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Zn(O,S) Buffer Layers and Thickness Variations of CdS Buffer for $\text{Cu}_2\text{ZnSnS}_4$ Solar Cells

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Abstract—To improve the conduction band alignment and explore the influence of the buffer-absorber interface, we here investigate an alternative buffer for $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) solar cells. The Zn(O,S) system was chosen since the optimum conduction band alignment with CZTS is predicted to be achievable, by varying oxygen to sulfur ratio.

Several sulfur to oxygen ratios were evaluated to find an appropriate conduction band offset. There is a clear trend in open-circuit voltage (V_{oc}), with the highest values for the most sulfur rich buffer, before going to the blocking ZnS, whereas the fill factor peaks at a lower S content. The best alternative buffer cell in this series had an efficiency of 4.6% and the best CdS reference gave 7.3%.

Extrapolating V_{oc} values to 0 K gave activation energies well below the expected band gap of 1.5 eV for CZTS, indicating that recombination at the interface is dominating. However, it is clear that the values are affected by the change of buffer composition and that increasing sulfur content of the Zn(O,S) increases the activation energy for recombination.

A series with varying CdS buffer thickness showed the expected behavior for short wavelengths in QE measurements but the final variation in efficiency was small.

Index Terms—current-voltage characteristics, $\text{Cu}_2\text{ZnSnS}_4$, kesterite, photovoltaic cells, Zn(O,S) buffer.

I. INTRODUCTION

The solar cell material $\text{Cu}_2\text{ZnSn(S,Se)}_4$ (CZTSSe) is a possible alternative to the commercially available Cu(In,Ga)Se_2 (CIGS). CZTSSe does not contain indium or gallium, and could therefore be a cheaper and more sustainable solar cell material for the future. Promising efficiencies of up to 11.1 % have been achieved [1], but more research is needed to understand what is preventing the devices from being as efficient as CIGS, which has record efficiencies just over 20%.

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Several causes for the lower performance have been proposed, such as a $\text{MoSe}_2/\text{MoS}_2$ layer at the back contact [2], secondary phases in the bulk [3], lack of shallow acceptors [4] and a non-favorable alignment of the conduction band at the absorber-CdS buffer interface [5].

To try to improve the conduction band alignment and to explore the influence of the buffer-absorber interface, we here investigate an alternative buffer for $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) solar cells. The Zn(O,S) system was chosen since it has been shown that the conduction band in this material can be changed by varying the ratio of oxygen to sulfur [6], and that the optimum conduction band alignment for CZTS should lie in between the ZnO and the ZnS values, see also Fig. 1. Pure ZnO is expected to give a negative conduction band offset with CZTS and has also been shown to give working devices on both CZTS and CZTSSe [7]-[8]. ZnS should, according to theory [9], cause current blocking due to a high barrier, which has also been observed in experiments [8].

In addition to studying the Zn(O,S) buffer, we performed a small optimization of the CdS buffer thickness on our absorbers. This could also give additional input to understanding the heterojunction formation on CZTS.

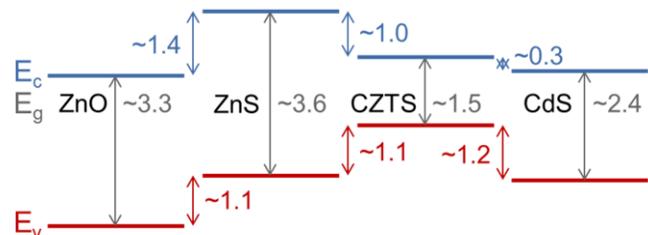


Fig. 1. Approximate conduction band offsets, valence band offsets and band gaps, derived from [5], [6] and [8] (values are in eV). The type of the CZTS-CdS conduction band offset is still disputed in the literature, it is shown here as a cliff, following [5]. ZnS forms a barrier towards CZTS and ZnO has a negative conduction band offset with CZTS. The conduction band position of Zn(O,S) has been shown to vary with the oxygen to sulfur ratio [6], so at an intermediate composition it is likely that the conduction band offset with CZTS is optimal.

II. EXPERIMENTAL

The Mo back contact was sputtered onto soda-lime glass substrates. The absorber was then reactively sputtered in H_2S using Zn and Cu:Sn (65:35) alloy targets as described in detail

in [10]. The sputtering time was 50 min, giving thicknesses around 2 μm . The precursors had Cu/Sn-ratios of 1.91-1.94 and were slightly Zn-rich with Zn/(Cu+Sn) equal to 0.39-0.40, as determined by X-ray fluorescence calibrated with Rutherford back scattering (RBS) measurements. The sulfur content was approximately 50 % according to energy-dispersive spectroscopy (EDS).

The precursors were annealed together with 20 mg sulfur in a small graphite box inside a tube furnace under a static argon atmosphere (35 kPa) at 560-565°C for 10 minutes. Due to limitations of sample size, the composition after annealing could not be measured for every piece, however, EDS measurement of a dedicated sample showed that the Cu/Sn ratio becomes 2.0, in agreement with our earlier results [11], and that the Zn/(Cu+Sn)-ratio is not changed.

The samples were etched in 5 wt% KCN solution for 120 s, rinsed in deionised water and then quickly transferred to either chemical bath deposition (CBD) of CdS or to the atomic layer deposition (ALD) system for deposition of Zn(O,S). The ALD was performed at 120 °C in our home-built system called MP3 described in [12], using diethyl zinc (DEZ) as the Zn precursor, H₂O as the O precursor and H₂S as the S precursor. The buffer composition was varied by changing the number of cycles of DEZ/N₂/H₂O/N₂ versus DEZ/N₂/H₂S/N₂ in the ALD process. This is also how the buffer samples are named: for example, the buffer Zn(O,S)4:1 completes four DEZ/N₂/H₂O/N₂ cycles for every DEZ/N₂/H₂S/N₂ cycle (note that this naming convention differs from some of our previous articles about Zn(O,S) buffer layers for CIGS). A total of 70 cycles was completed for each of the different buffers. For the buffer composition Zn(O,S)6:1, a sample with twice the number of cycles was also prepared.

Samples were prepared on 25 mm \times 25 mm substrates. To ensure that the differences observed indeed come from the change of buffer layer, a part of each sample was cut off and processed with the normal CBD CdS buffer. The CBD solution comprised of 1.1 M ammonia, 0.100 M thiourea, and 0.003 M cadmium acetate. The samples were kept in the solution for 8 min and 15 s at 60 °C, yielding a CdS film thickness of about 50 nm. In the CdS-thickness series, a sample with thinner CdS was produced by shortening the time to 6 min, which is predicted to give roughly half the thickness. For the samples with thick CdS, the CBD procedure was repeated a second time directly after the first, which is expected to give roughly double the thickness of the normal process.

The transparent front contact was deposited with RF-sputtering and consists of a thin intrinsic ZnO and a thicker Al-doped ZnO layer. For one of the samples with double CdS buffer thickness, the intrinsic ZnO was omitted.

The samples were characterized using an I-V-T setup with LED illumination and temperatures from 100 K to 330 K. Biased and unbiased quantum efficiency (QE) measurements were made in a setup calibrated by externally measured Hamamatsu Si and InGaAs solar cells. For certain samples, electron beam induced current (EBIC) and transmission

electron microscopy (TEM) were performed according to the methods described in [13].

Zn(O,S) layers on glass substrates, deposited in the same run as the buffer layers for the solar cells, were further investigated with X-ray reflectivity (XRR) and grazing incidence X-ray diffraction (XRD) in a Philips X'pert MRD diffractometer. The composition of the buffers on the glass substrates was measured with RBS with a 2 MeV He⁺-beam and a backscattering angle of 170°.

TABLE I
PROPERTIES OF THE Zn(O,S) BUFFERS

Sample name	Buffer	Thickness (XRR) [nm]	Density (XRR) [g/cm ³]	S/Zn (RBS)
B	Zn(O,S) 9:1	16	5.3	0.2
C	Zn(O,S) 6:1 T	33	4.8	0.3
C1	Zn(O,S) 6:1	16	4.5	0.3
D	Zn(O,S) 4:1	16	4.6	0.5

III. RESULTS AND DISCUSSION

A. Zn(O,S) buffer composition variation

For the alternative buffer system, several sulfur to oxygen ratios were evaluated to find an appropriate conduction band offset. The resulting S/Zn-ratios, measured by RBS on glass substrates, are presented in Table I. The oxygen content cannot be determined with this measurement and therefore the ratio can only be given with the precision presented in the table. The peak positions from XRD reflect the sample composition, as described in [6], and agree relatively well with our previous measurements on this buffer layer [14]. Measurements with XRR show that the thicknesses of the buffers on glass are the same for the different compositions and the densities are in the expected range (bulk densities being 5.6 g/cm³ for ZnO and 4.1 g/cm³ for ZnS). Doubling the number of ALD cycles roughly doubles the thickness, as seen when comparing sample C and C1. Sample C was also investigated by TEM and thickness measurements with this technique gave 30 \pm 3 nm which agrees well with the value from XRR.

Varying the composition of the Zn(O,S) buffer layer indeed has a large influence on the electrical properties of the cells, as seen in Table II and Fig. 2. Pure ZnS, as expected, blocks the current, and pure ZnO gives low open-circuit voltage (V_{oc}) values, probably due to a too large negative conduction band offset. The intermediate compositions have a clear trend in V_{oc} , with the highest values for the most sulfur-rich buffer. The currents also show the same, although weaker, trend. The parameter which limits the efficiency for the sulfur rich buffer Zn(O,S)4:1 is the fill factor (FF) which is only 42 % compared to 56% for the best alternative buffer, Zn(O,S)6:1.

Shunting seems to increase with higher oxygen content in the buffer. For the Zn(O,S)6:1 buffer, an increased layer thickness was tested in an attempt to decrease the shunt. This

TABLE II
SOLAR CELL PERFORMANCE FOR SAMPLES WITH VARYING Zn(O,S)-BUFFER LAYER COMPOSITION

Sample name	Buffer	V_{oc} [V]		J_{sc} [mA/cm ²]		FF [%]		Eff. [%]	
		Best	Avg.	Best	Avg.	Best	Avg.	Best	Avg.
A	ZnO	0.152	0.14	14.8	14.0	38.3	36.7	0.9	0.7
B	Zn(O,S) 9:1	0.348	0.26	16.4	15.2	42.6	34.2	2.4	1.5
C	Zn(O,S) 6:1 T	0.482	0.47	17.2	17.0	55.5	50.7	4.6	4.1
C1	Zn(O,S) 6:1	0.461	0.46	17.2	17.1	51.0	50.8	4.1	4.0
D	Zn(O,S) 4:1	0.598	0.55	17.8	17.7	42.4	41.8	4.5	4.0
E	ZnS	0.065	0.05	1.1	1.3	27.0	26.9	0.0	0.0
Ref	CdS	0.652	0.62	17.5	16.4	63.8	57.8	7.3	6.1

seemed to improve FF and V_{oc} slightly, see Table II. However, the shunt conductance, extracted from the dark JV curve by the method described in [15], was only improved from 2.5 to 1.9 mS/cm² for the best cells. Nevertheless, the thicker Zn(O,S)6:1 buffer, denoted T, yielded 4.6% in efficiency which was the highest value for the alternative buffers investigated, and is therefore the sample included in the more detailed measurements and results given here. The CdS reference samples for the complete series gave efficiencies between 4.5-7.3%.

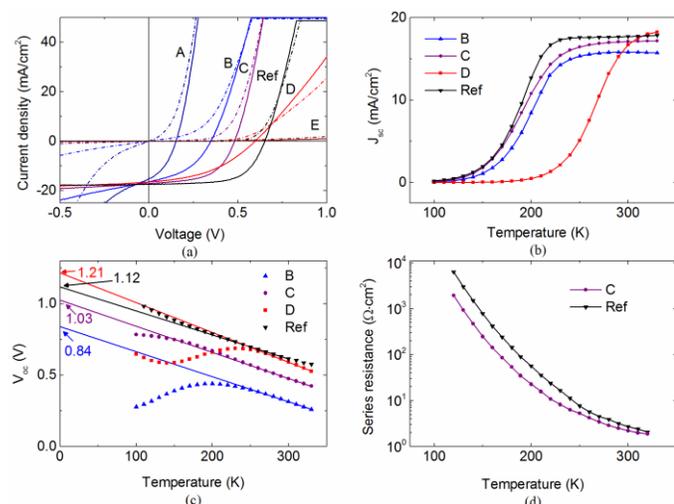


Fig. 2. a) JV-measurements on samples with different buffer layers, b) Short circuit current vs. T, c) Open circuit voltage vs. T and linear extrapolations to 0 K, d) Series resistance from fitting of JV-curves to a one-diode model. Sample names according to Table II.

Looking at JV-curves at different temperatures we notice that the Zn(O,S)4:1 sample is strongly affected by temperature variations already around room temperature. As seen in Fig. 2b), the other samples have a constant short circuit current density (J_{sc}) from 330 K to around 240 K, which then starts decreasing. The Zn(O,S)4:1 sample loses current already between 330 and 320 K. The low FF for this buffer together with the sensitivity to decreased temperature suggests that there is a barrier at the interface. Additionally, it has earlier been suggested that these buffer layers are slightly inhomogeneous both in depth and over the area [14]. The area inhomogeneity together with the sensitivity in the band

alignment could mean that an optimum alignment is found in some areas whereas other areas have a too high barrier and block the current unless the temperature is high.

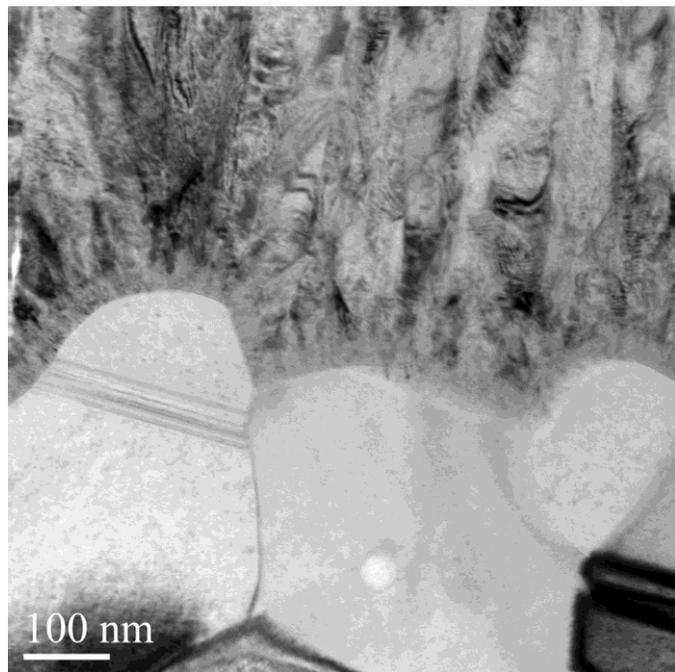


Fig. 3. Bright field TEM image of a cross section of sample C. The CZTS grains are seen in the lower part of the image. On top are first the buffer layer and then the ZnO window layer.

Plotting the V_{oc} against the temperature should yield the activation energy of the dominant recombination path when extrapolated to 0 K. This is described in for example [15], and can be seen in (1), where E_A is the activation energy, q is the elemental charge, A is the diode ideality factor, k is the Boltzmann constant, T is the temperature, J_{00} is the saturation current prefactor and J_L is the photocurrent density.

$$V_{oc} = \frac{E_A}{q} - \frac{AkT}{q} \ln\left(\frac{J_{00}}{J_L}\right) \quad (1)$$

As seen in Fig. 2c), the extrapolations show an increase in activation energy with increasing sulfur content of the Zn(O,S) buffer, but the E_A values are still well below the expected band gap value of 1.5 eV.

TABLE III

SOLAR CELL PERFORMANCE FOR SAMPLES WITH VARYING CdS-BUFFER LAYER THICKNESS (PROPERTIES OF THE BEST CELL GIVEN)

Sample name	CdS thickness	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	Eff. [%]
X	Thin	0.619	16.2	62.9	6.3
Xref	Normal	0.652	15.1	59.3	5.8
Y	Double	0.657	14.2	58.7	5.5
Yref	Normal	0.646	15.5	58.9	5.9
Z	Double (no i-ZnO)	0.638	14.8	66.3	6.2
Zref	Normal	0.657	16.0	62.3	6.5

This indicates that the band alignment for this buffer can be changed by the oxygen to sulfur ratio, also on the CZTS absorber, but that interface recombination is still dominant, possibly both due to defects and a still non-ideal band alignment.

Investigating the interface of the Zn(O,S)6:1 T sample with TEM (bright field in Fig. 3, and high resolution imaging), no obvious causes for bad electrical performance can be seen. The buffer conformally covers the CZTS grains and the crystallinity at the interface seems high. Also TEM-EDS across the interface shows a sharp interface without neither clear gradients across the buffer layer, nor diffusion of elements between the buffer and absorber.

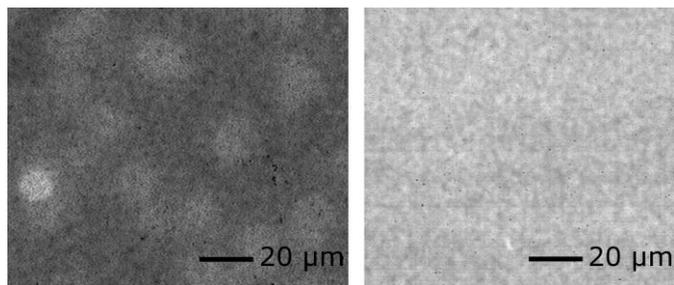


Fig. 4. EBIC on sample C (left) and CdS reference (right).

EBIC was performed on the Zn(O,S)6:1 T sample and the respective CdS reference. Both samples have an intensity variation on the level of the CZTS grain size. Additionally, there is an inhomogeneity on a larger scale for both samples, but, as can be seen in Fig. 4, it is different in shape and size. A TEM comparison between the dark and bright areas seen in the EBIC image, on the Zn(O,S)6:1 T sample, showed no clear differences in thickness, composition or morphology between the regions.

Trying to fit the JV-curves according to a one-diode model is dubious due to the non-ideal behavior especially at lower temperatures. However, the CdS reference and the best alternative buffer, the double-thickness Zn(O,S)6:1, give fairly reasonable fits. Interestingly, we see that the increase in series resistance for low temperatures, also seen by others [2], is similar for these two buffer layers, Fig. 2d), indicating that either the two different buffers cause a similar problem, or that the origin of the high series resistance at low temperatures is not the buffer.

Negatively biased QE measurements for the CdS buffer samples gave an increased collection for the long wavelength

photons; this is further discussed in the next section. The sample with Zn(O,S)4:1 buffer instead shows an increased QE for all wavelengths at -0.5 V, with only slightly more increase for long wavelengths, see Fig. 5.

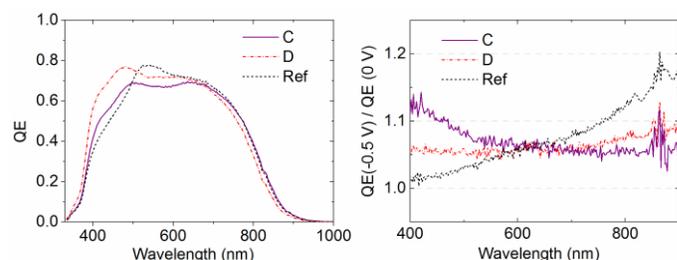


Fig. 5. Left: QE-measurements on samples with different buffer layers. Right: Ratio between negative biased (-0.5 V) QE and unbiased QE. Sample names according to Table II.

An explanation for this could be a photocurrent barrier at the buffer-absorber interface, in agreement with the low FF discussed above. For the Zn(O,S)6:1 T and Zn(O,S)6:1 samples, there is instead an additional increase of collection towards the short wavelength side. This could originate from the negative bias decreasing interface recombination of holes generated in the top part of the absorber and in the buffer [16].

B. CdS buffer thickness variation

The results from the CdS buffer thickness series are presented in Table III and Fig. 6, together with their respective references, which were taken from the same precursor and annealing run but processed with the standard CdS and window layers. As seen in Fig. 6, the QE signal behaves as expected for the different thicknesses, with higher response at the low wavelength side for the sample with a thin buffer and a decreased level for the samples with thick CdS buffer. The long wavelength part of the QE curve looks similar for the different samples, but the solar cell with thickest total window layer (double CdS and including i-ZnO) has a generally lower QE.

When comparing the QE measured without bias with the QE measured at -0.5 V, all samples show an increase in collection for the long wavelengths with negative bias. Such behavior was reported earlier for this material combination, for example in [2], and is usually explained by poor collection towards the back of the absorber [16], possibly due to short diffusion lengths in combination with a narrow space charge region. The behavior is very similar between the different

thicknesses of buffer layer which could indicate that the Fermi level at the interface is pinned by interface states.

The V_{oc} is slightly reduced for the thinnest CdS thickness. Comparing the thick CdS sample (Y) to its own reference also shows this trend, but when comparing to the reference samples in general there is no difference between the normal and the double thickness. A general increase of V_{oc} with increasing CdS thickness was seen in [17] for thicknesses from roughly 30 to 300 nm on monograins of CZTS, whereas the opposite trend was seen in [18], but no thickness range was given in the latter case.

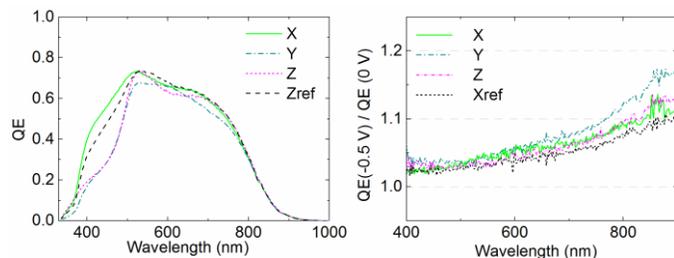


Fig. 6. Left: QE-measurements on samples with different thickness of the CdS buffer layer. Right: Ratio between negatively biased (-0.5 V) QE and unbiased QE. Sample names according to Table III.

We note that the fill factor (FF) for the sample without i-ZnO is one of the highest reported for the CZTS material in literature.

The efficiency difference is at most 1 % for this series, and the variation between the references is 0.7 %, indicating that the performance of the solar cell is rather robust to change of CdS buffer thickness in this range.

IV. CONCLUSIONS

In summary, we have shown that Zn(O,S) is a viable buffer system for CZTS, in which it is possible to vary the conduction band offset between the absorber and the buffer. The best cell with this alternative buffer had an efficiency of 4.6 % and was obtained for the Zn(O,S)6:1 buffer, the same optimum composition as for CIGS [12]. However, judging from the V_{oc} extrapolation to 0 K, a buffer with higher sulfur content gives a higher activation energy for recombination, indicating that the interface can be further improved. The large increase in series resistance at low temperatures is similar for the CdS and Zn(O,S)6:1 buffer samples.

We have also shown that increasing the CdS buffer thickness causes the expected decrease of short wavelength QE response but did not affect the efficiency values to a large extent, especially if the i-ZnO is omitted for the thickest CdS buffer layer sample.

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