COMMUNICATION

High efficiency $\text{Cu}_2\text{ZnSnS}_4$ solar cells over FTO substrate and its CZTS/CdS interface passivation via thermal evaporated Al_2O_3 .

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Abstract. We report the use of FTO/Mo(20nm) as a transparent substrate and Al_2O_3 as passivation film in CZTS solar cells. The best devices showed efficiencies of 7.7% (V_{oc} =677 mV) and, 7.3% (V_{oc} =700 mV). A complete morphological, structural and electrical analysis is discussed.

Introduction

Kesterite materials ($\text{CZTS}_x\text{Se}_{1-x}$), is a promising class of thin film photovoltaic absorbers, containing exclusively earth-abundant and low toxicity elements such as Cu, Sn, Zn, Se, and S [1]. One of its properties is the tunability of the bandgap of kesterite, up to 1.5 eV for sulfur compound CZTS, which makes it suitable for tandem solar cells application [2]. Tandem devices involving $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) have been fabricated [3], and similar strategies could be followed by kesterite. Bailie *et al.* [3] reported a tandem solar cell using CIGS and perovskite materials obtaining η =18.6%. The use of a transparent contact, often a transparent conductive oxide (TCO) as back contact, is critical in that context, and Nakada *et al.* [4] demonstrated the feasibility of such contact on CIGSe solar cells. The similarities between chalcopyrite and kesterite allows for a direct transfer of ideas and concepts, with possible refinements specific for each technology. Recently, Espindola-Rodriguez *et al.* [7] fabricated CZTS solar cells using FTO as back contact with a very thin-layer of molybdenum (Mo) (20 nm), promoting the formation of an MoSe_2 interfacial layer improving the contact's ohmicity, and leading to efficiencies of η =6.3% (front illumination) and, η =7.7% (bifacial illumination) [7]. The direct comparison of the ITO and FTO layers shows that the former could limit the performance of the solar cells due to a possible diffusion of indium atoms through the absorber layer, and, as a consequence, a degradation of the electrical conductivity of

ITO [5, 8, 9]. On the other hand, FTO showed a high stability up to 500°C before slightly degrading at higher temperatures [10,11]. Mainly, the FTO degradation is ascribed to the diffusion of fluorine atoms to the absorber film, which can be avoided, by adding a molybdenum layer as diffusion barrier, while the Mo reaction with sulfur forms MoS_2 [7,11,12].

On the other hand, reducing the V_{oc} deficit is currently the most important challenge faced by the kesterite community, and the perspective of wide bandgap top cell application in tandem devices makes this issue even more critical. Avoiding interface recombination (specifically, MoS_2/CZTS and CZTS/CdS) is a key strategy in that context. For instance, for the MoS_2/CZTS interface, Yan *et al.* [13] reported the use of Al_2O_3 to limit the growth of MoS_2 , obtaining an efficiency of 11%. In the case of the CZTS/CdS interface, Sun *et al.* [14] reported a V_{oc} of 657 mV using an Al_2O_3 thin film deposited by Atomic Layer Deposition (ALD). The use of H_2O vapor and Trimethyl-aluminium (TMA) in Al_2O_3 deposition by ALD questions whether hydrogen is the main passivation factor, rather than the Al_2O_3 layer. On the other hand, H. Xie *et al.* [15] investigated the chemical deposition of an ultrathin $\text{Al}(\text{OH})_3$ layer to passivate the surface of the CZTSSe . Xie *et al.* observed a reduction in the recombination at the CZTSSe/CdS interface, with an improvement in the shunt resistance. The authors also demonstrated an epitaxial relationship of $\text{Al}(\text{OH})_3$ with kesterite and CdS, corroborating an effective interface passivation with this chemical approach.

In this work, we study the effect of a passivation of absorber film using an Al_2O_3 layer deposited by thermal evaporation in CZTS/CdS interface. The deposition of Al_2O_3 by thermal evaporation avoid an extra chemical process (as was reported by Sun *et al.* [14] and Xie *et al.* [15]) and, as consequence, a possibly modification in composition and structure. All devices with thermally evaporated Al_2O_3 showed an increased V_{oc} but a slightly decreased fill factor (FF), suggesting an increase in the series resistance at the $\text{CZTS}/\text{Al}_2\text{O}_3/\text{CdS}$ interfaces. Promising record efficiencies of 7.7% (677 mV) and 7.3% (700 mV) are obtained for CZTS solar cell (without Al_2O_3 passivation) and CZTS solar cell (with Al_2O_3 passivation), respectively, giving proof for the promising use of Al_2O_3 . In the same way it was proof the use of FTO use as substrate in solar cells.

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Experimental details.

Substrates preparation (FTO and soda lime glass).

CZTS thin films were grown onto commercial FTO coated soda lime glass (SLG) substrates and SLG substrates by a sequential process within the same batch. The SLG substrates were used to characterization of kesterite films, exclusively. The thickness of the FTO is ~ 800 nm and sheet resistance $<10 \Omega/\square$ (Kaivo P001). FTO and SLG substrates were cleaned with isopropanol and then with deionized water in ultrasonic bath during 10 minutes in both cases. Immediately, after the cleaning process, 20 nm of Molybdenum (Mo) was deposited by DC magnetron sputtering (Alliance Concept CT100) on the FTO substrates.

Precursor synthesis. The stacked metallic films were deposited by DC magnetron sputtering (Alliance Concept 450) where Cu, Sn and Zn elemental targets were used. The stacked metallic films were deposited at the same time in both FTO and SLG substrates to avoid differences in composition. These depositions were optimized to produce Cu-poor and Zn-rich CZT precursor materials as it has been reported elsewhere [16]. The cationic ratios are $\text{Cu}/(\text{Zn}+\text{Sn}) = 0.7, 0.76$ and 0.73 & $\text{Zn}/\text{Sn} = 1.0, 1.1$, and 1.2 , labelled as samples A, B, and C, respectively. These variations in cationic ratios are due to tune the Cu-poor and Zn-rich CZT precursor. The cationic ratios were determined by X-ray fluorescence (Fisherscope XVD) on a reference sample without FTO (SLG substrate). Here the small variation of $\text{Cu}/(\text{Zn}+\text{Sn})$ ratio and a more significant change in Zn/Sn ratio were detected. After deposition, the CZT precursors were simultaneously sulfurized inside of a graphite box containing sulfur (100 mg) and tin (50 mg) powders, using a tubular furnace and the following two-step annealing: 15 min at 250°C (1 mbar Ar flux) and 30 min at 570°C (1 bar total Ar pressure). The thickness of the absorbers is $\sim 1.4 \mu\text{m}$ measured by X-ray fluorescence. **Solar cells fabrication (without and with Al_2O_3).** Prior to the Al_2O_3 deposition, the samples on FTO substrate was etched using KCN solution (2% w/v, 2 min) [17]. A ~ 3 nm Al_2O_3 layer was deposited by thermal evaporation (Univex 250) in some of the samples. The deposition by thermal evaporation was to avoid the use of hydrogen in Al_2O_3 deposition (commonly used in Al_2O_3 deposited by atomic layer deposition [13, 18–20]). Then, a 50 nm thick CdS buffer layer was then deposited by chemical bath deposition. Finally, the devices on FTO substrate were completed with i-ZnO (50 nm)/ITO (200 nm) layers deposited by DC magnetron sputtering (Alliance Concept CT100). In this way, two different architectures were studied: SLG/FTO/Mo(20nm)/CZTS/CdS/i-ZnO/ITO and SLG/FTO/Mo(20nm)/CZTS/ Al_2O_3 /CdS/i-ZnO/ITO as are shown in Fig. S1 (Supporting Information). Individual 9 mm^2 solar cells were isolated using a manual microdiamond scribe (OEG MR200) and characterized by means of J-V illuminated curves (AM 1.5) and external quantum efficiency (EQE). Neither antireflective coating (ARC) nor metallic grids were used on the solar cells. **CZTS films and CZTS solar cells characterization.** The as-grown CZTS-solar cells (FTO substrate) were analysed by Raman spectroscopy using a Horiba Jobin-Yvon FHR640 spectrometer coupled with CCD camera and excited by a diode-pumped solid-state laser of 532 nm. The measurements were performed in the backscattering configuration through a specific optical probe

designed at IREC. J-V curves were measured under light conditions using a Sun 3000 class AAA Abet Technologies solar simulator (1 sun illumination). The EQE measurements were obtained using a Bentham PVE3000 system calibrated with Si and Ge photodiodes. Top and cross section SEM images from the CZTS film and the solar cell structure were taken using a Zeiss Series Auriga microscope using 5 kV as acceleration voltage. Elemental depth profiles of the full CZTS solar cells were measured by time-of-flight secondary ion mass spectrometry (ToF-SIMS) V instrument from Ion-TOF GmbH with a Cameca IMS-6F Ion microprobe. The used primary beam was Bi ions at 30 keV. The analysed area was $100 \mu\text{m}^2$. The utilized secondary sputtering beam was Cs^+ primary beam with an impact energy of 2 keV. The area of the sputtered solar cells, $200 \times 200 \mu\text{m}^2$, was kept constant. The measured elements were $^{133}\text{Cs}^{16}\text{O}$, $^{133}\text{Cs}^{23}\text{Na}$, $^{133}\text{Cs}^{27}\text{Al}$, $^{133}\text{Cs}^{32}\text{S}$, $^{133}\text{Cs}^{63}\text{Cu}$, $^{133}\text{Cs}^{64}\text{Zn}$, $^{133}\text{Cs}^{98}\text{Mo}$, $^{133}\text{Cs}^{113}\text{In}$, $^{133}\text{Cs}^{114}\text{Cd}$, and $^{133}\text{Cs}^{120}\text{Sn}$. The elements were measured as $\text{M}^+ \text{Cs}$ cluster ions, where M is the element to be analysed, in order to reduce the matrix effect on the ionization. Finally, in the Supporting Information we present a complete analysis from the bare kesterite and solar cells samples.

Results and discussion.

In Fig. S2 (Supporting Information) is shown Raman spectra with an excitation of 532 nm. In the spectra measured under 532 nm only the peaks related to CZTS compound were detected [21], while the low width of the main peak denotes the high crystalline quality of the sample [21]. In Fig. S3 (Supporting Information) are shown the top-view SEM images. The samples showed big grains showing sizes between $0.6 \mu\text{m}$ and $2.6 \mu\text{m}$. This fact could affect the fill factor and decrease the shunt resistance. Likewise, the shunt paths can be avoided with the help of an Al_2O_3 layer acting as insulating layer.

After Raman and SEM analysis, CZTS solar cells were optoelectronically characterized. The solar cells over FTO are labelled as follow: solar cells ANA, BNA, and CNA (samples A, B, and C, respectively) without Al_2O_3 , and solar cells AWA, BWA, and CWA (samples A, B, and C, respectively) with ~ 3 nm of Al_2O_3 . In Fig. 1 are shown the J-V illuminated curves from BNA & BWA solar cells. The sample BNA showed the following parameters: $\eta = 7.7\%$, $V_{\text{oc}} = 677 \text{ mV}$, $J_{\text{sc}} = 17.8 \text{ mA}/\text{cm}^2$, and $\text{FF} = 63.8\%$, whereas the sample BWA showed the parameters $\eta = 7.3\%$, $V_{\text{oc}} = 700 \text{ mV}$, $J_{\text{sc}} = 18.2 \text{ mA}/\text{cm}^2$, and $\text{FF} = 57\%$. To the best of our knowledge, the efficiencies of 7.7% and 7.3% are close to the highest reported in kesterite solar cells using a TCO substrate [5–8,22]. In Fig. S4 (Supporting Information) are shown the box-plot diagrams from complete solar cells BNA and BWA (10 cells in each sample). The importance of Al_2O_3 as passivation layer is shown in sample BWA which showed less disperse values in V_{oc} and efficiency, indicating that the interface passivation significantly improves the reproducibility. In Fig. S5 (Supporting Information) are shown the J-V illuminated curves from CZTS solar cells without Al_2O_3 (Fig. S5 a) and with Al_2O_3 (Fig. S5 b). With the figures of merit from all the samples, we prove that Al_2O_3 layer helped to increase the V_{oc} .

Fig. 1. J-V curves from CZTS solar cell a) without Al_2O_3 (BNA) and b) with Al_2O_3 (BWA).

While the voltage is marginally improved by the introduction of an Al_2O_3 passivation, the degradation of the FF is ascribed to an increase in the series resistance at the interface; hence, it is possible that despite being only 3nm thick, this layer acts as a barrier hindering the transport of photoelectrons. Thus, even thinner passivation layers may have to be considered in future experiments. On the other hand, to obtain the electrical parameters from solar cells without Al_2O_3 and with Al_2O_3 : shunt conductance (G_{sh}), series resistance (R_s), ideality factor (A), and saturation current density (J_0) were calculated using dark J-V curves' fitting [23,24]. A summary of electrical parameters of the samples over FTO with and without Al_2O_3 are shown in Table S1. G_{sh} curves are shown in Fig.S6 (Supporting Information). The best value in conductance is 0.11 mS/cm^2 from BNA sample; this value means that shunt resistance (R_{sh}) is the biggest in comparison with the other two samples (ANA and CNA). This shunt conductance value benefits the efficiency, helping in the efficiency of 7.7% obtained. In the samples with Al_2O_3 (AWA, BWA, and CWA) the best value of conductance was 0.18 mS/cm^2 from sample BWA and, therefore, they showed a very good efficiency (7.3%). In the same regard, samples AWA & CWA showed G_{sh} values of 0.23 mS/cm^2 and 0.61 mS/cm^2 , both samples showing an improvement in shunt conductance due Al_2O_3 layer. With the passivation by Al_2O_3 , the shunt paths effect decreased, these shunt paths could help to some carriers can travel through the device [25]. R_s curves are shown in Fig.S7 (Supporting Information). The most important values in series resistances were for samples BNA ($6.0 \Omega\cdot\text{cm}^2$) and BWA ($6.8 \Omega\cdot\text{cm}^2$). In sample BNA the high V_{oc} could be due to a less quantity of grain boundaries and small R_s . On the other hand, only sample AWA showed a decrease in R_s value, whereas, samples BWA & CWA showed an increase in R_s value. This increase could be due to a major degradation of the back contact (FTO/Mo) due to the high temperature sulfurization (570°C). The samples that reported the highest efficiency were samples BNA (in the case of solar cells without passivation layer) and BWA (in the case of solar cell with passivation layer). In that regard, the ideality factor (A) was calculated from Fig. S8 (Supporting Information). The sample ANA showed an ideality factor of 2.1 and with the use of Al_2O_3 layer, the ideality factor changed to 1.7 (AWA).

Fig. 2. SEM Cross Section-view from the samples a) BNA and, b) BWA.

The samples BNA and BWA showed similar values: 1.7 and 1.8, respectively. On the other hand, the samples CNA and CWA showed values of 1.6 and 2.1, respectively. Those values in samples ANA (2.1) and CWA (2.1) means that the current transport is on the grain boundary region, and it is controlled by a recombination at a high density of defect states. Samples BNA, CNA, AWA, and BWA showed that the recombination current is the dominant charge transport mechanism [26]. In the same way, the J_0 was calculated from the same J-V dark curves (Fig. S8, Supporting Information). There is not a big difference in J_0 between the samples ANA, AWA, BNA, and BWA, indicating relatively similar recombination processes [27]. The biggest difference is between the samples CNA and CWA showing values of $5.5 \times 10^{-7} \text{ mA/cm}^2$ and $1.6 \times 10^{-3} \text{ mA/cm}^2$, respectively. In this case, the Al_2O_3 passivation layer could slightly decrease the J_0 value by reducing the recombination on the CZTS/CdS interface [28]. Despite of ideality factor of sample BNA, it showed the maximum reverse saturation current (J_0) indicating the highest carrier recombination rate [27]. In sample CNA the J_0 value is agree with ideality factor which showed both minimum J_0 and ideality factor. In the same Table S1 (Supporting Information), the $V_{\text{oc(SQ)}}$ deficit is shown. The $V_{\text{oc(SQ)}}$ parameter is the maximum thermodynamic Voc achievable for a given bandgap [1]. This parameter was calculated with respect to the maximum theoretic value represented by the Shockley-Queisser limit [29,30]. Naturally, the smallest $V_{\text{oc(SQ)}}$ deficit is for the sample BWA which has 523 mV; sample BNA shows a $V_{\text{oc(SQ)}}$ deficit of 561 mV. The $V_{\text{oc(SQ)}}$ value of sample BWA significantly increased, which gives the opportunity to a future improvement with the use of Al_2O_3 and a wide study in the use of TCO substrates. The 523 mV in $V_{\text{oc(SQ)}}$ deficit is close comparing with previously published results on record CZTS-based solar

cells, using the well established Mo as substrate and without passivation layer (501 mV [13], 503 mV [31], 495 mV [32]). Fig. 2 shows the cross-section view SEM images of the samples BNA and BWA. In Fig. 2a) it is shown the sample BNA showing big grains. In the rear contact (FTO/Mo/CZTS interfaces) big voids appear. These voids could be formed by liquid phase formation due to compositional nonuniformity during the annealing process, compositional mismatch of the metal precursor itself, and Zn volatilization during the process when using metal precursors [32,33]. In the same way, Fig 3b) shows the sample BWA. This image shows bigger voids compared with those of BNA sample. A clear degradation on FTO/Mo/CZTS interfaces is shown. This degradation could be related directly with the FF decrease, showing a 57%; in contrast, sample BNA showed a 63.8% in FF.

On the other hand, the external quantum efficiencies (EQE) and J_{sc} integrated from BNA and BWA samples are shown in Fig. S9 (Supporting Information). The response of both samples is very good, reaching 80% in response. However, sample BWA (Fig. S9 a) showed better response on the 500-600 nm region but, not a good response in the CZTS region (550-850 nm). Additionally, the increase in response in 500-600 nm region can be related to Al_2O_3 passivation layer and, as consequence, enhanced the photovoltaic performance which can be related to integrated J_{sc} value (17.46 mA/cm²). Examining both samples, BNA and BWA, there is not big difference between the J_{sc} measured and J_{sc} integrated (both showed difference of ~ 0.75 mA/cm²).

The EQE measurements from all the samples are shown in Fig. S10 (Supporting Information). The samples with Al_2O_3 layer showed a slightly increment in 500-600 nm range. Additionally, this passivation helps less recombination in the space charge region. In the same way, sample with the best response (BWA) not showed a good response in the CZTS region (550-850 nm). This fact could be attributed to destructive interferences in that spectral region [34].

On the other hand, with the use of Time-of-Flight secondary ion mass spectroscopy (ToF-SIMS) we can obtain a complete outlook about the depth composition of the solar cell. Fig. 3 shows SIMS measurements of samples BNA (Fig. 3a) and BWA (Fig. 3b). In sample BNA (Fig. 3a) it is shown a complete diffusion of sodium (Na) that could benefit the grain growth at the rear interface of the CZTS film [35,36]. It is shown that small quantity of oxygen (from FTO to CZTS) and indium (from the ITO-top contact to CZTS) were diffused. It was reported that indium diffusion on CZTS is no harmful for the kesterite solar cells [37,38]. Meanwhile, oxygen diffusion could be harmful for kesterite solar cells. Recently, Grini *et al.* reported a strong interaction between sodium and oxygen in kesterite solar cells, so proving the constant diffusion of Na-O (forming NaO complex or Na₂O complex) [39]. This could affect the performance of the solar cell forming deep defects. These NaO complexes are located mostly at the grain boundaries, as Haight *et al.* reported [40].

Fig. 3. SIMS measurements from the samples a) BNA and, b) BWA.

In Fig. 3b) it is shown the ToF-SIMS measurement of the sample BWA. Firstly, it is shown the Al_2O_3 layer, proving that the very-thin film lasted a possible etching from ammonium hydroxide as Park *et al.* [18] reported. Moreover, we can relate the increase of V_{oc} with Al_2O_3 passivation film. In the same regard, Na and O diffused along the entire solar cell, both being almost constant in concentration. This diffusion could be caused by the high temperature sulfurization (570°C), degradation of FTO and a possibly contamination of Mo [39-41]. This fact, could affect the performance of the solar cell, affecting directly G_{sh} and J_{sc} as we mentioned before and acting as a deep defect [39-41].

In summary, we report here the use of FTO as substrate in kesterite solar cells technology and the use of Al_2O_3 layer which acts as passivation film. V_{oc} was improved in sample B from 677 mV to 700 mV. With detailed compositional characterization, we demonstrate the role of the Al_2O_3 layer deposited by evaporation. Besides, this communication demonstrates the potential future of FTO as substrate in kesterite solar cells showing a solar cell efficiency of 7.7%. The efficiency could be increased with a thinner layer of Al_2O_3 or suppressing the quantity of voids in FTO/Mo/CZTS interfaces avoiding very high temperatures of sulfurization ($>570^\circ\text{C}$). Finally, the use of FTO as substrate opens new options as bifacial solar cells or tandem solar cells and, as consequence, obtaining high-efficiency devices.

Conflicts of interest

There are no conflicts to declare.

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