Atmospheric spatial atomic layer deposition of ZnOS buffer layers for flexible Cu(In,Ga)Se-2 solar cells

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Atmospheric spatial atomic layer deposition of ZnOS buffer layers for flexible Cu(In,Ga)Se₂ solar cells

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Zinc oxysulfide (ZnOS) is synthesized at atmospheric pressure in a laboratory-scale spatial atomic layer deposition setup by sequentially exposing the substrate to diethyl zinc and an H₂O/H₂S mixture, separated by a nitrogen gas curtain. The co-injection of H₂O and H₂S vapors in the same deposition zone enables an accurate control of the S/(O + S) ratio, the morphology, and the optoelectronic properties of the films. Next, the ZnOS deposition process is transferred to an industrial roll-to-roll spatial-ALD setup. ZnOS is applied as a buffer layer in flexible Cu(In,Ga)Se₂ solar cells, instead of the commonly used CdS, achieving a best efficiency of typically 13% in small area cells (0.57 cm²) and 9.2% in flexible mini-modules (270 cm²). These results show the viability of atmospheric spatial-ALD as a new technique for roll-to-roll manufacturing of flexible photovoltaics modules based on a Cu(In,Ga)Se₂ absorber. *Published by the AVS.*

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I. INTRODUCTION

Solar cells based on chalcopyrite Cu(In,Ga)Se₂ (CIGS) are becoming an established technology in the thin-film photovoltaic industry because they combine the advantages of a-Si thin films, i.e., low production costs and flexible modules, with high conversion efficiencies (>22%).¹ In recent years, zinc oxysulfide (ZnOS) has emerged as a valid alternative to the CdS buffer layer, because the use of toxic Cd is avoided and the quantum efficiency of the cells is enhanced in the blue wavelength region.²

Atomic layer deposition (ALD) is often used for the synthesis of Zn-based buffer layers, due to its ability to control the film composition at the atomic level and superior uniformity over nonplanar, large-area substrates with 3D topology.³ The low deposition rate (~0.01 nm/s) of conventional ALD can hinder the use of this technique in the solar cell industry where high throughput is needed to achieve low production costs. This drawback has been overcome by the spatial-ALD (S-ALD) technique.⁴ A schematic of the S-ALD concept is depicted in Fig. 1. The dosage of the precursors occurs in different space-divided zones of the reactor, and a moving substrate is sequentially exposed to each of these zones. Different reactor zones are separated by a nitrogen gas curtain so that a purge step is no longer needed and deposition rates as high as nanometers per second have been achieved. Several metal oxides (e.g., Al₂O₃, Al:ZnO, InGaZnO, and ZrO₂) have been synthesized in laboratory-scale S-ALD setups and successfully integrated in electronic devices.^{5–9} Sheet-to-sheet S-ALD Al₂O₃ is currently used in the photovoltaic industry to passivate the surface defects of c-Si wafers, thus boosting the solar cell efficiency.¹⁰ In this paper, we demonstrate

large-scale integration in the form of flexible CIGS modules (270 cm²) with a ZnOS buffer layer grown by roll-to-roll S-ALD.

II. EXPERIMENT

A schematic of the laboratory-scale spatial-ALD reactor is shown in Fig. 1. Two different inlets are installed in the cylindrical gas injection head; one for the metal precursors and another for the oxygen and sulfur precursors. The rigid substrate is placed on a circular substrate table, which rotates underneath the reactor head at a distance of typically 20–100 μm. The cylindrical table and the reactor head are built inside an oven to guarantee temperature uniformity and stability up to 300 °C. For the experiments reported in this paper, the substrate temperature is varied between 100 and 200 °C. Diethylzinc [Zn(C₂H₅)₂, (DEZ)], H₂O, and H₂S are used as precursors for zinc, oxygen, and sulfur, respectively. A 3.5% H₂S in the N₂ mixture is used as an H₂S source. The DEZ bubbler and H₂S cylinder bottle are kept at room temperature, while the H₂O bubbler is heated to 50 °C. Argon is used as the carrier gas for DEZ and H₂O. Vaporized precursors are transported to the reactor injection head through heated lines, to prevent condensation. The argon flow is set to 0.075 slm in the DEZ bubbler, while it is varied from 0 to 1 slm in the H₂O bubbler. The flow of the 3.5% H₂S/N₂ mixture is varied in the range from 0 to 0.030 slm and further diluted by an N₂ flow ranging from 0.720 to 1.420 slm. The exposure time of the substrate to the precursors (t_{exp}) is calculated as $t_{\text{exp}} = L / (2\pi r \times \text{RPM})$, where L is the width of the deposition zone (~1.5 cm), r is the radial distance from the center of the table, and RPM is the number of rotations per minute of the cylindrical table. The exposure time to both co-injected H₂O/H₂S and DEZ is varied from 30 to 52 ms.

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FIG. 1. (a) Schematic drawing of the laboratory-scale rotary spatial-ALD reactor. The DEZ and $\text{H}_2\text{O}/\text{H}_2\text{S}$ half-reaction zones are separated by gas bearings. By moving the substrate underneath the reactor, the two half-reactions take place subsequently to form a ZnOS monolayer. (b) Schematic drawing of the bottom side of the spatial-ALD reactor head, where the DEZ and $\text{H}_2\text{O}/\text{H}_2\text{S}$ half-reaction zones are integrated into inlets surrounded by exhaust zones and gas bearing planes. (c) Schematic drawing of the reactor.

The ZnOS deposition process has been transferred from the laboratory-scale S-ALD to the roll-to-roll S-ALD setup (50 cm wide) built by the VDL Enabling Technology Group, which is shown in Fig. 2. The machine consists of a rotating drum, containing several repetitions of two half-reaction zones [blue and red in Fig. 2(a)], where different vaporized precursors are injected. Nitrogen gas bearings [in green

(colors on line)] separate and surround the deposition zones, avoiding parasitic gas-phase chemical reactions between the different precursors and enabling the machine to operate at atmospheric pressure. The gas bearing ensures that there is no mechanical contact between the foil and the drum, thus preventing particles formation and/or scratches of the foil. The flexible substrate is exposed to the different precursors

FIG. 2. (a) Schematic of the roll-to-roll spatial-ALD concept developed at TNO, consisting of a central rotating drum that contains one or more combinations of metal vapors [red (colors on line)] and $\text{H}_2\text{O}/\text{H}_2\text{S}$ half-reaction zones [blue (colors on line)]. These zones are separated and surrounded by nitrogen gas bearings [green (colors on line)]. The foil to be coated is pulled over this drum, where the gas bearing ensures that the foil is kept at a fixed distance from the surface of the drum. If the foil is then moved over the drum, ALD deposition will take place, where the total thickness is determined by the rotation frequency of the drum in combination with the movement speed of the foil. (b) Picture of the roll-to-roll spatial-ALD setup built by the VDL Enabling Technology Group, based on the TNO concept.

by pulling it clockwise along the drum with a linear web speed of ~ 1 m/min and rotating the drum itself counterclockwise.¹¹ The precursors used for the deposition of ZnOS (i.e., DEZ, H₂O, and a 3.5% H₂S/N₂ mixture) are the same as those in the laboratory-scale S-ALD reactor. The exposure time of the foil to the precursors has been varied in the range from 20 to 40 ms in each deposition zone by varying the rotation frequency of the drum from 0.5 to 1 Hz and the foil speed from 0.5 to 1 m/s. The drum and the foil are warmed up to a temperature of 120 °C.

The ZnOS thickness is measured by *ex situ* Spectroscopic Ellipsometry, using a J.A. Woollam M2000 rotating compensator ellipsometer in the 300–1000 nm range. For these measurements, a *c*-Si wafer or a polyamide foil coated by Mo is used as a substrate. The composition of ZnOS is measured with an FEI Quanta 600 FEG SEM system equipped with an energy-dispersive x-ray (EDX) diagnostic system. A Philips X-pert SR5068 powder diffractometer equipped with a Cu K α source is used to determine the crystallographic structure of the films. A Shimadzu UV3600 spectrophotometer is used to measure the total reflection and transmission of ZnOS on a glass substrate.

CIGS devices consist of an Mo/CIGS/buffer layer/ZnO/Al:ZnO stack, where either chemical bath deposited (CBD) CdS or S-ALD ZnOS is used as a buffer layer. Co-evaporation technique is used to grow the CIGS absorber, while Mo, ZnO, and Al:ZnO are deposited by sputtering. A 50 cm wide polyamide foil is coated with an Mo/CIGS stack prior to the deposition of ZnOS by either the laboratory-scale (Fig. 1) or the roll-to-roll (Fig. 2) S-ALD setup. Flexible CIGS devices are then completed and characterized. The substrates are mechanically scribed to define individual solar cells with an area of about 0.5 cm² and mini-modules with an area of 270 cm².

III. RESULTS AND DISCUSSION

A. Layer deposition and characterization

Conventional ALD of multicomponent oxides is typically performed by alternating the growth of different binary oxides (i.e., supercycles).¹² ZnOS then consists of stacked ZnO and ZnS layers where the S/(O + S) ratio is controlled by the number of ALD cycles used to deposit each binary layer.³ Although the supercycle method enables a macroscopic control of film stoichiometry, microscopically it leads to out-of-plane compositional and structural nonuniformity.¹³

An alternative approach to the supercycles has been proposed for the synthesis of multicomponent oxides by S-ALD, which consists of exposing an oxygen-terminated surface simultaneously to different metal-organic precursors.⁷ In an S-ALD reactor, the evaporated precursors can be mixed while flowing continuously into the same deposition zone where the substrate is exposed to a constant concentration of both precursors. The full kinetics of the surface reactions can be studied by independently varying the exposure time and the precursors' concentration in the deposition zone. The method of co-injecting metal-organic precursors has been

successfully used to make device grade multimetal oxides (e.g., Indium-gallium-zinc oxide) in an S-ALD reactor.¹⁴ Oxides with a graded metal composition along the growth direction can be deposited by the co-injection method, making possible to develop advanced band-engineering schemes to control the electrical properties of interfaces.¹⁵

Co-injection of different precursors has also been investigated in laboratory-scale temporal ALD reactors.¹⁶ Here, the precursors do not flow continuously, but they are pulsed into the deposition chamber for a time which is much shorter than the exposure time. The precursors' concentration can vary during the exposure time, depending on the precursors' consumption at the substrate and reactor walls, the specific precursors' pulsing system or reactor design, and the diffusion rate of the precursors from their injection point to the substrate. This hinders the possibility of varying independently the exposure time and the concentration of co-injected precursors in a temporal ALD reactor, thus possibly limiting the control of layer composition when co-injecting precursors with a significantly different surface reactivity.

Only metal precursors that do not cause parasitic gas-phase reactions and with a similar vapor pressure can be effectively co-injected in an S-ALD setup. Undesired surface effects, such as steric hindrance, can limit the ability to control the film composition by the co-injection method or result in the incorporation of impurities in the layer.

Device grade ZnOS has been recently synthesized by S-ALD by co-injecting vaporized H₂O and H₂S.¹⁷ New insights on the growth mechanism and the properties of ZnOS are given in the first part of this paper. Later, the device characteristics of rigid and flexible CIGS with S-ALD ZnOS buffer layer will be described.

The effect of precursors' partial pressure, exposure time, and substrate temperature on the ZnOS composition is

FIG. 3. S/(S + O) ratio vs relative partial pressure of H₂S [i.e., $P_{\text{H}_2\text{S}}/(P_{\text{H}_2\text{S}} + P_{\text{H}_2\text{O}})$] times exposure time (i.e., t_{exposure}). For each value of the H₂S flow, the flow of the Ar carrier gas into the H₂O vessel is kept constant at 1 slm, while the exposure time is varied in the range from 30 to 52 ms. Inset: S/(S + O) ratio vs substrate temperature for a fixed $t_{\text{exposure}} = 30$ ms and $P_{\text{H}_2\text{S}}/(P_{\text{H}_2\text{S}} + P_{\text{H}_2\text{O}}) = 9 \times 10^{-4}$.

shown in Fig. 3. The H_2S flow is varied in the range from 0 to 20 sccm and mixed with a constant H_2O flow of 1 slm before being injected in the ALD reactor. For each chosen H_2S flow, the exposure time of the substrate to the vaporized precursors is varied in the range from 30 to 52 ms. The $\text{S}/(\text{S} + \text{O})$ ratio increases for a higher H_2S partial pressure relative to water [i.e., $P_{\text{H}_2\text{S}}/(P_{\text{H}_2\text{S}} + P_{\text{H}_2\text{O}})$] and a longer exposure time. The inset of Fig. 3 shows that the $\text{S}/(\text{S} + \text{O})$ ratio increases with a higher substrate temperature for a constant value of both $P_{\text{H}_2\text{S}}/(P_{\text{H}_2\text{S}} + P_{\text{H}_2\text{O}})$ (i.e., 9×10^{-4}) and exposure time (i.e., 30 ms).

The growth characteristics of ZnO, ZnS, and ZnOS have been investigated in the literature by quantum chemical methods, assuming the use of DEZ, H_2O , and H_2S as Zn, O, and S precursors, respectively.^{18,19} ALD of ZnS and ZnO is known to proceed via the following surface exchange half-reactions, respectively:

where Et is an ethyl group and Zn-Et denotes a surface species. The formation of intermediate complexes on the film surface via the exchange half-reaction between H_2O and surface ethyl groups [Eq. (2)] has a higher kinetic barrier (36.2 kcal/mol) than the corresponding dissociative chemisorption of H_2S at the same ethyl groups (25 kcal/mol).^{18,19} This implies that on a purely kinetic basis the formation of surface ZnS bonds is more favorable than ZnO, when H_2O and H_2S are co-injected in the same deposition zone and react simultaneously with surface ethyl groups. The $\text{S}/(\text{S} + \text{O})$ ratio is expected to increase with higher partial pressure of H_2S relative to H_2O [i.e., $P_{\text{H}_2\text{S}}/(P_{\text{H}_2\text{S}} + P_{\text{H}_2\text{O}})$], in agreement with the experimental data shown in Fig. 3.

Next, the O surface species bonded to Zn atoms can be replaced by S via the exchange reaction:

while the reverse exchange reaction:

is known to have a 2 orders of magnitude lower reaction rate.¹⁶ This implies that the $\text{S}/(\text{S} + \text{O})$ ratio increases with longer exposure times to a constant concentration of H_2S and H_2O vapor due to a progressive sulfurization of ZnOH surface species, in agreement with the experimental data shown in Fig. 3. The reaction of H_2S with the ethyl surface groups [Eq. (1)] and the sulfurization of ZnOH [Eq. (3)] are energetically more favorable than the corresponding H_2O -based surface reactions [Eqs. (2) and (4)], thus resulting in an increase of the $\text{S}/(\text{S} + \text{O})$ ratio with a higher substrate temperature as shown in the inset of Fig. 3. The simple reaction model in Eqs. (1)–(4) describes the measured variation

in ZnOS composition, but the full complexity of the chemical reactions and surface effects that occur when H_2S and H_2O precursors are co-injected, such as different sticking coefficients of the precursors or ligands repulsion, is beyond the scope of this publication.

The growth per cycle (GPC) of ZnOS is plotted in Fig. 4 as a function of the $\text{S}/(\text{S} + \text{O})$ ratio. The theoretical rule of mixture predicts the GPC of multicomponent oxides to be a linear combination of the GPC of each binary oxide in the film. In the case of ZnOS, the GPC is expected to be

$$\text{GPC} = \text{O}\% \text{GPC}_{\text{ZnO}} + (100 - \text{O}\%) \text{GPC}_{\text{ZnS}}, \quad (5)$$

where O% is the oxygen content in the film, GPC_{ZnO} and GPC_{ZnS} are the growth per cycle of ZnO (0.13 nm/cycle) and ZnS (0.15 nm/cycle) for the deposition conditions presented in this paper. The value of the GPC calculated according to Eq. (5) is plotted as a dotted line in Fig. 4. The net GPC of ZnOS follows the expected trend defined by Eq. (5) only for S-poor and S-rich layers, while it is much lower for films with an intermediate S content, i.e., $0.4 < \text{S}/(\text{S} + \text{O}) < 0.7$.

The XRD patterns of ZnOS with different values of the $\text{S}/(\text{S} + \text{O})$ ratio are plotted in Fig. 5. S-ALD ZnO and ZnS have a polycrystalline structure where (100) and (002) or (111) are the main crystallographic orientations, respectively. With increasing sulfur, the XRD peaks shift to the left, which can be attributed to the substitution of larger S^{2-} ions in place of O^{2-} ions (ionic radii of S^{2-} and O^{2-} are 184 and 140 pm, respectively).²⁰ Following the same consideration, a low concentration of O in ZnS induces a shift of the crystallographic peaks toward higher angles. When a low concentration of the additional anion (i.e., S in ZnO or O in ZnS) is incorporated in the polycrystalline lattice of the binary matrix layer, the GPC of ZnOS follows the trend as defined by the rule of mixture in Eq. (5). With increasing S concentration in ZnO (or O concentration in ZnS), the additional cation tends to form a lattice structure

FIG. 4. GPC vs $\text{S}/(\text{S} + \text{O})$ ratio for $P_{\text{H}_2\text{S}}/(P_{\text{H}_2\text{S}} + P_{\text{H}_2\text{O}}) = 9 \times 10^{-4}$ and $t_{\text{exposure}} = 35$ ms (red circles) and 52 ms (black squares). The “hashed” area in the picture highlights the range of $\text{S}/(\text{S} + \text{O})$ for which ZnOS has an amorphous structure, based on the XRD data shown in Fig. 5.

Fig. 5. XRD spectra of ZnOS layers for different values of $S/(S+O)$ ratios.

different from that of the hosting binary layer, thus disrupting the polycrystalline structure of the film and creating an amorphous lattice. For $0.4 < S/(S+O) < 0.7$, the ZnOS films are amorphous and their GPC sharply drops below the values predicted by the rule of mixture, possibly due to a lower density or a lower reactivity of the surface sites in the amorphous lattice.

The optical properties of ZnOS films have been characterized by measuring both the transmittance and reflectance in the wavelength range from 250 to 1500 nm. The absorption coefficient (α) is calculated as $\alpha = 1/t \ln[(1-R)^2/T]$, where t is the thickness of ZnOS, T is the transparency, and R is the reflectance of the film. The absorption coefficients of both ZnOS and CBD CdS are plotted in Fig. 6 as a function of the wavelength. The optical bandgap of ZnOS is calculated from the absorption coefficient (α) according to the procedure described in Ref. 16 and it is plotted in Fig. 7 as a function of the $S/(S+O)$ ratio. The bandgap of ZnOS bows with increasing $S/(O+S)$ ratio due to the narrow bandgap of amorphous ZnOS layers and the wide bandgap of both polycrystalline ZnO and ZnS layers. A similar trend is measured in ZnOS films synthesized by other deposition techniques, such as sputtering, temporal ALD, and chemical bath deposition.^{21–24} The optical bandgap of ZnOS is larger than that of CdS, irrespective of the $S/(S+O)$ ratio. The replacement of CdS with a wider bandgap ZnOS buffer layer can

Fig. 6. Absorption coefficient (α) vs wavelength of CdS, ZnO, and ZnOS with $S/(S+O) = 17, 40, 60, 75$, and 90 .

increase the overall efficiency of CIGS solar cells by enhancing the transmission of the solar spectrum in the short wavelength range.

B. Device characteristics

In the remaining part of the paper, we present the device characteristics of both rigid and flexible solar cells with an S-ALD ZnOS buffer layer. CIGS cells on $3 \times 3 \text{ cm}^2$ soda lime glass substrates consisting of an Mo/CIGS/CdS/i-ZnO/Al:ZnO layer stack have been synthesized at TNO. The solar cells have a size of 0.50 cm^2 . Several batches of CIGS cells on glass have been prepared in which the CBD CdS buffer layer is replaced by ZnOS, grown in the laboratory-scale S-ALD reactor. The open circuit voltage (V_{oc}), short circuit density (J_{sc}), fill factor (FF), and efficiency of CIGS cells with the ZnOS buffer layer are plotted in Fig. 8 as a function of the $S/(S+O)$ ratio, together with the reference cells where CBD CdS is used.

ZnOS has a wider bandgap than CdS resulting in lower adsorption losses in the blue wavelength region and a higher value of J_{sc} in CIGS cells with the ZnOS buffer layer

Fig. 7. Bandgap of ZnOS vs $S/(O+S)$ ratio, including CdS reference.

FIG. 8. Photovoltaic parameters of CIGS cell (0.52 cm^2) on glass where S-ALD ZnOS layers with different S/(S + O) ratios are used as a buffer layer: (top left) open circuit voltage (V_{OC}), (top right) short circuit current (J_{sc}), (bottom left) fill factor (FF), (bottom right) efficiency (ζ) vs S/(O + S) ratio. The patterned area in each graph represents the values of the photovoltaic parameters for cells with a CdS buffer layer grown by chemical bath deposition.

for $0 < S/(S + O) < 0.5$. The V_{oc} of CIGS cells increases with the S content of the buffer layer, possibly due to a passivation of CIGS/ZnOS interface defects by sulfur atoms, thus reaching a similar value of the reference cells for $S/(S + O) \sim 0.4$. A further increase in sulfur induces a sharp decrease in J_{sc} , V_{oc} , and fill factor due to the formation of a significant potential barrier at the ZnOS/CIGS interface, which hinders the electron transport from the CIGS layer to the front electrode.^{24,25} A best efficiency of 15.9% ($V_{oc} = 662 \text{ mV}$, $J_{sc} = 34.2 \text{ mA/cm}^2$, and $FF = 70.4\%$) is reached for a ZnOS buffer layer with $S/(S + O) \sim 0.4$, while the reference cells with the CdS buffer layer have an efficiency of 15.5% ($V_{oc} = 665 \text{ mV}$, $J_{sc} = 32.1 \text{ mA/cm}^2$, and $FF = 72.7\%$).

A cross section EDX analysis of a record cell is shown in Fig. 9. The Ga/(Ga + In) ratio in CIGS has a value of about

~ 0.4 . The S/(S + O) ratio has a value of ~ 0.4 , which is constant throughout the entire thickness of the buffer layer within the resolution limit of the EDX technique ($\sim 7 \text{ nm}$). The external quantum efficiencies (EQEs) of the record CIGS cell on glass with CdS and the CIGS cell with the ZnOS buffer layer are plotted in Fig. 10. As expected, the cell with ZnOS exhibits a large increase in EQE in the blue wavelength region, due to the wider bandgap of ZnOS, as compared to CdS. The CIGS cell with the ZnOS buffer layer suffers from a small decrease in EQE in the near-IR range from 800 to 1000 nm due to reflection losses in the front window (i.e., ZnOS/ZnO/Al:ZnO stack). EQE measurements show that an overall increase in J_{sc} of 2.1 mA/cm^2 is achieved in CIGS cells by replacing the CdS layer with ZnOS for $S/(S + O) \sim 0.4$.

The use of S-ALD ZnOS as a buffer layer for flexible CIGS cells has been tested both in the laboratory-scale setup and in the roll-to-roll S-ALD equipment. A polyamide foil coated by an Mo/CIGS has been prepared for the deposition of ZnOS. After that, the cell structure is finalized by sputter

FIG. 9. Composition of the front window layers (ZnOS/ZnO/Al:ZnO) for the best performing CIGS cells (0.52 cm^2) on glass.

TABLE I. Device characteristics of record solar cells with spatial-ALD ZnOS buffer layer.

Buffer layer	Substrate	Efficiency (%)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)
CBD CdS	Glass $30 \times 30 \text{ cm}^2$	15.5	665	32.1	72.7
Laboratory-scale S-ALD ZnOS	Glass $15 \times 15 \text{ cm}^2$	15.9	662	34.2	70.4
Laboratory-scale S-ALD ZnOS	Polyamide $15 \times 15 \text{ cm}^2$	13.1	652	32.8	61.2
Roll-to-roll S-ALD ZnOS	Polyamide 50 cm wide	10.2	563	30.1	60.0

Fig. 10. EQE and absorption ($1 - R$) of the best performing CIGS solar cells (0.52 cm^2) on glass with CdS (---) or S-ALD ZnOS (—) buffer layer.

deposition of the ZnO/Al:ZnO stack and the cells are characterized. The device characteristics of flexible CIGS cells and mini-modules are listed in Table I, together with the CIGS cells on the glass substrate, as previously described. A record efficiency of 13% is achieved in flexible CIGS cells (0.57 cm^2) with the ZnOS buffer layer deposited in the laboratory-scale S-ALD reactor. Next, a 50-cm wide CIGS/Mo/polyamide stack is coated by ZnOS in the roll-to-roll S-ALD reactor, resulting in a best cell efficiency of 10.2% and a mini-module (270 cm^2) efficiency of 9.2%. The efficiency of flexible cells can be further increased by enhancing the photocurrent generation in the CIGS absorber and by optimizing the S/(S+O) ratio in ZnOS for the specific composition of the CIGS layer.

IV. SUMMARY AND CONCLUSIONS

In summary, we have investigated the growth of ZnOS in a laboratory-scale S-ALD reactor operating at atmospheric pressure. The deposition process has been transferred to an industrial roll-to-roll S-ALD setup. ZnOS has been applied as the buffer layer in flexible CIGS solar cells, achieving a best cell efficiency of 13% and a mini-module efficiency of 9.2%. These results show the viability of atmospheric roll-to-roll S-ALD as a new manufacturing technique for low-cost and large-area photovoltaics based on CIGS.

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