Enhanced efficiency of Cu$_2$ZnSn(S,Se)$_4$ solar cells via anti-reflectance properties and surface passivation by atomic layer deposited aluminum oxide

Bingye Zhang, Lu Han, Shitian Ying, Yongfeng Li and Bin Yao

Reducing interface recombination losses is one of the major challenges in developing Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) solar cells. Here, we propose a CZTSSe solar cell with an atomic layer deposited Al$_2$O$_3$ thin film for surface passivation. The influence of passivation layer thickness on the power conversion efficiency (PCE), short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$) and fill factor (FF) of the solar cell is systematically investigated. It is found that the Al$_2$O$_3$ film presents notable antireflection (AR) properties over a broad range of wavelengths (350–1000 nm) for CZTSSe solar cells. With increasing Al$_2$O$_3$ thickness (1–10 nm), the average reflectance of the CZTSSe film decreases from 12.9% to 9.6%, compared with the average reflectance of 13.6% for the CZTSSe film without Al$_2$O$_3$. The Al$_2$O$_3$ passivation layer also contributes to suppressed surface recombination and enhanced carrier separation. Passivation performance is related to chemical and field effect passivation, which is due to released H atoms from the Al–OH bonds and the formation of Al vacancies and O interstitials within Al$_2$O$_3$ films. Therefore, the $J_{sc}$ and $V_{oc}$ of the CZTSSe solar cell with 2 nm-Al$_2$O$_3$ were increased by 37.8% and 57.8%, respectively, in comparison with those of the unpassivated sample. An optimal CZTSSe solar cell was obtained with a V$_{oc}$, J$_{sc}$ and $\eta$ of 0.361 V, 33.78 mA and 5.66%. Our results indicate that Al$_2$O$_3$ films show the dual functions of AR and surface passivation for photovoltaic applications.

1. Introduction

Recently, it has been proven that the conversion efficiencies of Cu(In,Ga)Se$_2$ (CIGS) thin film solar cells can reach 22.6%, which is comparable to their Si counterparts. However, the shortage and high material cost of indium and gallium restrict the development of CIGS solar cells. Kesterite Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) has attracted much more attention as a promising candidate for photovoltaic technology, including a Mo bottom electrode, a transparent conductive oxide (TCO) stack of indium tin oxide (ITO)/ZnO etc. Recently, the conversion efficiency record of CZTSSe solar cells has been proven to be 12.6% using a hydrazine solution based method. However, the efficiency of CZTSSe solar cells remains far from that of CIGS solar cells. To decrease the efficiency gap between CZTSSe and CIGS solar cells, one of the major challenges is reducing surface carrier recombination, which is caused by grain boundaries, defects and states. Various technologies have been utilized to fabricate high quality CZTSSe films, such as thermal coevaporation, sputtering, pulsed-laser deposition and other non-vacuum-deposition technologies (e.g. electrodeposition and solution processing). However, due to the complexity of multinary materials, it is difficult to obtain high quality CZTSSe films with a low density of defects and states at the interface between CZTSSe and CdS. Thus, CZTSSe devices suffer from an open-circuit voltage (V$_{oc}$) deficit caused by the significant recombination of photo-excited carriers due to the existence of large amounts of defects/states at the interface between CZTSSe and CdS. To solve this problem, it is necessary to induce a passivation layer to depress recombination. On one hand, a proper passivation layer can not only saturate dangling bonds to decrease the density of surface states in CZTSSe films (called chemical passivation), but also reduce the surface recombination velocity ($S_{surf}$) due to the existence of fixed charge in the passivation layer (called field effect passivation). On the other hand, passivation layers can

---

*a Department of Physics, Dalian University of Technology, Dalian, Liaoning, 116023, P. R. China. E-mail: byzhang@dut.edu.cn

*b Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun 130012, China. E-mail: binyao@jlu.edu.cn

Received 21st April 2018
Accepted 15th May 2018
DOI: 10.1039/c8ra03437k
rsc.li/rsc-advances
also prevent atomic interdiffusion between different layers in PV devices.\textsuperscript{16,17} Several dielectric materials have been used as passivation layers in CZTS-based solar cells and other PV devices (CIGS, Si solar cells etc.), such as Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, Si\textsubscript{3}N\textsubscript{4} and ZrO\textsubscript{2}.\textsuperscript{18-22} Among these materials, Al\textsubscript{2}O\textsubscript{3} has been regarded as a favorable material owing to its high dielectric constant, high transmission and large bandgap (6.3 eV), and is able to passivate p- and n-type semiconductors effectively.\textsuperscript{23-24} Recently, atomic layer deposition (ALD) has been proven to be an optimal technique for the synthesis of virtually pinhole-free inorganic thin films due to its low temperature deposition and precise thickness control. Moreover, atomic layer deposited Al\textsubscript{2}O\textsubscript{3} (ALD-Al\textsubscript{2}O\textsubscript{3}) can provide a state-of-the-art level of surface passivation for solar cells.

Furthermore, the barrier layer of p-i-n solar cells is also important for passivating the interface of the absorber and Al\textsubscript{2}O\textsubscript{3}/CIGS. These positive results for the Al\textsubscript{2}O\textsubscript{3} passivation layer and the beneficial technical aspects of ALD itself suggest that they would be appropriate for the passivation of CZTSSe solar devices.

As is well known, the thickness of Al\textsubscript{2}O\textsubscript{3} plays an important role in the density of interface states and the negative fixed charge for Si solar cells.\textsuperscript{25} Therefore, identifying the optimal thickness of Al\textsubscript{2}O\textsubscript{3} thin film has become the critical factor for obtaining high passivation performance for CZTSSe solar cells. However, few reports describe the influence of Al\textsubscript{2}O\textsubscript{3} thickness on the device performance of CZTSSe solar cells. Moreover, due to the differences in the structural, electronic and defect properties of CZTSSe and Si, as well as CIGS, the dominant passivation mechanism of Al\textsubscript{2}O\textsubscript{3} on CZTSSe is still unclear.

In this study, CZTSSe films (Cu/[Zn + Sn] = 0.81 and S/(S + Se) = 0.12) coated with various thicknesses of ALD-Al\textsubscript{2}O\textsubscript{3} (1–10 nm) film were fabricated. The influence of Al\textsubscript{2}O\textsubscript{3} thickness on the optical and electrical properties of CZTSSe solar cells was investigated in detail. We demonstrate that ALD-Al\textsubscript{2}O\textsubscript{3} thin films can not only provide a passivation effect, but also show excellent antireflection (AR) properties at short wavelengths for CZTSSe solar cells, which improves the power conversion efficiency (PCE), $V_{oc}$, FF and short-circuit current density ($J_{sc}$) of the CZTSSe solar cells. A CZTSSe solar cell with a PCE of 5.66% has been achieved via adjusting the thickness of the Al\textsubscript{2}O\textsubscript{3} thin film.

2. Experimental section

2.1. Materials and syntheses

**Preparation of CZTS precursor solution.** The CZTS precursor solution was prepared by dissolving Cu(CH\textsubscript{3}COO)\textsubscript{2}-H\textsubscript{2}O (1.198 g, 6 mmol), SnCl\textsubscript{2}-2H\textsubscript{2}O (0.745 g, 3.30 mmol), ZnCl\textsubscript{2} (0.5043 g, 3.70 mmol) and thiourea (1.97 g, 26 mmol) into N,N-dimethylformamide (10 mL, DMF) and then magnetically stirring for 2 h at room temperature. A CZT thin film with a thickness of ~1.1 μm was fabricated by spin-coating the CZTS precursor solution on molybdenum (Mo)-coated soda lime glass (SLG) substrates at a rotation rate of 3000 rpm for 30 s followed by drying in air at 300 °C for 3 min. The coating and drying processes were repeated 10 times.

**Synthesis of CZTSSe absorbers.** To obtain CZTSSe films, CZTS precursor films were sealed in a graphite box (~55 mm in diameter and ~40 mL in volume) with 200 mg of selenium. The selenization process was carried out in a rapid thermal processing (RTP) furnace (MTI, OTF-1200X-4-RTP), under nitrogen flow (80 mL min$^{-1}$) at 550 °C for 15 min with a ramping rate of 300 °C min$^{-1}$, and finally cooled down to room temperature naturally.

**Deposition of Al\textsubscript{2}O\textsubscript{3} thin films.** Al\textsubscript{2}O\textsubscript{3} thin films with varying thickness (1–10 nm) were deposited on CZTSSe by ALD, using trimethylaluminum (TMA), H\textsubscript{2}O and high-purity N\textsubscript{2} as Al and O sources, and carrying gas, respectively. The surface chemistry during Al\textsubscript{2}O\textsubscript{3} deposition can be described as follows:

\begin{equation}
\text{AlOH}^* + \text{Al(CH}_3)_3 \rightarrow \text{AlO} - \text{Al(CH}_3)_2 + \text{CH}_4
\end{equation}

\begin{equation}
\text{AlCH}_3^* + \text{H}_2\text{O} \rightarrow \text{Al} - \text{OH}^* + \text{CH}_4
\end{equation}

The ALD-Al\textsubscript{2}O\textsubscript{3} thin films were fabricated at 220 °C, and then annealed in situ at 400 °C for 10 min in N\textsubscript{2} to activate surface passivation. Various thicknesses of the Al\textsubscript{2}O\textsubscript{3} thin films were obtained via controlling the deposition cycles, and the growth rate of Al\textsubscript{2}O\textsubscript{3} was 0.7 Å per cycle. Each cycle consisted of a TMA pulse (0.03 s), an N\textsubscript{2} purge (12 s), a water pulse (0.06 s) and an N\textsubscript{2} purge (12 s).

**Fabrication of CZTSSe photovoltaic devices.** CZTSSe solar cells were fabricated with the structure SLG/Mo/CZTSSe/Al\textsubscript{2}O\textsubscript{3}/Cds/i-ZnO/indium tin oxide (ITO)/Al grid. 50 nm thick CdS buffer layers were deposited on the ALD-Al\textsubscript{2}O\textsubscript{3} thin films using chemical bath deposition (CBD), and then 50 nm i-ZnO and 250 nm ITO layers were deposited using RF and DC magnetron sputtering sequentially. Finally, top contact fingers were formed with an Al grid electrode (~2 μm) on the ITO layer. All of the solar devices had an active area of 0.20 cm$^2$, defined by mechanical scribing (~92% of the total device area, 0.22 cm$^2$).

2.2. Characterization

The structure, surface morphology and compositional ratio of CZTSSe films were measured using scanning electron microscope (SEM) measurements on a Hitachi S-4800 equipped with an energy-dispersive X-ray spectroscopy (EDS) system (EDAX Genesis 2000). The crystal structures of the CZTSSe films were characterized using an X-ray diffractometer (XRD) with Cu Kα radiation ($\lambda$ = 1.5406 Å). Optical reflectance of the CZTSSe films with ALD-Al\textsubscript{2}O\textsubscript{3} thin films was detected using a spectrophotometer with an integrating sphere. X-ray photoelectron spectroscopy (XPS) analysis was used to identify the actual composition and chemical state of the grown Al\textsubscript{2}O\textsubscript{3} thin films. For the PCE measurements of the CZTSSe solar cells, current–voltage curves were measured using a Keithley 2400 source meter and a solar simulator (Abet Sun 2000; AM 1.5). The light intensity was calibrated to 100 mW cm$^{-2}$ using a Newport optical power meter (model 842-PE) certified by Newport. The external quantum efficiency (EQE) curves were measured using
3. Results and discussion

In general, most passivation materials need a post deposition annealing (PDA) process to activate the passivation effect. In some cases, the annealing treatment can cause the deterioration of crystalline quality for the films deposited under low temperatures, leading to more defects and impurities. Thus, SEM and XRD measurements were carried out to specify whether PDA could cause degradation. Fig. 1 shows top-view and cross-sectional SEM images for the CZTSSe films and the devices. Both of the CZTSSe films, with and without the Al2O3 thin film, exhibit a compact and dense morphology with a grain size ranging from 1–2 μm, as shown in Fig. 1(a) and (b). Fig. 1(c) and (d) show cross-sectional SEM images of the CZTSSe solar cell, which consists of a 1 μm Mo film, a 1.17 μm CZTSSe film, a 2 nm Al2O3 thin film, and a 50 nm CdS film, as well as a 300 nm i-ZnO/ITO film. It can be seen that the compactness and domain size of CZTSSe coated with Al2O3 thin film aren’t obviously changed compared with the unpassivated sample, which demonstrates that the deposition and annealing processes of Al2O3 have a faint effect on the surface morphology and the grain growth of CZTSSe films. It should be noted that some holes exist at the interface between CZTSSe and Mo, which is assigned to the unstable nature of CZTSSe in contact with Mo.

Fig. 2 shows the XRD patterns of CZTSSe films, with and without Al2O3 thin film. The XRD patterns of the CZTSSe films show that all of the films can be indexed in kesterite-type structures with no secondary phases. With reference to JCPDS no. 00-026-0575 and 00-052-0868, three major diffraction peaks located at 27.34°, 45.45° and 53.81° are observed, which can be assigned to the (112), (220) and (312) planes, respectively, implying the good crystallinity of CZTSSe films. In addition, a minor peak located at 36.40° is also observed, corresponding to the (211) diffraction plane, as shown in Fig. 2(a). Fig. 2(b) shows the XRD pattern of the CZTSSe film with 2 nm Al2O3 thin film. Besides the diffraction peaks of CZTSSe, it can be clearly seen that no diffraction peak belonging to Al2O3 can be observed, suggesting the amorphous phase of the ALD-Al2O3 thin film. Moreover, the XRD peak position and full width at half-maximum (FWHM) of CZTSSe shows little change after the
Al2O3 deposition and PDA processes. These results indicate that the processes of Al2O3 deposition and PDA have no obvious influence on the crystalline quality of CZTSSe film, which is consistent with the SEM results.

For quantitative phase analysis, the full profile Rietveld refinement of the XRD pattern of the CZTSSe powder was carried out, as shown in Fig. 3. The structural model was refined on the basis of the tetragonal kesterite-type crystal structure [space group: I4 (no. 82)]. The obtained structural parameters of CZTSSe are a = 5.6573 Å, c = 11.301 Å, and c/a = 2.00. The corresponding weighted residual error (Rwp), residual of least-squares refinement (Rp) and χ² of the fittings are 5.87%, 4.46%, and 2.38, indicating good fits of the patterns. These lattice parameters (a and c) are slightly decreased compared to the reported values of CZTSe (ICSD#95117). This decreasing of the lattice parameters can be assigned to the shrinkage of the unit cell due to the substitution of Se atoms with S, which have a smaller ionic radius (1.84 Å) compared to that of Se (1.98 Å).48

Reducing optical losses is an important way to increase the density of photo-generated carriers for PV devices. Therefore, an AR layer is usually adopted to realize the low reflectance of solar cells, such as MgF2, SiO2 and SiN2:H in CIGS and Si PV devices.31,32 Several reports have proven that Al2O3 can have good AR properties with wide thickness ranges for Si solar cells.49 To verify the AR performance of Al2O3 in CZTSSe solar cells, the reflectance spectra of CZTSSe with various thicknesses of Al2O3 thin films were obtained for wavelengths from 350 nm to 1250 nm, as shown in Fig. 4(a). A remarkable decrease in the total reflectance of CZTSSe with Al2O3 thin films can be observed over a wide spectral range. The spectrum-weighted average reflectance (Rave) can be defined as:34

\[
R_{\text{ave}} = \frac{\int_{350}^{1250} R(\lambda) N(\lambda) \, d\lambda}{\int_{350}^{1250} N(\lambda) \, d\lambda}
\]

where \(R(\lambda)\) is the total reflectance and \(N(\lambda)\) is the solar flux under the standard conditions of AM 1.5. By calculation, the \(R_{\text{ave}}\) values of the as-deposited CZTSSe and CZTSSe with 1 nm, 2 nm, 5 nm and 10 nm Al2O3 thin films are 13.6%, 12.9%, 12.1%, 10.9% and 9.6%, respectively. With increasing Al2O3 thickness, the \(R_{\text{ave}}\) value of CZTSSe decreases by 32.4%, implying the good AR performance of Al2O3 thin film. The inset in Fig. 4(a) shows the CZTSSe solar cell with and without Al2O3 thin film, which shows a significant reduction in reflection losses for the CZTSSe solar cells. Fig. 4(b) shows the \(R_{\text{ave}}\) of CZTSSe/Al2O3 as a function of Al2O3 thickness and the ALD deposition cycles, and the inset shows digital photographs of CZTSSe film with various thicknesses of Al2O3 thin films. The \(R_{\text{ave}}\) exhibits an exponential reduction with increasing Al2O3 thickness, as shown in Fig. 4(b).

For the bare CZTSSe film, a high \(R_{\text{ave}}\) of 13.6% is observed. After depositing 1 nm Al2O3 thin film, the \(R_{\text{ave}}\) of CZTSSe/Al2O3 decreases about 0.7%. With increasing Al2O3 thickness, the \(R_{\text{ave}}\) of CZTSSe/Al2O3 decreases continuously, reaching 9.6% at the Al2O3 thickness of 10 nm. We have noticed that the reflectance of CZTSSe/Al2O3 decreases faster at short wavelengths (350–650 nm) than at long wavelengths (650–1100 nm) with increasing Al2O3 thickness. The reflectance of CZTSSe with 10 nm Al2O3 decreases beyond 60% at short wavelengths compared with 13% at long wavelengths. The discrepancy in reflectance at different wavelengths is mainly due to the dispersion of the Al2O3 refractive index.50 These results imply that the Al2O3 thin film can provide satisfying AR performance, especially in short wavelength regions, which can increase photo-generated carriers effectively.

Besides its AR properties, Al2O3 thin film can also provide an excellent passivation effect for both p- and n-type materials. In order to explore the origin of the passivation mechanism of Al2O3 on CZTSSe, the chemical states of Al and O were identified through XPS measurements. Fig. 5 shows the XPS spectra of Zn 2p, Al 2p and O 1s, respectively. The Zn 2p spectrum consists of two narrow peaks at 1022.5 eV and 1045.5 eV, corresponding to Zn 2p1/2 and 2p3/2, with a peak splitting of \(\Delta E = 23.0\) eV, in accordance with the standard splitting of 23 eV for Zn(0) state, as shown in Fig. 5(a).51 The O 1s core-level XPS spectra of Al2O3 thin film is shown in Fig. 5(b). The O 1s spectrum can be fitted into two peaks, located at 531.4 eV and 532.6 eV, which are attributed to Al–O–Al bonds and Al–OH bonds.52 The appearance of hydroxyl groups can be assigned to an incomplete reaction during eqn (1) and adsorbed H2O on the surface.53 Fig. 5(c) shows the Al 2p core-level XPS spectra of the as-deposited and annealed Al2O3 thin film. For the as-deposited sample, the Al 2p peak with a binding energy of 75.2 eV is assigned to the Al–O bond, which can be fitted into two sub-spectra located at 74.2 eV and 75.6 eV, corresponding to O–Al–O bonds and Al–OH bonds, respectively.54 After annealing, the component at 75.6 eV disappears, while the peak with a binding energy of 74.2 eV remains, indicating the disappearance of Al–OH bonds during the annealing process. According to previous literature, the residual O–H bonds would be broken easily to release interstitial O and interstitial H atoms during the annealing process.55 The interstitial H ions migrate through the Al2O3 matrix and arrive at the Al2O3/CZTSSe interface to...
passivate the dangling bonds or grain boundaries of the CZTSSe film. Meanwhile, the excess O ions released from hydroxyl groups are also helpful for the formation of O interstitials (Oi), which are responsible for the negative fixed charge in Al₂O₃ thin film, leading to the enhancement of field-effect passivation. Furthermore, negative fixed charge at the interface between CZTSSe and Al₂O₃ can effectively strengthen the built-in field of the p–n junction, which can enhance the carrier-separation efficiency.

To further understand the effects of passivation on device performance, the photovoltaic investigation of CZTSSe solar cells with the structure SLG/Mo/CZTSSe/Al₂O₃/CdS/i-ZnO/ITO/Al was carried out. Fig. 6 displays current density–voltage (J–V) curves for CZTSSe solar cells with various thicknesses of Al₂O₃ under standard AM 1.5 illumination (100 mW cm⁻²). The detailed device parameters are listed in Table 1. It was found that the unpassivated CZTSSe solar cell achieved a PCE of 2.24%, and the Vₜₙ, Jₘ and FF values are 0.262 V, 21.42 mA cm⁻² and 38.22%, respectively. After Al₂O₃ deposition, the PCE increased sharply and then decreased with increasing Al₂O₃ thickness from 1 nm to 5 nm. The PCE reached the highest value of 5.66% at a film thickness of 2 nm. The Vₜₙ, Jₘ and FF change similarly to the PCE, revealing the highest values of 0.361 V, 33.78 mA cm⁻² and 48.98%, respectively. Compared with CZTSSe solar cells without Al₂O₃ passivation, the Vₜₙ, Jₘ and FF values of the CZTSSe with 2 nm Al₂O₃ thin film were increased by 37.8%, 57.8% and 28.2%, respectively. This improvement in device performance can be assigned to the AR

Fig. 4 (a) The reflectance spectra of CZTSSe thin films without Al₂O₃ thin film and with Al₂O₃ thin film at various thicknesses. The inset is the reflectance spectra of CZTSSe solar cells without Al₂O₃ thin film and with 5 nm Al₂O₃ thin film. (b) The Rₘe of CZTSSe thin films coated with Al₂O₃ thin films as a function of Al₂O₃ thickness and ALD cycles. The inset is digital photographs of CZTSSe thin films with Al₂O₃ thin film at various thicknesses.

Fig. 5 XPS spectra of (a) the Zn 2p core level of the CZTSSe film, (b) the O 1s core level of as-deposited Al₂O₃, and (c) the Al 2p core-level of as-deposited and annealed Al₂O₃.

Fig. 6 Current–voltage curves for CZTSSe solar cells with Al₂O₃ thin film at various thicknesses, in comparison with unpassivated CZTSSe solar cells. The inset is the schematic of the device structure.
performance of Al2O3 thin film and the reduction of the density of acceptor-like states at the interface between CZTSSe/Al2O3, resulting in the decreased compensation of photo-generated carriers.11

Fig. 7(a) displays the EQE spectra of CZTSSe solar cells with various thicknesses of Al2O3 passivation layers. For comparison, a CZTSSe solar cell without an Al2O3 passivation layer is also added as a reference. All of the CZTSSe solar cells present a distinct spectral response, and with increasing Al2O3 thickness, the EQE value shows a similar trend to that of the PCE results. The CZTSSe solar cell with 2 nm Al2O3 exhibits the highest value of around 80% in the wavelength region of 500 nm to 900 nm. It is found that the EQE is improved at all wavelengths with increasing Al2O3 thickness, especially in the long wavelength region. The improvement in EQE indicates the improvement in the collection length of photo-generated carriers, which is due to the passivation of the CZTSSe surface and/or grain boundaries by Al2O3 films.24 In addition, the bandgap of the CZTSSe films is determined by plotting $[E \times \ln(1 - \text{EQE})]^2$ versus $E$ using the EQE spectra of the CZTSSe solar cell, as shown in Fig. 7(b). It is found that the bandgaps of all of the CZTSSe films have the value of 1.07 eV, which indicates that the ALD process has no influence on the stoichiometric ratio of the CZTSSe film, especially the S/Se ratio, which is consistent with the XPS and EDS results. Therefore, it is deduced that the improvement of the performance of CZTSSe solar cells mainly originates from decreases in the reflectance of CZTSSe and the surface passivation of Al2O3.

Based on the above discussions, it can be concluded that the development of CZTSSe solar cells originates from two aspects. On one hand, the deposition of Al2O3 thin films can reduce the reflectance of CZTSSe films and increase photo-generated carriers, leading to an improvement in device performance, especially the $J_{sc}$ value. On the other hand, Al2O3 thin films can not only saturate the defects and dangling bonds at the interface between CZTSSe and CdS, but also produce a large amount of negative fixed charge to reduce interface recombination and increase the carrier separation efficiency, resulting in an increased $V_{oc}$ value. In addition, although thicker Al2O3 thin films are beneficial for obtaining lower reflectance for the CZTSSe films, the optimal CZTSSe PV device was obtained at the Al2O3 thickness of 2 nm in the present work, which can be explained as follows. According to our results and other literature on Si and CIGS solar cells, a thicker passivation layer causes reduction in the fixed charge, leading to the debasing of field-effect passivation. Therefore, the Al2O3 passivation layer should be kept thin enough so that the photo-excited electrons are able to effectively tunnel through the layer in the device.

### Table 1

| Al2O3 thickness (nm) | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF (%) | Eff. (%) |
|---------------------|-------------|------------------------|--------|---------|
| 0                   | 0.262       | 21.42                  | 38.22  | 2.24    |
| 1                   | 0.301       | 26.84                  | 39.45  | 3.12    |
| 2                   | 0.361       | 33.78                  | 48.98  | 5.66    |
| 5                   | 0.312       | 30.68                  | 46.14  | 4.39    |
| 10                  | —           | —                      | —      | —       |

### 4. Conclusions

In summary, Al2O3 thin films of various thicknesses were deposited on the top of CZTSSe prior to CdS deposition by ALD. The influence of the thickness of Al2O3 thin films on the reflectance and PCE values of CZTSSe solar cells was investigated in detail. The CZTSSe without the Al2O3 thin film achieved an $R_{ave}$ of 13.6%. After deposition of the Al2O3 thin films, the $R_{ave}$ values of CZTSSe films with 1 nm, 2 nm, 5 nm and 10 nm Al2O3 were 12.9%, 12.1%, 10.9% and 9.6%, respectively. This decrease in $R_{ave}$ demonstrates that Al2O3 thin films can provide favorable AR properties. The XPS results indicate the existence of a large amount of Oi, which is believed to be the origin of field effect passivation caused by the negative fixed charge. The appearance of Oi can not only provide field effect passivation to depress surface recombination, but also enhance the built-in field of the p-n junction to increase the carrier-separation efficiency. The $V_{oc}$, $J_{sc}$, and $\eta$ of CZTSSe solar cells with 2 nm Al2O3 thin film achieved the highest values of 0.361 V, 33.78 mA and 5.66%, respectively, in comparison with 0.262 V, 21.42 mA and 2.24% for the CZTSSe solar cell without passivation.

---

Fig. 7  (a) EQE spectra of CZTSSe solar cells with Al2O3 thin film at various thicknesses. (b) Band gap values of CZTSSe solar cells, with Al2O3 thin film at various thicknesses, determined by the $[E \times \ln(1 - \text{EQE})]^2$ vs. $E$ curve.
Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 61604029 and 61774075) and the Fundamental Research Funds for the Central Universities (Grant No. DUT18LK48).

References

1 P. Jackson, D. Hariskos, R. Wuerz, O. Kiowski, A. Bauer, T. M. Friedlmeier and M. Powalla, Phys. Status Solidi RRL, 2015, 9, 28–31.
2 P. Jackson, R. Wuerz, D. Hariskos, E. Lotter, W. Wite and M. Powalla, Phys. Status Solidi RRL, 2016, 10, 583–586.
3 N. Shibayama, Y. W. Zhang, T. Satake and M. Sugiyama, RSC Adv., 2017, 7, 25347–25352.
4 Z. Y. Xiao, B. Yao, Y. F. Li, Z. H. Ding, Z. M. Gao, H. F. Zhao, L. G. Zhang, Z. Z. Zhang, Y. R. Sui and G. Wang, ACS Appl. Mater. Interfaces, 2016, 8, 17334–17342.
5 S. Y. Chen, A. Walsh, X. G. Gong and S. H. Wei, Adv. Mater., 2013, 25, 1522–1539.
6 A. Walsh, S. Y. Chen, S. H. Wei and X. G. Gong, Adv. Energy Mater., 2012, 2, 400–409.
7 J. Kim, H. Hiroi, T. K. Todorov, O. Gunawan, M. Kuwahara, T. Gokmen, D. Nair, M. Hopstaken, B. Shin, Y. S. Lee, W. Wang, H. Sugimoto and D. B. Mitzi, Adv. Mater., 2014, 26, 7427–7431.
8 D. B. Mitzi, O. Gunawan, T. K. Todorov, K. Wang and S. Guha, Sol. Energy Mater. Sol. Cells, 2011, 95, 1421–1436.
9 K. Ramasamy, M. A. Malik and P. O'Brien, Chem. Commun., 2012, 48, 5703–5714.
10 Q. Tian, Y. Cui, G. Wang and D. Pan, RSC Adv., 2015, 5, 4184–4190.
11 Z.-Y. Xiao, Y.-F. Li, B. Yao, Z.-H. Ding, R. Deng, H.-F. Zhao, L.-G. Zhang and Z.-Z. Zhang, RSC Adv., 2015, 5, 103451–103457.
12 W. Wang, M. T. Winkler, O. Gunawan, T. Gokmen, T. K. Todorov, Y. Zhu and D. B. Mitzi, Adv. Energy Mater., 2014, 4, 1301465.
13 A. Ahmad, K. B. Reuter, O. Gunawan, L. Guo, L. T. Romankiw and H. Deligianni, Adv. Energy Mater., 2012, 2, 253–259.
14 M. E. Erkan, V. Chawla and M. A. Scarpulla, J. Appl. Phys., 2016, 119, 194504.
15 G. Sozzi, S. D. Napoli, R. Menozzi, B. Bissig, S. Buecheler and A. N. Tiwari, Sol. Energy Mater. Sol. Cells, 2017, 165, 94–102.
16 K. Herz, A. Eicke, F. Kessler, R. Wachter and M. Powalla, Thin Solid Films, 2003, 431, 392–397.
17 B. A. Chambers, G. G. Andersson, J. S. Quinton, J. Jasieniak, B. I. MacDonald, M. Ionescu, A. Deslandes, J. S. Quinton, J. J. Jasieniak and G. G. Andersson, Sol. Energy Mater. Sol. Cells, 2014, 125, 164–169.
18 R. Kotipalli, B. Vermang, J. Joel, R. Rajkumar, M. Edoff and D. Flandre, AIP Adv., 2015, 5, 077101.
19 J. Löckinger, S. Nishiwaki, T. P. Weiss, B. Bissig, Y. E. Romanyuk, S. Buecheler and A. N. Tiwari, Sol. Energy Mater. Sol. Cells, 2018, 174, 397–404.
20 S. Gatz, T. Dullweber, V. Mertens, F. Einsele and R. Brendel, Sol. Energy Mater. Sol. Cells, 2012, 96, 180–185.
21 W.-C. Wang, M. C. Tsai, J. Yang, C. Hsu and M.-J. Chen, ACS Appl. Mater. Interfaces, 2015, 7, 10238–10237.
22 L. Q. Zhu, Q. Fang, X. J. Wang, J. P. Zhang, M. Liu, G. He and L. D. Zhang, Appl. Surf. Sci., 2008, 254, 5439–5444.
23 G. L. Lu, F. Zheng, J. Q. Wang and W. Z. Shen, Prog. Photovoltaics, 2017, 25, 280–290.
24 P. Casper, R. Hünig, G. Gomard, O. Kiowski, C. Reitz, U. Lemmer, M. Powalla and M. Hetterich, Phys. Status Solidi RRL, 2016, 10, 376–380.
25 W.-W. Hsu, J. Y. Chen, T.-H. Cheng, S. C. Lu, W.-S. Ho, Y.-Y. Chen, Y.-J. Chien and C. W. Liu, Appl. Phys. Lett., 2012, 100, 023508.
26 P. Poedt, A. Lankhorst, F. Roozeboom, K. Spee, D. Maas and A. Vermeer, Adv. Mater., 2010, 22, 3564–3567.
27 N. M. Terlinden, G. Dingemans, M. C. M. Van de Sanden and W. M. M. Kessels, Appl. Phys. Lett., 2010, 96, 112101.
28 L. Meng, B. Yao, Y. F. Li, Z. H. Ding, Z. Y. Xiao, K. S. Liu and G. Wang, J. Alloys Compd., 2017, 710, 403–408.
29 K. Wang, B. Shin, K. B. Reuter, T. Todorov, D. B. Mitzi and S. Guha, Appl. Phys. Lett., 2011, 98, 051912.
30 S. W. Shin, J. H. Han, Y. C. Park, G. L. Agawane, C. H. Jeong, J. H. Yun, A. V. Moholkar, J. Y. Lee and J. H. Kim, J. Mater. Chem., 2012, 22, 21727.
31 H.-J. Jeong, Y.-C. Kim, S. K. Lee, Y. Jeong, J.-W. Song, J.-H. Yun and J.-H. Jang, ACS Appl. Mater. Interfaces, 2017, 9, 25404–25411.
32 S.-Y. Han, C. Q. Pan, D.-H. Kim and C.-H. Chang, RSC Adv., 2015, 5, 24712–24717.
33 L. Q. Zhu, Y. H. Liu, H. L. Zhang, H. Xiao and L. Q. Guo, Appl. Surf. Sci., 2014, 288, 430–434.
34 P. Menna, G. Di Francia and V. La Ferrara, Sol. Energy Mater. Sol. Cells, 1995, 37, 13–24.
35 Y. T. Qu, G. Zoppi and N. S. Beattie, Prog. Photovoltaics, 2016, 24, 836–845.
36 C. Van der Marel, M. Yildirim and H. R. Stapert, J. Vac. Sci. Technol., A, 2005, 23, 1456.
37 V. Naumann, M. Otto, R. B. Wehropohn, M. Werner and C. Hagendorf, Energy Procedia, 2012, 27, 312–318.
38 Y.-W. Cheng, F.-L. Tang, H.-T. Xue, H.-X. Liu and B. Gao, Appl. Surf. Sci., 2017, 394, 58–62.