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N. Barreau

S. Marsillac
Old Dominion University, Smarsill@odu.edu

J. C. Bernède

L. Assmann

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Evolution of the band structure of β-$In_2S_{3-3x}O_{3x}$ buffer layer with its oxygen content

N. Barreau, S. Marsillac, J. C. Bernède,[a] and L. Assmann
LPSE, Faculté des Sciences et des Techniques, Université de Nantes, 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France

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The evolution of the band structure of β-$In_2S_{3-3x}O_{3x}$ (BISO) thin films grown by physical vapor deposition, with composition x, is investigated using x-ray photoelectron spectroscopy. It is shown that the energy difference between the valence-band level and the Fermi level remains nearly constant as the optical band gap of the films increases. As a consequence, the difference between the conduction band level and the Fermi level increases as much as the optical band gap of the films. The calculation of the electronic affinity χ of the BISO thin films shows that it decreases linearly from 4.65 to 3.85 eV when x varies from 0 to 0.14. This will facilitate fabrication of efficient Cu(InGa)Se_2-based solar cells having different absorber layer band gap. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1565823]

I. INTRODUCTION

Knowledge of the band structure of semiconductors is essential for their understanding and improvement of solar cells since the transport properties can depend on interface characteristics: potential barrier height, interfaces states, and band discontinuities. In the present work, we will focus on chalcopyrite thin-film-based solar cells. For cells with Cu(In,Ga)Se_2 absorber and CdS buffer layers, photovoltaic conversion efficiencies exceeding 18% have been achieved.[1] It has been shown that such high conversion efficiencies are facilitated in part due to a minimal conduction band offset between Cu(In,Ga)Se_2 and CdS.[2] However, from the environmental safety point of view in manufacturing settings, it would be preferable to substitute the CdS buffer layer by a different, Cd-free, material. One goal in developing such a buffer layer is to obtain minimal band offsets with absorber layers of different band gap. Moreover, the efficient CdS buffer layers are deposited onto the absorber by chemical bath deposition (CBD), whereas the other layers constituting the solar cells are grown following vacuum processes. In order to improve the large scale production of such solar cells, it would also be preferable to deposit the buffer layer by a vacuum process.

We have shown in a previous work that polycrystalline n-type β-$In_2S_{3-3x}O_{3x}$ (BISO) thin films can be grown at 200 °C by physical vapor deposition (PVD).[3] The most interesting property of these films is that their direct optical band gap linearly increases from 2.10 to 2.90 eV when x varies from 0 (pure β-In_2S_3) to 0.14. We have fabricated Cu(In,Ga)Se_2-based solar cells with a 2.90-eV BISO films and efficiencies higher than 10% have been reached.[4]

In this work, the evolution of the conduction and valence band levels when the optical band gap of the films increases is investigated. The results obtained are discussed first in terms of β-$In_2S_{3-3x}O_{3x}$ intrinsic property, then in terms of its application as buffer layer in Cu(InGa)Se_2-based solar cell.

II. EXPERIMENTAL PROCEDURE

A. The semi-direct XPS technique

The method used in the present study to estimate the valence band discontinuity is known as the semidirect x-ray photoelectron spectroscopy (XPS) technique.[5–10] In order to determine the evolution of the band structure of the BISO thin films versus x, the evolution of the valence band discontinuity ΔE_v at the interface n^+-SnO_2/n-BISO has been studied. Since SnO_2 is a highly degenerated semiconductor, its bands remain flat, and the entire band bending at the interface n^+-SnO_2/n-BISO is located in the resistive BISO film.[5] The semidirect method consists of first measuring the In 4d and Sn 4d core levels as well as the valence band maximum (VBM) E_v of the BISO and SnO_2, respectively. These values can be measured by XPS acquisitions on each kind of film deposited onto a glass substrate. The position of the In 4d and Sn 4d core levels is then determined at the interface of the heterostructure n^+-SnO_2/n-BISO. These last values are obtained from XPS acquisitions on the bilayer glass/SnO_2/BISO with a very thin BISO film, typically 2 nm. The valence band discontinuity ΔE_v, at the heterostructure interface can be calculated as

$$\Delta E_v = (E_{\mathrm{Sn}\,4d} - E_{v\,\mathrm{SnO_2}}) - (E_{\mathrm{In}\,4d} - E_{v\,\mathrm{BISO}}) - \Delta E_{\mathrm{CL}}, \tag{1}$$

where $\Delta E_{\mathrm{CL}} = E_{i\text{-}\mathrm{Sn}\,4d} - E_{i\text{-}\mathrm{In}\,4d}$ (difference between Sn 4d and In 4d at the interface SnO_2/BISO), $E_{\mathrm{Sn}\,4d}$ and $E_{\mathrm{In}\,4d}$ are the binding energies in the bulk of SnO_2 and BISO, respectively, and $E_{v\mathrm{SnO_2}}$ and $E_{v\mathrm{BISO}}$ are the valence band maximums in the bulk of SnO_2 and BISO, respectively. The conduction band discontinuity ΔE_c can then be deduced from

$$\Delta E_c = \Delta E_v - E_{g\,\mathrm{BISO}} + E_{g\,\mathrm{SnO_2}}, \tag{2}$$

[a]Electronic mail: jean-christian.bernede@physique.univ-nantes.fr

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TABLE I. XPS binding energies of the core levels and VBM of SnO_2 and BISO, and the SnO_2/BISO interface.

	Glass/SnO_2			Glass/BISO			Glass/SnO_2/BISO		
$E_{g\ \mathrm{BISO}}$ (eV)	$E_{\mathrm{Sn}\ 4d}$ (eV)	$E_{v\ \mathrm{SnO_2}}$ (eV)	$E_{\mathrm{Sn}\ 4d}-E_v$ (eV)	$E_{\mathrm{In}\ 4d}$ (eV)	$E_{v\ \mathrm{BISO}}$ (eV)	$E_{\mathrm{In}\ 4d}-E_v$ (eV)	$E_{i-\mathrm{In}\ 4d}$ (eV)	$E_{i-\mathrm{Sn}\ 4d}$ (eV)	ΔE_{CL} (eV)
2.10	27.10	3.50	23.60	18.65	1.50	17.15	18.60	26.90	8.30
2.50				18.60	1.50	17.10	18.60	26.95	8.35
2.90				18.55	1.50	17.05	18.60	27.00	8.40

where, $E_{g\ \mathrm{BISO}}$ and $E_{g\ \mathrm{SnO_2}}$ are the optical band gaps of the BISO and SnO_2 films, respectively. These values were determined by spectrophotometer measurements.[3] A band bending effect may affect the XPS spectra in the XPS probing region and thus varies ΔE_{CL}. However, when the dopant density is low, the surface band bending of the upper layer can be neglected in the XPS probing region.[6] In current work, the BISO thin films are highly resistive and it can be estimated that their density carrier is lower than $5\times10^{16}\,\mathrm{cm}^{-3}$, which is sufficiently low to neglect the band bending effect. The accuracy of this indirect method has been discussed by Chichibu *et al.*[7] and Hashimoto *et al.*[6] The XPS data acquisitions have been performed using the Mg K_α line as an x-ray source with a Leybold–Heraeus spectrometer (LHS 12) at the University of Nantes, CNRS. After subtraction of the background by the Shirley method,[9] the core level energy position was defined to be the center of the peak width at half of the peak height, which made it unnecessary to resolve the splitting of the relatively narrow Sn 4*d* and In 4*d* levels to obtain high precision peak position.[10] The accuracy of each measurement is estimated to be ±0.05 eV.

B. Thin-film growth

The process used to grow the BISO thin film has previously been reported[3] and will only be shortly described here. The process consists first of the deposition of indium and sulfur onto substrates where temperature is T_s ($20\,^\circ\mathrm{C}\leqslant T_s\leqslant200\,^\circ\mathrm{C}$). These structures are then annealed *in-situ* at 200 °C for 30 min. The oxygen content of the films (x) depends on the temperature T_s during the deposition process: the higher the T_s, the smaller the x. The values of x have been measured by microprobe analysis. The oxygen content of the BISO thin films and therefore their optical band gap (E_g) increases from 2.10 to 2.90 eV when x varies from 0 to 0.14.[3]

The substrates used were soda-lime glass and SnO_2-coated, provided by SOLEMS.[11] The electrical conductivity of the n-type SnO_2 layer is $10^2\,\mathrm{S\,cm}^{-1}$ and the carrier density is $n=10^{20}\,\mathrm{cm}^{-3}$. The optical band gap of these films is 3.90 eV. Before the deposition, the soda-lime glass substrates have been chemically cleaned as previously reported;[11] however the SnO_2 -coated glass substrates have been cleaned as follows: ultrasonification with acetone, then treatment at 80 °C with a H_2O:H_2O_2(30%):NH_4(25%) solution (5:1:1), finished by rinsing with distilled water.

III. RESULTS AND DISCUSSION

BISO films with different band gaps were deposited onto soda-lime glass and SnO_2-coated glass substrates: $E_g=2.10$ eV ($x=0$), $E_g=2.50$ eV ($x=0.07$), and $E_g=2.90$ eV ($x=0.14$). The measured binding energies of the different In 4*d* and Sn 4*d* core levels and the VBM are summarized in Table I. The absolute value of the energy has been corrected using the C 1*s* signal (C 1*s* = 284.80 eV). Figure 1(a) plots the spectrum obtained from the heterointerface SnO_2/BISO in the case of a 2.10-eV thin film. Both In 4*d* and Sn 4*d* peaks are present on the spectrum, indicating that the measurement effectively occurs at the interface. Figure 1(b) shows the XPS valence band spectrum for a 2.10-eV film deposited onto glass substrate; the measurement of the VBM by linear extrapolation of the leading edge is illustrated. From the measurements summarized in Table I, the value of ΔE_v has been calculated following Eq. (1) for each kind of BISO thin film (see Table II). The calculated values of ΔE_v are similar for all, suggesting that the substitution of sulphur atoms by oxygen atoms in the crystalline matrix of β-In_2S_3 has only a small influence on the position of the valence band level of the material.

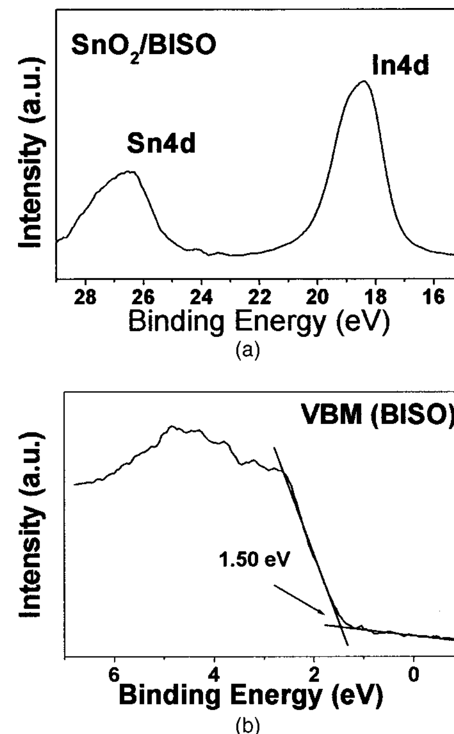

FIG. 1. (a) Illustration of the measurement of ΔE_{CL}: XPS spectrum at the interface SnO_2/BISO (case of a 2.10-eV BISO film). (b) Measurement of the VBM by linear extrapolation of the leading edge of the valence band XPS spectrum (case of a 2.10-eV BISO film).

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TABLE II. Values of the valence band (ΔE_v) and conduction band (ΔE_c) discontinuities at the interface SnO_2/BISO and of the electronic affinity (χ) of the BISO.

$E_{g\ \mathrm{BISO}}$ (eV)	ΔE_v (eV)	ΔE_c (eV)	χ (eV)
2.10	−1.85	−0.05	4.65
2.50	−1.85	−0.45	4.25
2.90	−1.85	−0.85	3.85

Robles *et al.*[12] have shown that the sulphur orbitals participate in both conduction and valence bands of β-In_2S_3. On another hand, Matar *et al.*[13] have shown that the oxygen orbitals also contribute to both conduction and valence bands of β-In_2O_3. Therefore, in the case of an increase of the optical band gap due to an electronic effect, both valence and conduction bands should shift, contrary to what we observed. Robles *et al.* have also shown that the compression of the β-In_2S_3 lattice induces an increase in its optical band gap. In the case of the BISO thin films, we have observed that the introduction of oxygen, substituted for sulphur in the crystalline matrix of β-In_2S_3, induces a decrease of its lattice parameters.[3] From these results, it seems that the increase of the optical band gap of the BISO thin films with x is not due to the presence of oxygen orbitals, but instead is simply due to the decrease of the lattice parameter induced by its introduction.

The value of the conduction band discontinuity ΔE_c for each film studied has been calculated from Eq. (2), and the values are reported in Table II. With ΔE_v being constant, one can see that ΔE_c increases linearly with x. A schematic energy-level diagram of the calculated BISO films band structure is shown in Fig. 2.

Because SnO_2 is a degenerated n-type semiconductor, its Fermi level is very close to its conduction band minimum.[5]

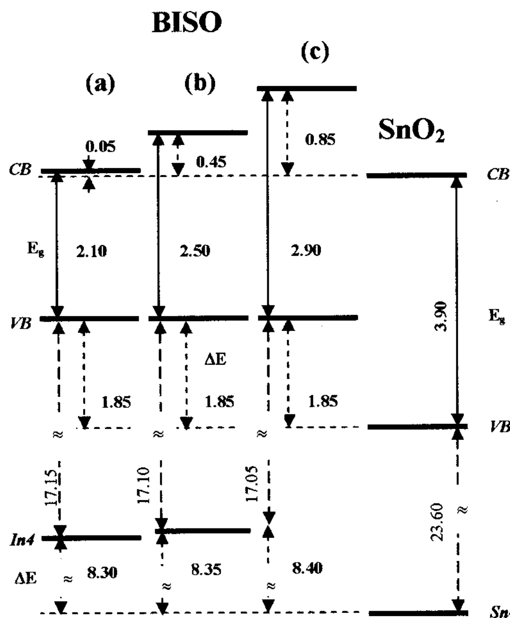

FIG. 2. Schematic energy-level diagram of SnO_2 and BISO (the values are in eV): (a) $E_g = 2.10$ eV, $x = 0$; (b) $E_g = 2.50$ eV, $x = 0.07$; (c) $E_g = 2.90$ eV, $x = 0.14$.

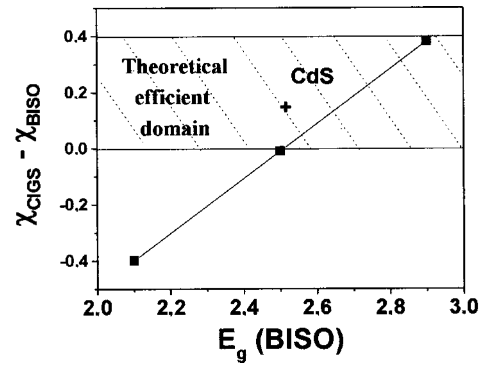

FIG. 3. Evolution of the electronic affinity difference $\chi(CuIn_{0.7}Ga_{0.3}Se_2) - \chi$(BISO) versus the optical band gap of the BISO. The value for CBD-CdS is also reported.

Therefore, it can be assumed that its electronic affinity is equal to its work function. The variation of the work function of a conductive oxide with its surface treatment has been extensively studied.[14,15] It has been shown that treatment with hydrogen peroxide, the process used here, leads to work function, that is, electronic affinity, of 4.70 ± 0.20 eV.[14] We will therefore use this value later in the discussion. The electronic affinity χ of the BISO films is then calculated by

$$\chi\,(\mathrm{BISO}) = \chi\,(SnO_2) - |\Delta E_c|. \tag{3}$$

Similarly to ΔE_c, χ (BISO) varies linearly with x. It decreases from 4.65 to 3.85 eV when x increases from 0 to 0.14.

The conduction band offset between the absorber and the buffer layer is an important parameter influencing conversion efficiency of solar cells. Minemoto *et al.*[16] have shown that for $Cu(InGa)Se_2$-based solar cells, the conduction band offset [χ (absorber) $-\chi$ (buffer)] must theoretically be between 0 and 0.40 eV to achieve high-efficiency devices. The electronic affinity of $Cu(In_{1-y}Ga_y)Se_2$ can be calculated versus y.[16] For the best cells,[1] as for the cells realized with BISO as buffer layer, y is close to 0.3, corresponding to an electronic affinity χ of about 4.25 eV. The evolution of the electronic affinity difference, $\chi(CuIn_{0.7}Ga_{0.3}Se_2) - \chi$(BISO), versus the optical band of the BISO thin film is reported in Fig. 3. One can observe in this figure that the conduction band offset between BISO and $CuIn_{0.7}Ga_{0.3}Se_2$ is well adapted when the optical band gap of the BISO thin film is between 2.50 and 2.90 eV. The value for the CBD-CdS buffer layer is also reported. Its electronic affinity corresponds to a 2.70-eV BISO film. The interests in such Cd-free BISO buffer layers compared to CdS are that they are grown by PVD (vacuum process). It is speculated if the conduction band offset between $Cu(In,Ga)Se_2$ and buffer layer is a limiting factor in solar cells efficiency, then comparable efficiency should be obtained with BISO. Experiments comparing these different buffer layers are presently under way. Furthermore, for the same conduction band offset (0.20 eV), BISO films should induce less absorption losses in the blue region due to their wider band gap.

However, the efficiencies reached with a wide band gap $Cu(InGa)Se_2$ absorber (that is, Ga/(Cu+Ga) larger than 0.5), are lower than the theoretically expected values. One of

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the reasons for the degradation of the cells performances (low open-circuit voltage and fill factor) is the conduction band offset between CdS and $Cu(InGa)Se_2$.[16,17] Effectively, the increase of gallium induces a decrease of the electronic affinity of $Cu(InGa)Se_2$. We have shown in the discussion that the electronic affinity of the BISO thin films can be controlled easily between 4.65 and 3.85 eV. It should be therefore possible to adapt the conduction band offset of the BISO/$Cu(InGa)Se_2$ heterostructure to achieve efficient solar cells.

IV. CONCLUSION

In this work, we have studied the evolution of the band structure of β-$In_2S_{3-3x}O_{3x}$ (BISO) thin films with the value of x by the semidirect XPS method. The results have shown that the increase of the material optical band gap leads essentially to a decrease of the electronic affinity, with the energy between the valence band and the Fermi level remaining constant. The electronic affinity of the BISO decreases linearly from 4.65 to 3.85 eV when x increases from 0 to 0.14. This property should make possible the control of the conduction band offset in BISO-based heterostructures. From the values obtained, it can be suggested that the most efficient solar cells based on $Cu(InGa)Se_2$/BISO heterostructure may be achieved with a 2.70-eV BISO thin film. Furthermore, the use of wide band gap BISO thin films as buffer layer may allow an improvement in the performance of high band gap $Cu(InGa)Se_2$-based solar cells due to a better conduction band offset matching.

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