CADMIUM-FREE CIGS MINI-MODULES WITH ALD-GROWN Zn(O, S)-BASED BUFFER LAYERS

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ABSTRACT: We present the first results from our work on cadmium-free CIGS solar cells and mini-modules on 12.5×12.5 cm^2 substrates. The buffer layers in these cells and modules consist of Zn(O,S) grown by atomic layer deposition (ALD) in a new home-built reactor. The CIGS absorber of the cells and modules presented in this article was deposited in our inline micro-pilot evaporator with a deposition time of 15 minutes. In this study, we focus on issues which are relevant to the manufacturing of 100 cm^2 sized mini-modules with ALD Zn(O,S) buffer layers manufactured in our lab. We have achieved independently certified aperture area efficiencies of 18.5 % for 0.5 cm^2 cells and 14.7 % for a 76.8 cm^2 mini-module.
Keywords: Buffer Layer, Cu(In,Ga)Se2, Manufacturing and Processing, Zn(O,S)

1 INTRODUCTION

State-of-the-art Cu(In,Ga)Se_2 (CIGS) based thin film solar cell modules contain a buffer layer of cadmium sulfide, CdS. The amount of about 0.2 g/m^2 cadmium in the active layers is beyond the tolerated amount of 0.01 wt-% of cadmium in homogeneous materials according to the Directive of the European Parliament on the Restriction of Hazardous Substances (RoHS) [1].

Even though the definition of *homogeneous materials* or *electrical and electronic equipment* is not yet clearly defined in the context of solar cell modules, alternative materials for the buffer layer are in the focus of intensive research. These new materials should of course not lead to a decrease in solar cell performance as compared to the established CdS layers. Neither should the deposition process be more time consuming or more costly than the established technology.

Alternatives to CdS buffer layers, based on zinc oxide, ZnO, and zinc oxysulfide, Zn(O,S), grown by atomic layer deposition (ALD) have been studied in our group for more than a decade [2-4]. Recently, we have demonstrated solar cell efficiencies for cadmium-free CIGS cells which are close to, and above our CdS-containing baseline references [3,4]. The properties of Zn(O,S) as buffer layer makes it a promising candidate for the application in CIGS solar cells.

In the ALD process the precursor gases for the group II and group VI elements are sequentially introduced into the reaction chamber. Ideally, a monolayer of group II and group VI element containing molecules forms on the substrate, respectively, and reacts with the previously deposited molecules to form the desired compound. The unreacted precursor gases and remaining ligands are then removed from the reaction chamber by purging with an inert gas. This layer-by-layer growth gives precise control over the thickness and composition of the deposited layers, as well as good step coverage and conformal coating [5].

Our aim at Ångström Solar Center is to choose and develop process steps which are scalable for the use in module fabrication. In order to show the scalability of the ALD process for buffer layer deposition and its applicability within a module process we have built a new ALD system to extend our expertise in the field of cadmium-free buffer layers.

2 EXPERIMENTAL

2.1 Baseline process

The CIGS absorber layers for this study were deposited in our micro-pilot system onto 12.5 × 12.5 cm^2 soda-lime glass substrates with a sputtered molybdenum backside contact. The nominal thickness of the CIGS absorber layer is 1.7 μm, and the nominal composition is Cu/(In+Ga) = 0.9 and Ga/(In+Ga) = 0.4.

The processing of the modules follows the previously described baseline recipe with laser-scribed molybdenum backside contacts and mechanically scribed contact vias and front contact isolations [6].

Baseline reference cells with chemical bath deposited CdS buffer layers are made from CIGS material of the same deposition run as the ALD grown buffer layers.

The front contact of the solar cells consists of a bilayer of aluminum doped zinc oxide (ZnO:Al) on top of a thin layer of undoped or intrinsic zinc oxide (i-ZnO). These layers are deposited by sputtering from ceramic targets, as described in [6].

2.2 ALD system

A new ALD system was built in order to process full sized 12.5 × 12.5 cm^2 samples. The process chamber is made of stainless steel and gives room to a gas volume of about 2 mm height over the full size of the substrate. The substrate itself is introduced as part of the rear side of the process chamber.

Nitrogen is used as carrier gas at a nominal pressure of 2 mbar during the ALD process. The precursor gases are introduced into the nitrogen stream by means of fast switching valves. Diethyl zinc, DEZn, is used as zinc precursor, hydrogen sulfide, H_2S, and water vapor, H_2O, are used as group VI precursors, respectively.

The flow rate of the carrier gas is controlled by mass flow controllers and can be changed during pulse and purge cycles of the ALD process. The amount of precursor introduced into the chamber during the pulses is controlled by the opening time of the switching valves, which is nominally in the order of 200 ms. The layer composition and thickness is controlled by the pulsing sequence of the precursor gases and by the number of pulsing cycles, respectively.

Numerical computer simulations of the gas flow inside the reaction chamber were made in order to assess inhomogeneities in the thickness of the grown layers, which we observed in our initial deposition experiments. These were identified as regions of CVD growth because of incomplete removal of precursors during the purge cycles, and as regions of impeded growth due to the lack of one precursor species, respectively. The results from the computer simulation helped us to choose process parameters which gave good lateral homogeneity in terms of thickness and composition of the deposited layers.

3 RESULTS AND DISCUSSION

3.1 ALD grown Zn(O,S) layers

Initial studies of the performance of the new ALD system involved the growth of Zn(O,S) layers on uncoated and on molybdenum coated glass substrates. We used these samples in combination with the computer simulations of the carrier gas flow inside the ALD chamber to adjust the process parameters, especially the gas flow and pulse times, in order to obtain a uniform layer thickness over the whole substrate area.

Since ALD growth is a non-equilibrium process where only one precursor is available at any time during the growth, exchange reactions between the gas phase and the already deposited layers are expected. In the case of Zn(O,S) especially the exchange reaction

$$ZnO + H_2S \Leftrightarrow ZnS + H_2O$$

is likely to take place. Not only does this influence the actual composition of the deposited material, it can also lead to gradients in the sulfur concentration, both laterally and vertically. The band gap of $ZnO_{1-x}S_x$ depends strongly on the composition and shows a minimum for $x = 0.5$. From the earlier results published by Platzer-Björkman, we estimate the band gap of the Zn(O,S) in our buffer layers to be around 3 eV [5].

Thickness series with different numbers of ALD cycles were used to analyze the initial stages of the ALD growth. The surface properties are different prior to the ALD growth and once a continuous layer has started to form. This nucleation phase is often observed as an incubation time in the beginning of the ALD deposition. The XRF analysis of the zinc contents as a measure for the thickness of the ALD films grown with 0 to 500 ALD cycles is shown in Figure 1. We observe a short incubation time in the order of 10 ALD cycles and a linear dependence of the deposited film thickness on the number of ALD cycles. An actual growth rate of about 40 nm per 100 ALD cycles was deduced from the measurement of etched steps in deposited films on glass substrates.

3.2 CIGS cells with ALD Zn(O,S) buffer layer

We obtained the best and most reproducible cell results with a recipe of 70 ALD cycles (group II + group VI precursor and purging), where every seventh cycle contained an H_2S pulse for the group VI precursor instead of the H_2O pulse of the remaining cycles. The optimum deposition temperature is in the range of 117 to 120 °C, measured on the outside of the reaction chamber. The net deposition time for the buffer layer is about 20 minutes. From the linearity measurements of the ALD growth we estimate a film thickness of 25 nm.

The good step coverage of the deposited ALD buffer layer can be seen in the cross section TEM image in Figure 2. The thickness of the Zn(O,S) layer, seen as a dark band between the CIGS grains and the sputtered ZnO front contact, appears to be less than 25 nm in the TEM image. Until now it is unclear whether this is caused by the TEM sample preparation or by a lack of contrast between the Zn(O,S) layer and the i-ZnO, which is sputtered directly on top of it.

Because of the wider band gap of the Zn(O,S) buffer layer the CdS absorption edge below 500 nm is absent and the quantum efficiency curve of cells with Zn(O,S) buffer layer is more box-shaped, as shown in Figure 3. We also noticed an increase in the quantum efficiency in the wavelength range between 600 nm and 1000 nm for the cells with Zn(O,S) buffer layer. This could be attributed to a wider space charge region in the cells with

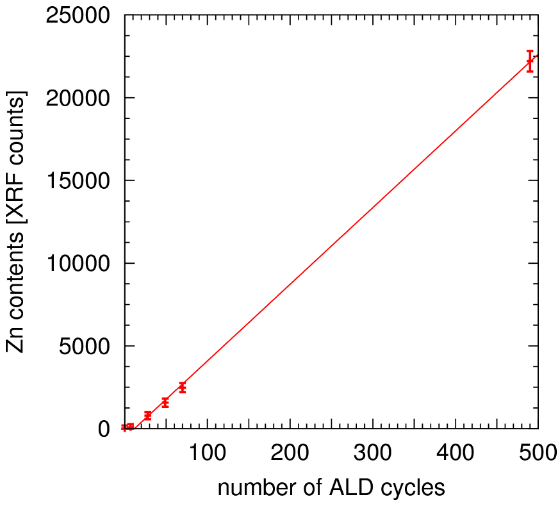

Figure 1: XRF analysis of the Zn contents in ALD films deposited with different numbers of ALD cycles. The drawn line is a linear regression to the measurement data. Considering a background level of 2200 XRF counts the incubation time is in the order of 10 ALD cycles.

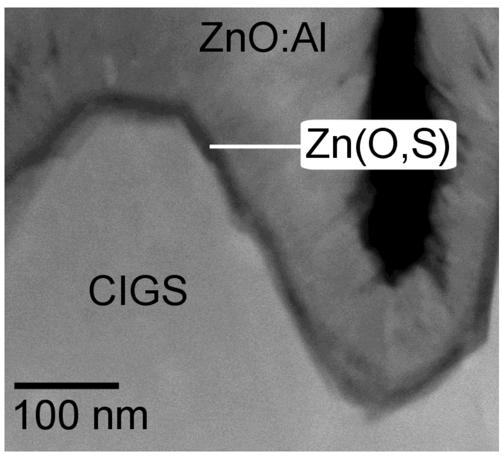

Figure 2: Cross section TEM image of a CIGS solar cell with ALD grown Zn(O,S) buffer layer. The buffer layer is the dark band between the CIGS grains and the columnar ZnO:Al front contact layer. The dark area to the right is a void.

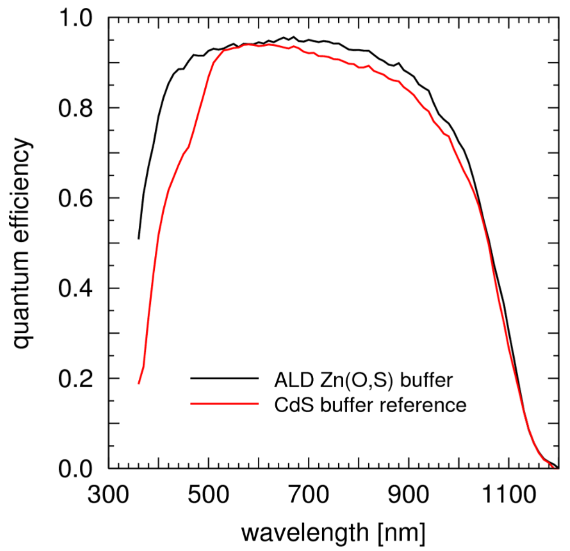

Figure 3: Quantum efficiency measurement for a cell with ALD Zn(O,S) buffer layer and a reference cell with CdS buffer.

Zn(O,S) buffer layer, leading to an improved carrier collection for long wavelengths. Together these effects result in a current gain in the order of 2 mA/cm^2 as compared to reference cells with CdS buffer layer.

An independent measurement at NREL certifies an efficiency of 18.53 % for a 0.5 cm^2 cell with ALD Zn(O,S) buffer layer and MgF antireflection coating, see Table 1. The neighboring cells on the same sample all show comparable efficiencies above 18 %.

Table 1: Solar cell parameters of seven neighboring CIGS cells with ALD Zn(O,S) buffer layer and 0.5 cm^2 area, as measured by NREL. The cells have MgF antireflection coating.

sample	Jsc [mA/cm^2]	V_{oc} [V]	FF [%]	efficiency [%]
2898-5	35.490	0.685	76.12	18.51
2898-6	35.233	0.687	75.97	18.37
2898-7	35.511	0.689	75.77	18.53
2898-8	35.488	0.689	75.71	18.52
2898-9	35.371	0.690	75.85	18.51
2898-10	35.287	0.689	75.67	18.38
2898-11	35.062	0.688	75.49	18.20

3.3 ALD layer uniformity

A uniform distribution of the electrical solar cell parameters is necessary for the successful manufacturing of monolithically interconnected modules.

Figure 2 shows the distribution of the open circuit voltage, V_{oc}, the short circuit current density, J_{sc}, the fill factor and cell efficiency over the full substrate size of 12.5 × 12.5 cm^2 measured on 220 individual solar cells of 0.5 cm^2 area, each. A full size sample was split into four parts after the ALD Zn(O,S) buffer deposition. The four pieces were then processed in our baseline cell process.

The solar cell performance drops significantly within an approximately 15 mm wide zone along all four outer edges of the substrate. This area is not used as active area in

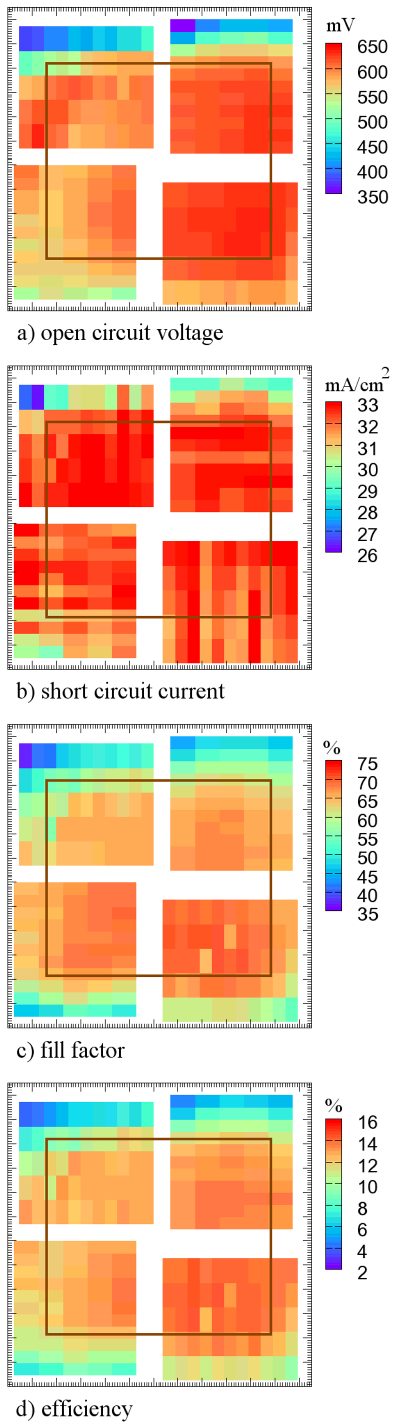

Figure 4: Solar cell parameter mapping over a full 12.5 × 12.5 cm^2 substrate, showing the open circuit voltage (a), the short circuit current density (b), the fill factor (c) and efficiency (d) of 220 individual 0.5 cm^2 solar cells. The drawn rectangle indicates the position of the aperture area of a typical mini-module on the substrate.

Table 2: Electrical measurements on CIGS mini modules. The mini modules consist of 16 series interconnected cells with a width of 5 mm each. Modules 3100 and 3101 have been laminated with a cover glass and EVA before the measurement. Measurements were taken at NREL and at our own lab, respectively.

sample	buffer material	aprt. area cm^2	I_{sc} mA	Jsc mA/cm^2	V_{oc} V	V_{oc}/cell V	FF %	efficiency %	measured at
3100*	Zn(O,S)	76.8	147.2	30.7	11.0	0.685	70.3	14.8	NREL
3101*	Zn(O,S)	77.6	146.2	30.1	10.9	0.680	68.3	14.0	NREL
3102	Zn(O,S)	76.8	150.9	31.4	10.5	0.659	69.7	14.5	ÅSC
3126	CdS	76.8	148.4	30.9	9.8	0.614	69.9	13.3	ÅSC

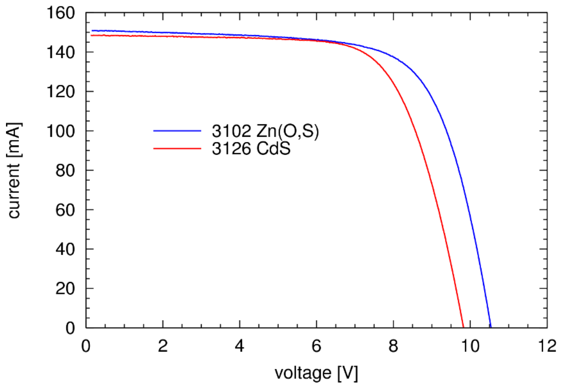

Figure 5: Current voltage characteristics of a 16-cell mini-module with ALD Zn(O,S) buffer layer (3102) in comparison to a reference module with CdS buffer (3126). More data for the two moduls is listed in Table 2.

our mini-modules, but instead serves as contact area and module-edge isolation. The aperture area of our mini-modules is indicated as a black rectangle in the maps in Figure 4 and falls within a region of sufficient uniformity.

3.3 Mini modules

We used modules with 16 and 20 series interconnected, 5 mm wide cells to investigate the suitability of the ALD buffer layers for a module process. The same Zn(O,S) process recipe as utilized as for the cells described in the previous section.

The comparison between mini-modules with Zn(O,S) buffer layer and a reference module with CdS buffer layer is shown in Figure 5. Detailed electrical measurements are listed in Table 2. The cadmium free modules show both a higher open circuit voltage V_{oc} and a higher short circuit density J_{sc} than the CdS reference module. The fill factor for both types of modules is around 70 % and the best aperture area efficiency of 14.8 % for module 3100 in Table 2 was confirmed in an independent measurement at NREL.

The short circuit current density in the modules with Zn(O,S) buffer layer is around 30 mA/cm^2, calculated over the aperture area of the module. This is about 16 % lower than the J_{sc} of our cells with the same buffer layer. The fill factor of the modules is about 10 % lower than the typical fill factor for our cells, both for the Zn(O,S) buffer layers and for the CdS references. Several electrical and optical mechanisms contribute to these additional losses. We will continue to identify these losses and further improve our module process.

4 CONCLUSIONS

We have demonstrated the manufacturing of cadmium-free CIGS solar cells with efficiencies of above 18 % on 12.5×12.5 cm^2 large substrates. We have shown that the uniformity of our Zn(O,S) ALD process is sufficient to manufacture mini-modules with aperture areas of 77 cm^2 and aperture area efficiencies of above 14.5 %.

We will further develop and optimize our module process in order to understand and resolve the issues which limit our module performance as compared to our cell results. We have also just started to investigate the long-term stability of cells and modules with cadmium-free buffer layers.

The interface between the CIGS absorber and the buffer layer is of major importance for the performance of the CIGS solar cell. A detailed investigation of the interface has not been part of this study. Our group will continue to further analyze this interface for different cadmium-free buffer layers.

ACKNOWLEDGMENT

The authors would like to thank all the other members of the solar cell group for active participation in the research work. The study was financed by the Swedish Energy Agency.

We are also grateful for the independent electrical measurements on our cells and modules which were done at the National Renewable Energy Laboratory in Golden, Colorado/USA. Thanks also to Jarmo Skarp for valuable discussions in the design phase of the ALD system and Ernesto Coronel for the TEM work.

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