INDUSTRIAL APPLICATION OF CHEMICAL BATH DEPOSITION: CdS BUFFER LAYERS IN Cu(In,Ga)(S,Se)₂ SOLAR CELLS T. P. Niesen, J. Lorenz, W. Stetter, and V. Probst Shell Solar GmbH Otto-Hahn-Ring 6, 81739 München, Germany

Aiming at a low cost, high efficiency thin film solar cell process, we are currently developing a two step stacked elemental layer process for Cu(In,Ga)(S,Se)₂ (CIGSSe) thin films of $60x90 \text{ cm}^2$ size, applying Cu(Ga)-In-Se precursor deposition by magnetron sputtering and subsequent rapid thermal processing (RTP) in a sulfur containing ambient (fig. 1, 2).¹ Such devices yield the highest efficiencies with thin CdS buffer layers deposited by Chemical Bath Deposition (CBD) while vapor deposition techniques led to inferior results.

In the present paper, the CBD-CdS processing in our pilot line is described. Deposition is done in a programmable, automatically driven equipment with tanks for substrates of 30x30 cm² in size. Separate compartments for deposition, rinsing, and drying are included. Thiourea is decomposed in presence of cadmium acetate in aqueous ammonia solution at 60°C. To reach best homogeneity of the coatings, the substrates are moved up and down during deposition by an automatically driven manipulator. In addition, a filtering system is used to remove CdS particles from the solution, and ultrasonication is applied to reduce undesired particle agglomeration. Due to the toxicity of cadmium compounds coating should only be applied on the active area of the final device. This is successfully reached by special designed substrate holders.

The development of the CBD-CdS process is driven by optimizing the solar cell parameters (e.g. efficiency) which includes a look at the buffer layer composition (i.e. impurities), film thickness and lateral homogeneity, and reproducibility of the deposition process. For each deposition film thickness is controlled ex-situ by x-ray fluorescence analysis on a test substrate (fig. 3). Likewise the lateral homogeneity of the coatings is determined.

Depth resolved x-ray photoelectron spectroscopy is used to analyze the film composition and impurities therein. Carbon and nitrogen impurities are below the detection limits, therefore cadmium cyanamide $(Cd(CN)_2)$ – as a side product of thiourea decomposition – is only rarely formed in our process. Oxygen is found to be between 3.8 and 6.0 at-%, and optimal solar cell parameters are found with the lowest oxygen content (fig. 4). The amount is directly correlated to the used thiourea concentration in CBD, as a higher sulfide concentration decreases the incorporation of oxide or hydroxide species. However, bulk precipitation of CdS particles occurs at high thiourea concentration which makes a permanent filtration of the solution during the deposition inevitable.

¹ J. Palm, V. Probst, W. Stetter, R. Tölle, T. P. Niesen, S. Visbeck, O. Hernandez, M. Wendl, H. Vogt, H. Calwer, B. Freienstein, and F. Karg, Thin Solid Films *special issue E-MRS 2002, symposium B* (submitted).



Fig. 1. Process scheme for CIGSSe-modules with monolithic integration of series connected cells



Fig. 2. Schematic cross section through integrated series connection in CIGSSe modules



Fig. 3. CdS film thickness data reached in repeated CBD processes



Fig. 4. Direct correlation of oxygen content in CdS film and cell efficiency