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Evaluation of different intrinsic ZnO and transparent conducting oxide layer combinations in Cu(In,Ga)Se₂ solar cells

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ABSTRACT

We studied the interaction of four different window layer combinations in Cu(In,Ga)Se₂ solar cells. Intrinsic ZnO (i-ZnO) layers were grown on CdS by either chemical vapor deposition (CVD) or magnetron sputtering. These were combined with sputtered ZnO:Al or In₂O₃:H grown by atomic layer deposition as transparent conducting oxides (TCO). It was found that the thickness of the CVD i-ZnO layer affects the open circuit voltage (V_{oc}) significantly when using In₂O₃:H as TCO. The V_{oc} dropped by roughly 30 mV when the i-ZnO thickness was increased from 20 to 160 nm. This detrimental effect on V_{oc} was not as prominent when a ZnO:Al TCO was used, where the corresponding decrease was in the range of 5 to 10 mV. In addition, the V_{oc} drop for the CVD i-ZnO/In₂O₃:H structure was not observed when using the sputtered i-ZnO layer. Furthermore, large fill factor variations were observed when using the In₂O₃:H TCO without an i-ZnO layer underneath, where already a thin (20 nm) CVD i-ZnO layer mitigated this effect. Device simulations were applied to explain the experimentally observed V_{oc} trends.

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1. Introduction

The state-of-the-art Cu(In,Ga)Se₂ (CIGS) solar cells are normally manufactured by using the conventional CdS/i-ZnO/n-ZnO buffer-window stack. Efficiencies above 21% have been reached with this structure [1,2]. Magnetron sputtered ZnO:Al (AZO) is often used because of a low manufacturing cost while high conversion efficiencies can be achieved [3]. However, ZnO:Al exhibits quite low mobility that makes high doping a requirement in order to reach low resistivity. This high doping level results in a parasitic free charge carrier absorption, which encouraged the introduction of new transparent conducting oxide (TCO) materials during the past decade. Recently, the potential of In₂O₃:H (IOH) as high mobility TCO layer has been demonstrated, and an increased short circuit current density (J_{sc}) for CIGS solar cells was reported [4].

The function of the i-ZnO layer has been the focus of numerous reports [5–8]. Nevertheless, it is hard to see strong systematic trends on how the i-ZnO thickness affects the device performance. Furthermore, the i-ZnO process has shown to behave differently with alternative buffer materials [9,10]. No studies on the effect of the i-ZnO layer thickness when In₂O₃:H films are used as a TCO have yet been reported.

In this work, we studied the interaction of i-ZnO layers grown by chemical vapor deposition (CVD) and by radio frequency magnetron sputtering (PVD), in combination with two different TCO materials, namely sputtered ZnO:Al and In₂O₃:H grown by atomic layer deposition

(ALD). Complementary SCAPS-1D [11] simulations, applying a rudimentary model, was used to explain the experimental observations.

2. Methods

2.1. Experimental details

The solar cell devices investigated in this study had a SLG/Mo/CIGS/CdS/i-ZnO/TCO layer structure, where i-ZnO was deposited by either CVD or sputtering and the TCO material was either ALD In₂O₃:H or sputtered ZnO:Al. All CIGS absorber films originate from a single deposition, made by an inline co-evaporation process at Solibro Research AB, which resulted in a 2.0 μm thick absorber with an average composition of [Cu]/([In] + [Ga]) = 0.83 and [Ga]/([In] + [Ga]) = 0.43 as determined by X-ray fluorescence spectrometry (Epsilon 5, Panalytical). The absorbers are graded and the surface gallium content yields a surface band gap close to 1.2 eV, which is commonly used. The CIGS had been capped with CdS immediately after deposition to avoid oxidation of the surface. This capping layer was etched off, by immersion for 1 min in 2 M HCl, before a new CdS buffer layer was deposited using the current ÅSC baseline process [12].

Both the ALD In₂O₃:H and CVD i-ZnO were performed in an F-120 ALD reactor (ASM Microchemistry). N₂ was used as carrier gas in both processes. The In₂O₃:H layer was deposited at 145 °C, and the precursors used were cyclopentadienylindium(I) [In(C₅H₅) or InCp] and a mixture of deionized water and oxygen gas. For further details we refer to Refs. [4,13]. In this study, 1600 cycles were used for all In₂O₃:H depositions,

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resulting in a layer thickness of around 160 nm. In the thermally activated CVD ZnO process, layers were deposited at 95 °C from diethylzinc [Zn(C₂H₅)₂ or DEZ] and water. This process yields a growth rate of 14 nm/min, at the given temperature, and the CVD i-ZnO thickness was varied between 0 and 370 nm. Further details on the CVD process can be found in Ref. [14].

Radio frequency magnetron sputtering of i-ZnO (*d* = 0–390 nm) and ZnO:Al (*d* = 225 nm) were performed by using a Von Ardenne sputtering system. No external heating or supply of oxygen gas was added during the deposition.

The resistivity of the individual window layer films was determined by measuring the sheet resistivity using an automatic four point probe stage (CMT-SR2000N, Advanced Instrument Technology). The i-ZnO thicknesses were determined by X-ray fluorescence spectrometry (Epsilon 5, Panalytical), calibrated by profilometry (Dektak 150, Veeco).

Illuminated current density-voltage (J-V) measurement was performed on each cell, using a tungsten halogen lamp as light source at a sample temperature of 25 °C. From these measurements, the *J*_{sc}, open circuit voltage (*V*_{oc}), fill factor (*FF*) and conversion efficiency (*η*) were extracted. The external quantum efficiency of each sample variation was measured in a custom-built system to calibrate the light intensity of the J-V measurements to correct for the spectral mismatch.

2.2. Modelling

The software SCAPS (version 3.3.02) was used for electrical modeling. A simple model was created, consisting of a linearly graded CIGS layer with bulk defects concentrated near the interface. Interface defects were placed mid-gap, in order to enable single-level recombination near the interface. The CdS layer doping concentration was chosen so that the depletion region extends into the intrinsic layer. The doping concentration and thickness of the i-ZnO layer were varied to reproduce the experimental trends. Lastly, TCO properties were set constant and correspond to commonly used values for ZnO:Al. The used input values are listed in Table 1.

3. Results and discussion

It was found that i-ZnO thickness could significantly affect *V*_{oc}, depending on the combination of layers in the window layer structure. This can be seen in Fig. 1, which presents the best *V*_{oc} values from

Table 1

Material parameters used in the SCAPS-1D simulations. *d* is the layer thickness, *E*_g is the band gap, *χ* is the electron affinity, *ε*_r is the relative permittivity, *N*_{doping} is the doping density, *N*_C and *N*_V are the effective density of states in the conduction band and valence band respectively, *v*_{th} is the thermal velocity for electrons and holes, *N*_{defect} is the neutral defect density, and *σ*_e and *σ*_h are the capture cross section for electrons and holes respectively.

Property	CIGS	CIGS/CdS interface	CdS	i-ZnO	TCO
<i>d</i> (nm)	2000	–	50	Varied	400
<i>E</i> _g (eV)	1.3–1.1 ^(LG)	–	2.4	3.4	3.3
<i>χ</i> (eV)	4.3–4.5 ^(LG)	–	4.2	4.35	4.45
<i>ε</i> _r	13.6	–	10	9	9
<i>N</i> _{doping} (cm ⁻³)	2 · 10 ^{16(A)}	–	4.5 · 10 ^{16(D)}	Varied	10 ^{20(D)}
<i>N</i> _C (cm ⁻³)	2.2 · 10 ¹⁸	–	2.2 · 10 ¹⁸	2.2 · 10 ¹⁸	2.2 · 10 ¹⁸
<i>N</i> _V (cm ⁻³)	1.8 · 10 ¹⁹	–	1.8 · 10 ¹⁹	1.8 · 10 ¹⁹	1.8 · 10 ¹⁹
<i>v</i> _{th} (cm/s)	10 ⁷	–	10 ⁷	10 ⁷	10 ⁷
<i>N</i> _{defect} (cm ⁻³)	10 ¹⁰ –10 ^{14(PG)}	4 · 10 ¹⁴	10 ¹⁷	10 ¹⁶	10 ¹⁶
<i>σ</i> _e (cm ²)	10 ⁻¹³	10 ⁻¹⁵	10 ⁻¹³	10 ⁻¹²	10 ⁻¹²
<i>σ</i> _h (cm ²)	10 ⁻¹⁵	10 ⁻¹⁵	10 ⁻¹³	10 ⁻¹²	10 ⁻¹²

^(LG)Linear gradient.

^(PG)Parabolic gradient with highest density at CIGS/CdS interface.

^{(A)/(D)}Acceptor/donor type doping.

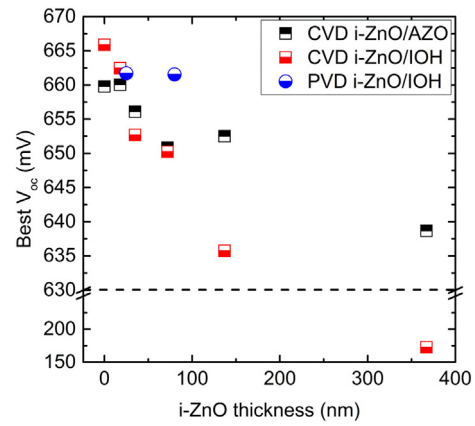


Fig. 1. Best *V*_{oc} values for different i-ZnO thicknesses. Different trends are observed for different combination of layers in the window structure.

each i-ZnO thickness, for different i-ZnO/TCO combinations. In addition, all extracted J-V parameters can be found in Table 2. For CVD i-ZnO/In₂O₃:H, a significant decrease in *V*_{oc} was observed with increasing thickness of the CVD i-ZnO layer. The best *V*_{oc} dropped by 27 mV when the i-ZnO thickness was increased from 20 to 160 nm. This detrimental effect on *V*_{oc} was not as prominent when a ZnO:Al TCO was used, in which case the corresponding decrease is in the range of 5–10 mV. The difference between the TCO layers in terms of *V*_{oc} becomes pronounced for very thick CVD i-ZnO films. The *V*_{oc} dropped with only 21 mV for ZnO:Al when the CVD i-ZnO thickness was increased to 370 nm, while the cells with In₂O₃:H merely showed a weak diode behavior. However, no significant *V*_{oc} change was observed when a sputtered i-ZnO layer was used, for neither of the TCO choices. The results for sputtered i-ZnO/ZnO:Al are not shown in Fig. 1 because a different CdS layer was used.

The average and best fill factor values for different CVD i-ZnO thicknesses when using the ALD In₂O₃:H TCO are shown in Fig. 2. Lower and more varying fill factors were observed when using the ALD In₂O₃:H TCO deposited directly on the buffer layer, with no i-ZnO layer in-between. Possibly due to shunting paths created by In₂O₃:H deposited in CdS pin holes, which is likely due to the high conformality of ALD. However, only a thin (20 nm) CVD i-ZnO layer was needed to ensure low variations in fill factor. The *FF* decrease observed for thicker i-ZnO layers are due to the shift of the J-V curve to lower *V*_{oc} values [15].

Quite large *J*_{sc} variations were observed between the different samples. This was partly due to a shift in reflection fringes due to varying layer thicknesses. However, this effect would be mitigated in an encapsulated module. More relevant are differences caused by parasitic absorption. In this study, it is again shown that *J*_{sc} increases when using the high mobility ALD In₂O₃:H TCO, as was previously reported [4,16]. Similarly, parasitic absorption occurs in the i-ZnO layer. Our CVD i-ZnO has a slightly higher optical band gap than our sputtered equivalent, resulting in lower absorption in the high wavelength region [14]. Consequently, the CVD i-ZnO/In₂O₃:H window layer combination is predicted to yield the highest current density in this study. The best cell produced was with this constellation, and had conversion efficiency of 16.2%.

The possibility that diffusion of species to or from the interface region was the cause to the *V*_{oc} drop was considered. However, it is deemed unlikely that it is the case, because of the low ZnO growth temperature of 95 °C. In addition, control experiments were performed and show that the *V*_{oc} drop was not inflicted by annealing effects in the ZnO CVD or In₂O₃:H ALD processes. Instead, the bulk properties of the different layers must be considered, in order to understand the observed *V*_{oc} decrease.

The resistivity measurements showed that the sputtered i-ZnO films have a resistivity of 0.6 Ω cm, while the resistivity of the CVD grown i-

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