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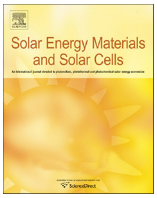

Large process-dependent variations in band alignment and interface band gaps of Cu_2ZnSnS_4/CdS solar cells

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ABSTRACT

Electron–hole recombination at the Cu_2ZnSnS_4/CdS interface is believed to play a major role in limiting the efficiency of Cu_2ZnSnS_4 solar cells. In this work, we experimentally determine detailed Cu_2ZnSnS_4/CdS interface band diagrams as a function of process conditions, and correlate them to chemical processes occurring during interface formation and subsequent post-annealing. The newly devised experimental method involves a combination of photoemission spectroscopy and spectroscopic ellipsometry. Our measurements reveal that, under most process conditions, the band gaps of both Cu_2ZnSnS_4 and CdS decrease by several hundred meV near the interface. Furthermore, interface band bending and conduction band offsets are highly process-dependent and roughly correlated to the amount of chemical interdiffusion. The interface electronic properties are found to be unfavorable under all process conditions studied in this work, either due to a cliff-like conduction band offset, or to substantial band gap narrowing in Cu_2ZnSnS_4, or to both effects. According to the present study, the least harmful process conditions for the interface electronic properties are a low CdS deposition temperature without post-annealing. Even in such a case, a minimum open circuit voltage loss of 230 mV is expected due to interface- or near-interface recombination.

1. Introduction

The Cu_2ZnSnS_4/CdS interface appears to be of crucial importance for the performance of Cu_2ZnSnS_4 (CZTS) solar cells. In fact, the open circuit voltage extrapolation to 0 K temperature, as reported by different research groups on different state-of-the-art CZTS/CdS solar cells, is consistently lower than the bulk band gap of CZTS, even when recombination from band tails in CZTS is taken into account [1–3]. The reason for this experimental finding is still debated and can be attributed, for example, to a cliff-like conduction band alignment (CBO) between CZTS and CdS [4], to band gap narrowing of ideal CZTS surfaces [5], and to interdiffusion-driven band gap narrowing of CZTS near the interface with CdS [6,7]. Even though problems with band alignment and band gap narrowing could also occur at the back contact interface (MoS_2/CZTS), recent results point to a low work function of the back contact as the main issue [8].

To further complicate the issue, the properties of the CZTS/CdS interface could in principle be influenced by growth process conditions [7]. However, process-dependent interface properties have only been studied for special cases, such as intentional Zn alloying in the CdS bulk [9], intentional Cd alloying in the CZTS bulk [3], and KCN etching of CZTS before CdS deposition [10]. One possible reason for the lack of systematic studies is the difficulty of determining the band gaps of the two materials near the heterointerface *after* interface formation. In fact, typical band alignment measurements based on direct photoemission spectroscopy can determine valence band offsets directly, but they usually rely on optical measurements of the two separate, bulk materials to determine their bulk band gaps [9,3]. They assume therefore that the bulk band gaps of the two materials are equal to their band gaps in the interface region after interface formation. Even if complementary inverse photoemission spectroscopy measurements are performed to determine the *surface* band gaps of the two separate materials [10], the real interface band gaps may still be different from the surface band gaps due to interface-related phenomena such as interdiffusion, epitaxial growth, and early-stage growth mechanisms [7]. A post-annealing treatment of the as-deposited interfaces may further enhance the differences in electronic properties between the bulk materials and their near-interface region [6] (Table 1).

In order to characterize interface band gaps after interface preparation, we perform complementary spectroscopic ellipsometry

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Table 1
Numerical values of the quantities measured in this work, which are also plotted in Fig. 7. See Fig. 1(c) for a key to the symbols.

CdS deposition T (°C)	$E_{\mathrm{vb,CZTS}}$ (eV)	$E_{\mathrm{vi,CZTS}}$ (eV)	$E_{\mathrm{vb,CdS}}$ (eV)	$E_{\mathrm{vi,CdS}}$ (eV)	VBO (eV)	$E_{\mathrm{gb,CZTS}}$ (eV)	$E_{\mathrm{gi,CZTS}}$ (eV)	$E_{\mathrm{gb,CdS}}$ (eV)	$E_{\mathrm{gi,CdS}}$ (eV)	**CBO (eV)**
As deposited CdS										
55	0.50	0.90	2.10	1.88	0.98	1.56	1.56	2.33	2.30	**− 0.24**
75	”	0.80	”	1.82	1.02	1.41	1.31	”	2.31	**− 0.02**
95	”	0.66	”	1.78	1.12	1.54	1.35	”	2.26	**− 0.21**
Post-annealed CdS										
55	0.50	0.73	2.10	1.67	0.94	1.56	1.33	2.33	2.27	**+0.00**
75	”	0.64	”	1.74	1.10	1.58	1.33	”	2.27	**− 0.16**
95	”	0.55	”	1.73	1.18	1.54	1.45	”	2.17	**− 0.46**

measurements on CTZS/CdS film stacks. The ellipsometry spectra are sensitive to changes in the optical functions of the materials perpendicularly to the substrate plane; thus a band gap gradient in the out-of-plane direction can be detected by fitting the ellipsometry spectra to an appropriate multi-layer optical model [11,12]. Complete interface band diagrams can then be drawn by combining the measured interface band gaps with the valence band offsets measured by x-ray photoemission spectroscopy. The goal of this paper is to determine those interface band diagrams as a function of process conditions, and correlate them to interfacial chemical processes.

2. Experimental details

CZTS thin films (about 100 nm thick) were deposited on a soda lime glass substrate by pulsed laser deposition from a single stoichiometric CZTS target, tuning the laser fluence to obtain the desired Cu-poor, Zn-rich composition as described previously [13]. Deposition of the typical Mo back contact was omitted in order to limit the number of free parameters necessary for fitting ellipsometry spectra [11]. The CZTS films are thinner than in typical solar cells in order to keep their roughness low. This precaution is important because high surface roughness can depolarize the incident beam used in the ellipsometry measurement and render subsequent analysis impossible [14,15,11]. With such thin films, there is a risk that interdiffusion from CdS into CZTS might occur over the full absorber thickness. However, it will be shown later in this paper that the depth of elemental interdiffusion into CZTS is only tens of nm, in agreement with previous studies [7]. The possibly higher Na concentration in 100 nm-thick CZTS compared to thicker absorbers deposited on Mo-coated glass is not expected to significantly alter the optoelectronic properties, because the effects of Na incorporation into CZTS depend on Na concentration only below a certain concentration threshold (about 10^{19} cm^{-3}), which has to be achieved in order to obtain efficient solar cells [16]. The as-deposited CZTS films were post-annealed in a sulfur-containing atmosphere at 550 °C for 10 min. Additional process details and film characterization are available elsewhere [13]. CdS thin films (20–40 nm) were deposited on CZTS by chemical bath deposition at 55 °C, 75 °C, and 95 °C on nominally identical glass/CZTS substrates. The solvent for CdS deposition was milli-Q water, the Cd source was 1.5 mM CdSO$_4$, and the sulfur source was 70 mM thiourea. To prevent homogeneous Cd(OH)$_2$ precipitation, an ammonia solution was added to the bath as a complexing agent. 1.7 M, 2.0 M and 2.4 M ammonia was used at 55, 75, and 95 °C deposition temperature respectively, in order to account for the increasing OH$^-$ concentration with increasing temperature and thus keep deposition rate roughly constant with temperature [17]. If the ammonia content is not adjusted at the different deposition temperatures, the resulting higher rate of homogeneous precipitation at higher temperature may have a stronger influence on the interface properties than the increase in temperature itself [17]. In order to avoid temperature transients in the deposition, thiourea was only added after the solution reached the desired temperature. A deposition time around 5 min yielded CdS films of 31 nm average thickness, with 8 nm standard deviation across samples. After CdS deposition, each of the three samples was cut in two halves, and one half of each sample was further annealed at 300 °C for 20 min in Ar, as reported previously [6]. This yielded a total of six samples for interface electronic characterization. Note that the CZTS bulk in one of the six samples is more Cu-rich than what was intended. This could be due to the reproducibility issues of PLD discussed in [13] or to the dependence of film composition on the exact position of the substrate in the PLD chamber. The three samples that were not post-annealed will be denoted “as-deposited” in the following.

Variable-angle spectroscopic ellipsometry measurements were performed to obtain the CZTS band gap in the bulk $E_{\mathrm{gb,CZTS}}$, and the CZTS (CdS) band gaps near the interface $E_{\mathrm{gi,CZTS}}$ ($E_{\mathrm{gi,CdS}}$) as shown in Fig. 1(a). The measurement was performed with a rotating compensator

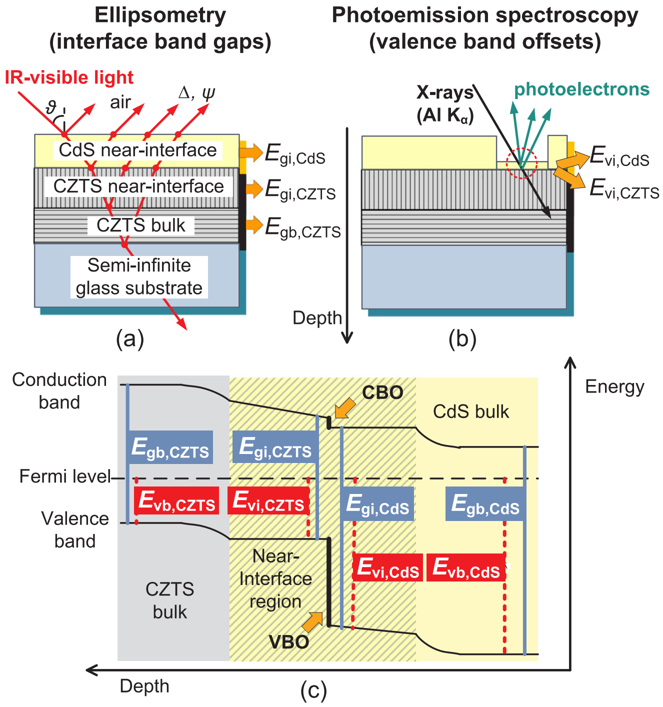

Fig. 1. (a): Scheme of the optical model employed to extract band gaps by fitting ellipsometry spectra $\Psi(E)$ and $\Delta(E)$. The CZTS layer is split into sub-layers of equal thickness with independent band gaps. (b): Scheme of the XPS measurement employed to determine the valence band energy with respect to the Fermi level at different depths. The depth resolution is achieved by alternating an ion beam etching step with a photoemission measurement step. An additional output of the measurement is the depth-dependent chemical composition of Cd, Cu, Zn, Sn, S. (c): Key to interpret the interface band diagrams plotted in this study. The quantities colored red (blue) are obtained by the XPS (ellipsometry) measurement. More details about the experimental method are available elsewhere [12]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).