV), which can be explained by adsorbates. Also, the Sn^{2+} surface species disappears. However, the initial electronic structure including the Sn^{2+} species could be reversibly restored by annealing the sputtered sample after mere exposure to air as well as after the cleaning procedure.

Figure 2b compares the effect of the cleaning and vacuum annealing treatments for Tec15, Tec15B and a sputtered SnO_2 sample (Argon atmosphere). The spectra of Tec15 and Tec15B undergo the same changes during annealing. The spectra of all three types of samples recorded after annealing in vacuum exhibit the tail of the VB states already presented above, all of them at the same energy. In contrast, the onset of the steep part of the VB is affected by the heating step in the case of the sputtered SnO_2 but not in the case of the commercial samples. This can be understood by the relatively small number of states created by adsorbates which are easily compensated by the high number of electrons in the CB of the degenerate SnO_2 . But for the weakly doped films, only few free charge carriers are present in the bands for charge compensation.

Figure 3 summarises the observed effects in schematic band diagrams for the 4 types of samples.

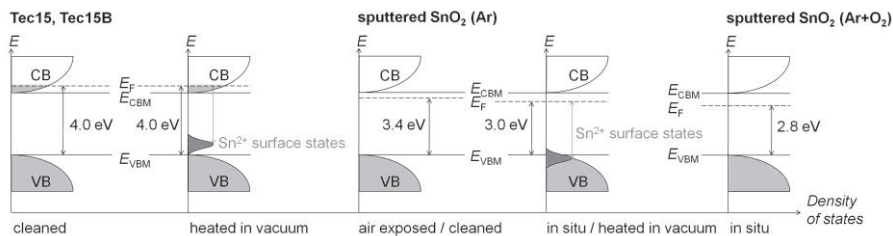


Fig. 3. Schematic energy band diagrams of the investigated samples and their dependence of the sample treatments.

4. Conclusions

Different types of SnO₂ samples were characterised by XPS. Although not doped intentionally, the commercial samples are not intrinsic. In fact, no difference could be found between the Fermi level position of the samples with (Tec15B) and without (Tec15) additional “buffer”. In contrast, sputtered SnO₂ films show Fermi level positions characteristic for weakly n-doped SnO₂. The influence of air exposure, cleaning sequence, and heating in vacuum was investigated. For all samples, annealing in vacuum leads to a reduction of the surface indicated by the formation of a Sn²⁺ surface component which results in a tail of states extended into the band gap. In the case of the degenerate commercial samples, annealing does not change the position of the onset of the VB. In the case of the sputtered sample, the Fermi level is shifted towards the CB after exposure to air and cleaning liquids; still the film remains weakly n-doped. The initial Fermi level position of the sputtered sample could be restored to its in situ appearance by annealing the film in vacuum, while the same treatment did not affect the Tec15 and Tec15B samples.

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