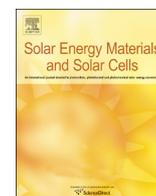




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# Atmospheric spatial atomic layer deposition of Zn(O,S) buffer layer for Cu(In,Ga)Se<sub>2</sub> solar cells



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## ABSTRACT

Zinc oxysulfide has been grown by spatial atomic layer deposition (S-ALD) and successfully applied as buffer layer in Cu(In, Ga)Se<sub>2</sub> (CIGS) solar cells. S-ALD combines high deposition rates (up to nm/s) with the advantages of conventional ALD, i.e. excellent control of film composition and superior uniformity over large-area and even non-flat substrates. Diethylzinc, water and hydrogen sulfite (H<sub>2</sub>S) have been used as zinc, oxygen and sulfur precursor, respectively. The S/(S+O) ratio in the film is accurately controlled by exposing the substrate simultaneously to both H<sub>2</sub>O and H<sub>2</sub>S precursors, which are pre-mixed and co-injected in the same deposition zone. The optoelectronic and morphological properties of Zn(O,S) are characterized as a function of the S/(S+O) ratio. Zn(O,S) buffer layers with different values of S/(S+O) ratio are applied in CIGS solar cells. An optimum value of S/(S+O) ratio of about 0.4 is found for which both the short circuit current density ( $J_{sc}=34.2$  mA/cm<sup>2</sup>) and cell efficiency ( $\eta=15.9\%$ ) increase, as compared to reference cells with CdS buffer layer ( $J_{sc}=32.1$  mA/cm<sup>2</sup>,  $\eta=15.5\%$ ).

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## 1. Introduction

Solar cells based on chalcopyrite Cu(In, Ga)Se<sub>2</sub> (CIGS) are becoming an established technology in the thin film photovoltaic industry because they combine the advantages of Si thin films, i.e. low production costs and flexible modules, with high conversion efficiencies (> 21%) [1,2]. State-of-the-art CIGS solar cells are based on a Mo/CIGS/CdS/ZnO/Al:ZnO stack with a Mo back contact, ZnO/Al:ZnO transparent front contact and a CdS buffer layer. In recent years there has been a growing interest in developing alternative buffer layers to CdS, to avoid the use of Cd which is toxic [3]. The replacement of the CdS buffer layer with a wider band gap material (> 2.4 eV) has the potential to increase the overall cell efficiency by enhancing the quantum efficiency in the blue wavelength region, where CdS absorbs most of the light. Zn(O,S) is emerging as a valid alternative to CdS, being a non-toxic material with a wider band gap than CdS [4–7]. The successful application of Zn(O,S) as buffer layer requires to control the composition and morphology of the CIGS/Zn(O,S) interface at a nanoscale level to minimize the interface recombination of light-induced charge carriers [8].

Atomic layer deposition (ALD) is an ideal technique to control the composition of thin films at atomic level and achieve superior uniformity over non-flat, large-area substrates [9]. However, the

low deposition rate ( $\approx 0.01$  nm/s) of ALD can hinder the use of this technique in the solar cell industry where high-throughput is needed to achieve low production costs. Conventional ALD is characterized by a time-sequenced injection of precursors in the deposition zone, where selective and self-limiting half-reactions occur on the substrate. In between precursor injections, the reactor is purged with an inert gas to remove all unreacted precursor and reaction products. Purging of the reactor is a time consuming step which severely limits the deposition speed of conventional ALD. This drawback has been overcome by the spatial ALD technique, where 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. By spatially dividing the zones by a nitrogen gas curtain, a purge step is no longer needed and deposition rates as high as nanometers per second have been achieved [10].

ALD of multi-component films is typically carried out by alternating the self-limiting growth of binary layers, resulting in films where both the composition and the physical properties are strongly inhomogeneous along the growth direction [9,11]. ALD Zn(O,S) is a nano-laminate with alternating ZnO and ZnS composition, where the S/(S+O) ratio is tentatively controlled by varying the relative thickness of the ZnS and ZnO layers [12]. However, the lattice mismatch or the different morphology of the binary layers as well as non-ideal surface reactions at layers interface can hinder a precise control of both thickness and stoichiometry of multi-component films [11,12]. In S-ALD, the growth of multi-metal oxides (e.g. Al:ZnO, InGaZnO) is typically performed by

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alternatively exposing the substrate to water vapor and to the precursors of the metal elements (e.g. Al, Zn) which are pre-mixed and co-injected in the same deposition zone [13–15]. The co-injection of metal-organic precursors with similar molecular size and vapor pressure (e.g. TMA, DEZ) allows a precise control of the metal content in the film and it enables the deposition of Zn-based multi-metal oxides with uniform composition along the growth direction [14,15]. In this paper, we investigate the S-ALD of Zn(O,S) by co-injecting the vaporized H<sub>2</sub>S and H<sub>2</sub>O precursors. The structural and optoelectronic properties of Zn(O,S) are characterized as a function of the S/(S+O) ratio and the application of Zn(O,S) as buffer layer in CIGS solar cells is demonstrated.

## 2. Experimental

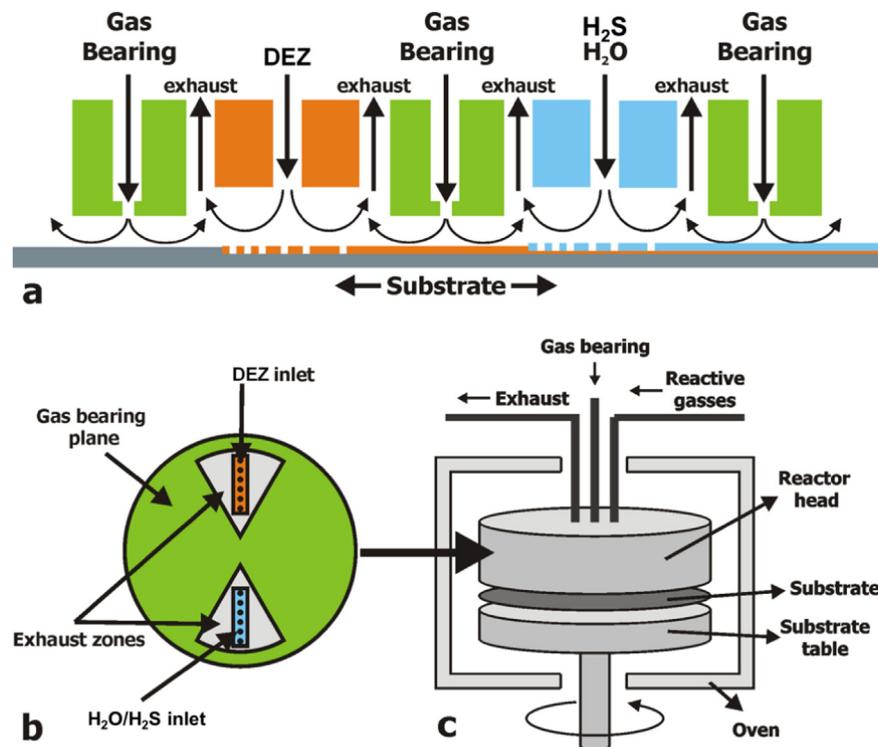
A schematic of the atmospheric spatial ALD reactor used for the deposition is shown in Fig. 1 [10,16]. Two different inlets are installed in the circular gas injection head, one for the metal precursors and another for the oxygen precursor. The substrate is placed on a circular table which rotates underneath the reactor head at a distance of typically 20–100 μm. During each rotation, the substrate is exposed sequentially to each precursor. Between and around the reactant inlets, shields of inert gas (N<sub>2</sub>) separate the precursor flows and seal off the reaction zones, thus making the reactor completely independent of the environment, enabling operation under atmospheric pressure conditions. The entire reactor is installed in a conventional oven which can be heated up to 400 °C.

For the conditions reported in this paper, diethylzinc [Zn(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, (DEZ)], H<sub>2</sub>O and H<sub>2</sub>S are used as precursors for zinc, oxygen and sulfur respectively. DEZ and deionized water are evaporated from bubblers, using argon as carrier gas and transported to the reactor injection head through heated lines, to

prevent condensation. A 3.5% H<sub>2</sub>S/N<sub>2</sub> mixture is used as H<sub>2</sub>S source. The DEZ bubbler and H<sub>2</sub>S bottle are kept at room temperature, while the H<sub>2</sub>O bubbler is heated to 50 °C. The H<sub>2</sub>O and H<sub>2</sub>S flows are mixed and then injected into the deposition zone through the same inlet, after being diluted by argon. The Ar carrier flow through the H<sub>2</sub>O and DEZ bubbler is varied in the range from 0 to 1 slm and from 10 to 150 sccm, respectively. The H<sub>2</sub>S flow to the reactor varies in the range from 0 and 30 sccm. The experiments described in this manuscript are carried out by setting the exposure time of the substrate for both the DEZ and H<sub>2</sub>O/H<sub>2</sub>S mixture to 30 ms. The substrate temperature is set at 120 °C.

Zn(O,S) is deposited on *c*-Si wafers to measure its thickness and composition, while a glass substrate is used to determine the crystallographic structure and the transparency of the films. The Zn(O,S) thickness is measured by ex-situ Spectroscopic Ellipsometry, using a J.A. Woollam M2000 rotating compensator ellipsometer in the 300–1000 nm range. The composition of the films is measured with a FEI Quanta 600 FEG SEM system equipped with an energy-dispersive X-ray (EDX) diagnostic. A Philips X-pert SR5068 powder diffractometer equipped with a Cu Kα source is used to determine the crystallographic structure of the films. TEM studies are performed using a JEOL ARM200F operated at 200 kV, equipped with a 100 mm<sup>2</sup> SSD EDS detector. A Shimadzu UV3600 spectrophotometer is used for total reflection and transmission measurements with an integrating sphere.

Solar cells are fabricated by co-evaporating 2 μm thick CIGS films on 10 × 10 cm<sup>2</sup> soda lime glass substrates, coated by Mo. The glass substrate is kept at a temperature of 550 °C during the CIGS deposition. Reference solar cells have a 60 nm thick CdS buffer layer, grown by chemical bath deposition. All devices are completed with a RF sputtered 50 nm thick ZnO and a 250 nm thick ZnO:Al layer. Ni/Al contact grids are evaporated through a shadow mask. The individual solar cells with an area of 0.5 cm<sup>2</sup> are defined by mechanically scribing the substrates.



**Fig. 1.** (a) Schematic drawing of the spatial ALD reactor; from [10]. The DEZ and H<sub>2</sub>O/H<sub>2</sub>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 Zn(O,S) monolayer. (b) Schematic drawing of the bottom side of the spatial ALD reactor head, where the DEZ and H<sub>2</sub>O/H<sub>2</sub>S half-reaction zones are integrated into inlets surrounded by exhaust zones and gas bearing planes. The colors correspond to those in (a). (c) Schematic drawing of the reactor. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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