On the beneficial effect of Al_2O_3 front contact passivation in Cu(In,Ga)Se_2 solar cells

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A B S T R A C T

This study reports on the beneficial effect of an absorber surface passivation by Al_2O_3 on the performance of Cu(In, Ga)Se_2 (CIGSe) solar cells. Here the Al_2O_3 layer is deposited by atomic layer deposition (ALD) subsequently to a CdS buffer layer. It is shown that a very thin film of about 1 nm efficiently reduces the interface recombination rate if the buffer layer is too thin to not fully cover the CIGSe absorber. An Al_2O_3 thickness of 1 nm is sufficiently low to allow current transport via tunneling. Increasing the thickness to > 1 nm leads to a detrimental blocking behavior due to an exponentially decreasing tunnel current. Losses in open circuit voltage (V_{oc}) and fill factor (FF) when reducing the buffer layer thickness are significantly mitigated by implementing an optimized Al_2O_3 layer. It is further shown, that the heat treatment during the ALD step results in an increase in short circuit current density (J_{sc}) of about 2 mA/cm^2. This observation is attributed to a widening of the space charge region in the CIGSe layer that in turn improves the collection probability of electrons. For not fully covering CdS layers the decrease in interface defect density by the passivation contributes as well, leading to a gain of about 5 mA/cm^2 for cells without a buffer. Finally, the leakage current of the solar cell devices could be reduced when applying the Al_2O_3 layer on insufficiently covering CdS films, which proves the capability of mitigating the effect of shunts or bad diodes.

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1. Introduction

In recent years the passivation of interfaces in the layer stack of CIGSe solar cells found an increased interest and several approaches, applying different material combinations, have been investigated. The latest sudden boost in efficiency for the best devices was achieved by the implementation of a post-deposition KF treatment [1–4]. It was suggested that this improvement originates from the formation of a several nanometer thin (K)-In-Se surface layer that improves the junction quality, either by an enhanced in-diffusion of Cd or S, a better buffer coverage or/and a passivation effect by a significant band gap widening [5,6]. By a fine-tuned KF post deposition process it is further possible to grow a passivating surface layer which exhibits nano-sized openings (after treatment) and thereby allows the creation of CdS point contacts [7].

Furthermore, the potential of thin Al_2O_3 layers for passivating possible interfaces with the CIGSe absorber layer (including CIGSe/air) has been evaluated. It was found that by depositing several nanometer thin layers of Al_2O_3 on top of the commonly used Mo back contact, the back surface recombination velocity was effectively reduced. This effect is supposed to originate from reducing the interface defect density and the creation of an effective field that repulses the minority charge carriers, caused by the established fixed negative charge inside the Al_2O_3 layer. The back contact passivation is reported to be increasingly beneficial for decreasing absorber thicknesses and a distinct improvement in J_{sc} and V_{oc} is evident for corresponding devices [8–10]. Photoluminescence (PL) measurements have shown an increased PL intensity when the CIGSe surface was passivated by Al_2O_3, which is explained by a reduction in interface defect density of 35% compared to the unpassivated CIGSe surface [11]. It was found that an Al_2O_3 passivation of the CIGSe surface also prevents degradation with air exposure time (illustrated by a non-decreasing PL yield) [12]. Furthermore, the polarity of the fixed charge in the Al_2O_3 layer seems to be dependent on the deposition conditions and a possible post-treatment. It is claimed that aluminum-rich growth conditions result in a positive (by Al_i defects) and Al-poor conditions in a negative fixed charge (by V_{Al} or O_i defects) [13]. Another model explains the negative fixed charge by the local atomic bonding environment of Al in amorphous Al_2O_3 (i.e.

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tetrahedrally or octahedrally coordinated Al sites) [14,15]. Furthermore hydrogen is proposed to cause a negative charge in Al_2O_3 [16]. Kotipalli et al. reported that as grown ALD Al_2O_3 layers establish a positive fixed charge while thermally annealed (510 °C) films exhibit negative charging [17].

One main goal in CIGSe solar cell research is to reduce the parasitic absorption in the buffer layer. This can be achieved by using high or indirect band gap materials [18] or by reducing the layer thickness of the commonly used CdS. Especially when considering large scale fabrication, thinning down the CdS buffer layer can be crucial, because a homogeneous coverage of the entire CIGSe absorber surface might not be given. Already small openings could thereby cause a severe reduction in solar module performance, which is mainly due to the appearance of unfavorable ZnO/CIGSe interface regions.

In this contribution the potential of very thin Al_2O_3 films (≤ 2 nm) deposited by ALD on top of CdS buffer layers with varied thicknesses (i.e. partly and fully covering) is investigated and the effect on the solar cell performance is presented.

2. Materials and methods

2.1. Sample fabrication

The CIGSe solar cells investigated in this study were manufactured as a stack of SLG/Mo/CIGSe/CdS/(optional Al_2O_3)/i-ZnO/ZnO:Al. Here, the electrodes were deposited by RF-sputtering, resulting in a thickness of about 80 nm for the i-ZnO and 270 nm for the ZnO:Al (i.e. roughly 30 Ω/sq) layer. Since the cell area was chosen small enough to avoid any resistive losses (A=0.05 cm^2), no metal grid was applied. The CdS buffer layer was grown in a chemical bath (CBD) heated to 60 °C that consists of 1.1 M ammonia, 0.1 M thiourea and 0.003 M cadmium acetate. The buffer layer thickness/coverage was tuned by varying the deposition time between 0 min and 8:15 min, while the corresponding thickness was estimated by measuring the Cd signal intensities by X-ray fluorescence (XRF, spot size 2.2 cm) spectrometry (Spectro X-Lab 2000) and calibrating these to the thickness of the thickest CdS layer (55 nm) deduced by transmission electron microscopy (TEM) on the cell cross section. The CIGSe films were deposited by an inline co-evaporation process at Solibro Research AB, exhibiting an overall composition of [Ga]/([Ga]+[In])=0.43 and [Cu]/([Ga]+[In])=0.83 determined by XRF. In order to ensure stable and comparable absorber properties during the entire time span of experiments, all samples have been processed preliminary with a capping layer of CdS layer on top of the absorber and stored in a N_2 cabinet. Prior to each "fresh" buffer deposition the protective CdS layers were etched in a diluted HCl solution (HCl concentration c=5 wt%) for 2 min, which guaranteed its complete removal without significantly affecting the absorber properties [19].

The Al_2O_3 passivation layer was deposited in a Picosun Sunale R200 ALD reactor at 200 °C, using trimethylaluminium (TMA) and water as precursors. The growth rate was ~1 Å/cycle, showing almost no nucleation time (estimated to ≈ 2 cycles).

For each sample configuration 16 solar cells were structured and analyzed subsequently. The given error bars in the presented results are related to the corresponding standard deviations and are thereby reflective of a single sample.

2.2. Characterization methods

Scanning electron microscopy (SEM, Zeiss 1550) was employed to investigate the CdS growth/coverage on the CIGSe surface. Transmission electron microscopy analysis was done on a FEI Tecnai F30 ST TEM (acceleration voltage=300 kV). Electron energy loss spectroscopy (EELS) was performed in STEM mode. The TEM electron

transparent lamella is prepared using the in-situ lift-out method.

External quantum efficiency (EQE) measurements were performed by a home-build system. The resulting J_{sc} values have been taken to calibrate the light intensity to 1 sun (mismatch corrected) for current-voltage (IV) measurements at T=25 °C under illumination by an ELH lamp. The IV measurements were conducted on 16 solar cells for each sample variation discussed in this study. The reflectance on the solar cells was determined by using a Perkin Elmer Lambda 900 spectrometer with an integrating sphere.

Capacitance-voltage (CV) measurements were conducted in darkness and at room temperature applying a frequency of f=100 kHz and an oscillation voltage of V_{ac}=30 mV in a voltage range of -1 V to $+0.5$ V.

3. Results and discussion

3.1. Growth of CdS on CIGSe absorber and Al_2O_3 passivation

The thickness dependence of the CdS buffer layers on the CBD time is illustrated in Fig. 1 for all different CdS thicknesses used in this study. It is obvious that the growth starts delayed by about 2 min (mainly due to the heat up time of the chemical bath after insertion). After that, a more or less linear growth takes place (~9 nm/min). It should be mentioned here, that the given thickness is an average value, assuming conformal planar growth.

In order to characterize the corresponding morphology and coverage of the CdS layers on top of the CIGSe absorber, SEM investigations were conducted in top-view (perpendicular to the surface). A selection of the resulting images is presented in Fig. 2 (7:15 min is not shown because it does not provide additional information). It is visible that in the beginning of the growth, CdS is not covering the CIGSe absorber completely and it starts growing alongside the facets of the CIGSe topography. Here, the coverage varies a lot laterally from grain to grain, which is probably caused by different nucleation kinetics on different CIGSe surface orientations (slower nucleation on {112} surfaces) [20]. With increasing deposition time the exposed CIGSe area is reduced until almost 100% coverage is reached for CBD times $\geq 5:15$ min (i.e. between 20–30 nm) and only very few dispersed pinholes could be detected. Moreover, after complete coalescence of the buffer layer islands, the surface roughness is reduced with increasing CdS thickness by smoothening the CIGSe topography. It has to be mentioned at this point, that the SEM investigations provide only a qualitative estimation of the CdS buffer coverage which does not allow for a quantitative analysis. An absolute determination could be conducted by an extensive and time-
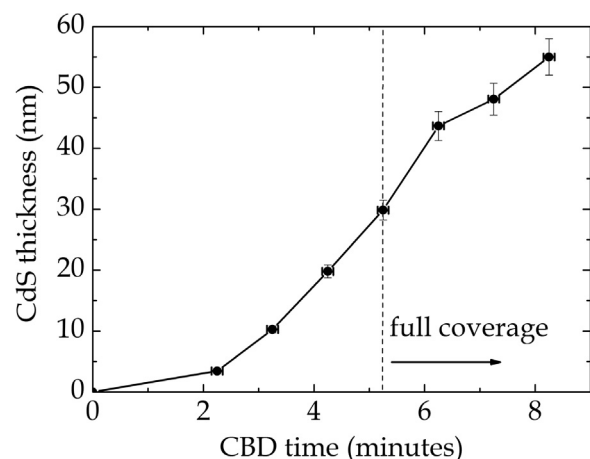

Fig. 1. Dependency of CdS buffer thickness on CBD time as measured by XRF/TEM.