

A First Approach to the Interface Analysis of Chemical Bath Deposited $\text{In}(\text{OH},\text{O})_x\text{S}_y$ Buffer Layers and CuInS_2 in Thin Film Solar Cells

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Chemical bath deposition (CBD) of $\text{In}(\text{OH},\text{O})_x\text{S}_y$ is a subject of ongoing research - mainly due to the objective of developing Cd-free, chalcopyrite based thin film solar cell devices [1,2]. The solution chemistry, the deposition mechanism and the characteristics of CBD- $\text{In}(\text{OH},\text{O})_x\text{S}_y$ thin films have been investigated to a large extent [3,4,5]. The interplay between chemical bath, i.e. deposition conditions, and the performance of resulting solar cells has, however, largely remained unclear. Here we present first results concerning the analysis of the $\text{In}(\text{OH},\text{O})_x\text{S}_y/\text{CuInS}_2$ interface and its sensitivity to changes in the chemical environment during the deposition process. Solar cell performances of the investigated devices are also reported.

$\text{In}(\text{OH},\text{O})_x\text{S}_y$ layers were deposited at 70°C for approximately 17min onto CuInS_2 , etched in 10% KCN for 3 min. The chemical bath composition was: 25mM InCl_3 , 0.005M HCl and 0.1M thioacetamide [3,6]. The deposited layers were investigated using angle resolved X-ray photoelectron spectroscopy (ARXPS) after different deposition times and were also employed as buffer layers for CuInS_2 solar cell processing.

In previous work two deposition phases have been identified for the $\text{In}(\text{OH},\text{O})_x\text{S}_y$ CBD deposition process: an initial hydroxyoxide rich nucleation phase and a consecutive phase of fast sulphur rich growth. The first of these two has shown to be beneficial for the development of the V_{oc} of the finished device [2]. Furthermore it was shown that $[\text{In}(\text{H}_2\text{O})_6]^{3+}$, polynuclear complexes as for example $[\text{In}(\text{In}(\text{OH})_2)_n]^{3+n}$ or even colloidal $\text{In}(\text{OH})_3$ are present in the chemical bath during the initial stage and that they may contribute significantly to the growth initialisation of $\text{In}(\text{OH},\text{O})_x\text{S}_y$ [3]. In view of a process optimisation leading to solar cells of optimum efficiency it is hence of interest to investigate how the presence of such species influences the resulting device characteristics as for example the band line up at the $\text{In}(\text{OH},\text{O})_x\text{S}_y/\text{CuInS}_2$ interface. This was done using a ‘cold’ start and a ‘hot’ start deposition process. For the ‘cold’ start process the sulphur source was added to the otherwise complete chemical bath at room temperature and the solution was heated over the deposition time. For the ‘hot’ start process the sulphur source was added once the bath had been kept for some time at the deposition temperature. As demonstrated in earlier work, heating the indium salt containing solution to 70°C will increase the concentration of the species in question [3].

For the $\text{In}(\text{OH},\text{O})_x\text{S}_y$ layers the optical energy band gaps are determined at 2.2eV and 3.2eV, indirect and direct respectively. Similar values can be found in the literature [7,8]. XPS results have shown that the material deposited in the initial stage of the CBD process is richer in oxides than the one formed during the second deposition phase, a characteristic, which is enhanced by using the ‘hot’ start process. The band line-up at the $\text{In}(\text{OH},\text{O})_x\text{S}_y/\text{CuInS}_2$ interface, deduced from the determination of the valence

band discontinuity ΔE_{VB} , was found to be affected as shown in Figure 1. Characterisation of the resulting solar cell devices, so far did not permit further conclusions (see Table 1). However, a device optimisation is consistently achieved when the ‘hot’ start CBD process with the higher initial concentration of the critical indium complexes is used.

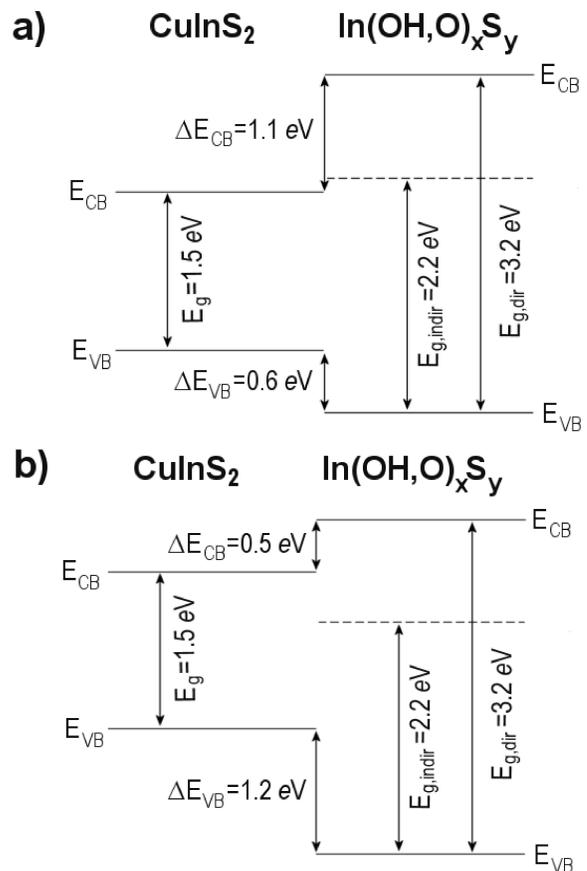


Figure 1. Energy band line-up between the CuInS_2 absorber and the $\text{In}(\text{OH},\text{O})_x\text{S}_y$ buffer layer, deposited via a) a ‘cold’ and b) a ‘hot’ CBD process.

Table 1. Characteristic I-V corner point values for solar cells with $\text{In}(\text{OH},\text{O})_x\text{S}_y$ buffer layers, deposited via a ‘cold’ or ‘hot’ CBD process, in comparison with the CdS reference devices.

Process	I-V Corner Point Values				% of CdS
	V_{oc} [mV]	j_{sc} [mA/cm ²]	FF[%]	η [%]	
‘cold’	703	24.0	58.4	9.9	84
CdS	717	22.7	73.3	11.8	
‘hot’	753	24.4	57.6	10.6	95
CdS	712	21.5	68.8	11.2	
‘hot’	705	23.6	63.3	10.5	91
CdS	718	22.4	72.4	11.6	

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- [1] D.Braunger, D.Hariskos, T.Walter and H.W.Schock, *Sol. Energy Mater. Sol. Cells* **40**:97-102 (1996)
- [2] C.Kaufmann, S.Neve, W.Bohne, J.Klaer, R.Klenk, C.Pettenkofer, J.Röhrich, R.Scheer, U.Störkel and P.J.Dobson, *28th IEEE PVSC*, Anchorage, Sept. 2000
- [3] C.Kaufmann, R.Bayón, W.Bohne, J.Röhrich, R.Klenk and P.J.Dobson, *J. Electrochem.Soc.* **149**(1):C1-C9 (2002)
- [4] R.Bayón and J.Herrero, *Thin Solid Films*, **387**:111-114 (2001)
- [5] R.Bayón, C.Maffiotte and J.Herrero, *Thin Solid Films* **353**:100-107 (1999)
- [6] T.Yoshida, K.Yamaguchi, H.Toyoda, K.Akao, T.Sugiura, H.Minoura and Y.Nosaka, *Electrochem. Soc. Proc.* **97-20**:37-57 (1997)
- [7] E.B.Yousfi, T.Asikainen, V.Pietu, P.Cowache, M.Powalla and D.Lincot, *Thin Solid Films* **361-362**: 183-186 (2000)
- [8] W.T.Kim and C.D. Kim, *J. Appl. Phys.* **60**(7):2631-2633 (1986)