

XPS, TEM AND NRA INVESTIGATIONS OF THE $\text{Cu(In,Ga)(S,Se)}_2/\text{ZnSe}$ HETEROSTRUCTURE FOR HIGHLY EFFICIENT SOLAR CELLS

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Thin film solar cells based on Cu(In,Ga)Se_2 (CIGS) have achieved photovoltaic conversion efficiencies beyond 18 % on laboratory scale [1]. Standard CIGS devices contain a buffer layer consisting of CdS deposited by CBD. However, for a large-scale manufacturing of this type of solar cell, a replacement of the toxic CdS would be desirable. Alternative buffer layers such as ZnS [2] and many others have been investigated. Previously, we have reported on CIGSS solar cells with efficiencies of over 14 % containing a $\text{Zn(Se,OH)/Zn(OH)}_2$ buffer layer deposited by CBD [3]. Here we present a study on the structural and compositional properties of these CBD- $\text{Zn(Se,OH)/Zn(OH)}_2$ buffer layers deposited on CIGSS substrates.

The $\text{Zn(Se,OH)/Zn(OH)}_2$ buffer layer was grown in an aqueous alkaline solution using CBD. For the deposition, two solutions were prepared: Solution A contained ZnSO_4 (0.8 M), $(\text{NH}_2)_2$ (25 %), NH_3 (25 %) dissolved in tri-distilled water under stirring, heated to 70 °C, solution B contained $\text{SeC(NH}_2)_2$ (0.08 M) and Na_2SO_3 (0.08 M) dissolved in tri-distilled water. Prior to the deposition of the Zn(Se,OH) layer, a zinc-treatment was performed leading to the growth of an amorphous Zn(OH)_2 layer with a thickness of several nm [6]. This is why these buffer layers are called $\text{Zn(Se,OH)/Zn(OH)}_2$. For the Zn-treatment the CIGSS absorbers were immersed in the colorless, heated solution A and were constantly rotated. Then solution B was added and the solution turned milky after 30 sec. After the deposition of the buffer layer, the CIGSS substrate was cleaned with tri-distilled water and air dried.

The Zn-treatment allows for favorable modification of the absorber surface [4]. Also an intermixing at the interface reported by Heske et al. [5] has a positive effect on the solar cell performance. The grown Zn(OH)_2 layer could be responsible for the positive effect of the treatments on the solar cell performance as well due to protection of the

absorber during ZnO-sputtering or introduction of a charged layer on the absorber surface [7]. The experimental details of the TEM, XPS, NRA analysis and device fabrication are described elsewhere [3, 6, 8]. For the SEM images a LEO1530 (Gemini) FE-SEM with Schottky field emission and a voltage of 7 kV is used.

Solar cells with a $\text{Zn(Se,OH)/Zn(OH)}_2$ buffer yield high efficiency values comparable to CIGSS/CdS devices (total area = 0.5 cm², Tab. 1).

	? [%]	FF[%]	Isc [mA/cm ²]	Voc [mV]
ZnSe	14.5	72.3	35.2	570
CdS	14.6	73.7	33.7	588

Tab. 1: Parameters of CIGSS devices (tot. area 0.5 cm²) with $\text{Zn(Se,OH)/Zn(OH)}_2$ and CdS buffer layers

In the cross-sectional SEM image (Fig. 1) small

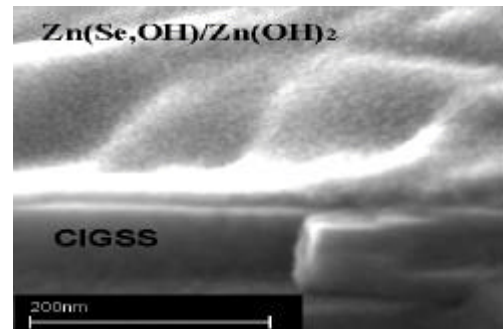


Fig. 1: SEM image: $\text{Zn(Se,OH)/Zn(OH)}_2/\text{CIGSS}$

white particles can be seen in the film which covers the absorber uniformly. The cross-sectional TEM image (Fig. 2) shows that these particles consist of small crystallites (Region 1). Fourier transform analysis of the lattice planes yields a spacing of 3.2 Å, which can be attributed to ZnSe. Fig. 1 suggests that an aggregation of ZnSe nanocrystals formed by the homogenous process in the milky solution could take place during CBD. They are adsorbed on the already existing amorphous layer (Region 2), consisting of Zn(OH)_2 , which is formed during the Zn-treatment [6]. Region

3 represents the lattice planes of the CIGSS absorber, region 4 is part of the glueline.

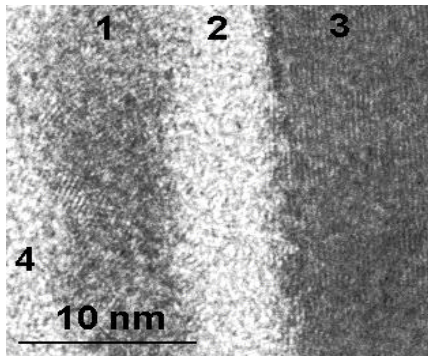


Fig. 2: TEM picture of a Zn(Se,OH)/Zn(OH)₂/CIGSS structure, U = 120 kV

Fig. 3 shows a XPS O1s spectrum of a Zn(Se,OH)/Zn(OH)₂ buffer layer on CIGSS with a thickness of 10 nm. Appreciable levels of oxygen are incorporated into the ZnSe film in the forms of Zn(OH)₂, ZnO and H₂O, justifying the nomenclature Zn(Se,OH) for this part of the buffer layer. Furthermore contributions of C-O bonds, H₂O and OH-groups from contamination of the film surface are expected. The main contribution to the O1s peak comes from Zn(OH)₂ incorporation in the

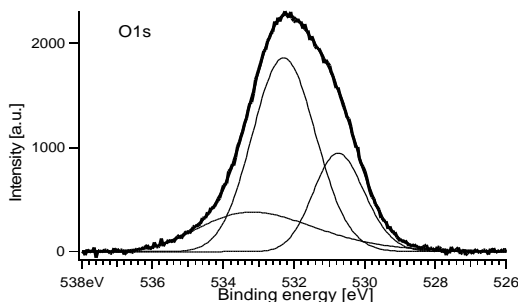


Fig. 3: O1s core level of Zn(Se,OH) using a Mg K_α source (1253.6 eV), p = 2x10⁻⁸ Pa

ZnSe layer (main peak at 532.3 eV). The underlying amorphous Zn(OH)₂ layer (Fig. 2, region 2) contributes little to the signal due to the surface sensitivity of XPS. The smaller peak of the Gauss-Lorenz fit at 530.75 eV can be attributed to ZnO formed from Zn(OH)₂. H₂O and C-O bonds contribute to the smallest peak at 533.2 eV [2].

Fig. 4 shows a hydrogen depth profile of a Zn(Se,OH)/Zn(OH)₂ buffer layer on CIGSS. The buffer contains a high amount of hydrogen, whereas the absorber contains almost no hydrogen. Since the absorber surface is rough, there is a slow decrease of the profile into the absorber. The hydrogen content in the Zn(Se,OH) layer is higher than in the Zn(OH)₂

layer indicating that part of the Zn(OH)₂ is converted to ZnO.

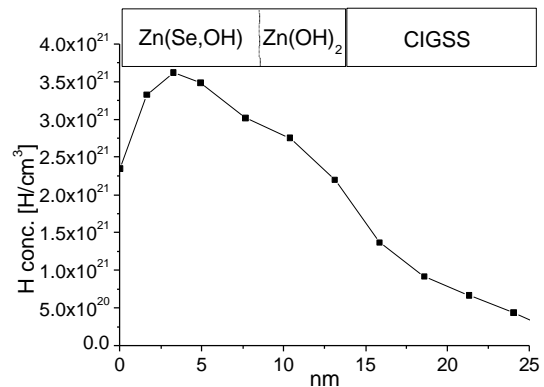


Fig. 4: Hydrogen depth profile with NRA

CBD- Zn(Se,OH)/Zn(OH)₂ buffer layers are grown on CIGSS substrates with a nanocrystalline and amorphous structure to a thickness of approximately 10 nm. A high amount of oxygen and hydrogen is incorporated in the ZnSe film mainly in form of Zn(OH)₂, ZnO and H₂O.

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