CdS- and Cd(OH)$_2$-formation during Cd-treatments of Cu(In,Ga)(S,Se)$_2$ thin film solar cell absorbers

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INTRODUCTION

For thin film solar cells based on Cu(In,Ga)(S,Se)$_2$ (CIGSSe) record efficiencies of 18.8 % [1] have been reached. The standard structure of these solar cells contains a CdS buffer layer between the CIGSSe absorber and a ZnO window layer, which is undesirable because of the large amount of Cd-containing waste produced during its chemical bath deposition (CBD). Therefore, a Cd-free solar cell structure is the goal of current investigations, which is not an easy task because the CdS layer and the CBD process itself play an important role for high cell efficiencies. Important effects are the protection of the absorber surface against damage caused by the sputter deposition of the ZnO window layer as well as a removal of absorber surface contaminations by the ammonium hydroxide-containing chemical bath. Recently, cells without CdS buffer layer have reached similar efficiencies as corresponding cells with CdS layer [2], using a soft ZnO deposition technique ("Ion Layer Gas Reaction", ILGAR) and by treating the absorber with an ammonium hydroxide solution containing Cd^{2+} prior to the ZnO deposition. This treatment improves all relevant cell parameters. There is still Cd involved in this process, but the amount of waste is largely reduced compared to the CBD process, since the solution can be reused. Despite its success, the Cd^{2+}-treatment is an "empirically" introduced step and its impact on the absorber surface is still largely unknown. Therefore, we have performed a detailed investigation using X-ray Photoelectron Spectroscopy (XPS), X-ray excited Auger Electron Spectroscopy (XAES) and X-ray Emission Spectroscopy (XES).

EXPERIMENTAL

The investigated absorbers were taken from the Shell Solar base line process consisting of a rapid thermal annealing of elemental layers on Mo-coated soda-lime glass in a sulfur containing atmosphere. We have investigated absorbers treated with different solutions containing between 0 mM and 12 mM CdSO$_4$ dissolved in 1.5 M aqueous NH$_3$. The absorbers were treated for 10 mins while employing a temperature ramp between room temperature and 80°C. For XPS and XAES experiments, Mg K$_\alpha$ excitation and a VG CLAM 4 electron spectrometer were used. The XES spectra were taken at the SXF endstation of beamline 8.0.
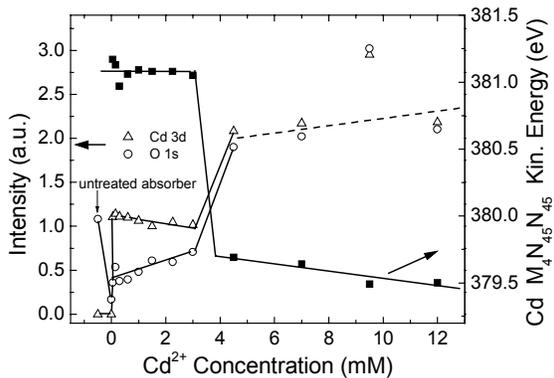
Figure 1. XPS-intensities of Cd 3d (open triangles) and O 1s (open circles) as a function of Cd^{2+} concentration before and after treatment of a $Cu(In,Ga)(S,Se)_2$ absorber (left ordinate). The corresponding Cd $M_4N_{45}N_{45}$ Auger line positions are shown with filled squares (right ordinate).

Figure 2: Sulfur $L_{2,3}$ x-ray emission spectra of (a) an untreated and (b) a Cd^{2+} treated $Cu(In,Ga)(S,Se)_2$ absorber (1.5 mM Cd^{2+} concentration), normalized to the maximum count rate. Spectrum (c) shows the enlarged (x25) difference between (a) and (b). Spectra (d), (f), and (g) are obtained by subtracting 96% of spectrum (a) from the spectra of absorbers after Cd^{2+} treatment with different Cd^{2+} concentrations. For comparison, spectrum (e) was recorded for a CdS reference film.

RESULTS

Independent of the Cd^{2+} concentration, our XPS and XES measurements show that Na, located at the absorber surface, is removed (i.e., dissolved in the aqueous NH_3 solution). Furthermore, we find a reduction of C and, depending on the Cd^{2+} concentration (as disscussed below), O surface contaminations. For all treatments containing Cd^{2+}, our XPS and XAES measurements show a deposition of Cd at the absorber surface. This deposition takes place in two concentration regimes, as shown in Fig. 1. For Cd^{2+} concentrations of 1.5 mM or below we observe a nearly concentration-independent amount of Cd at the absorber surface. A quantitative evaluation of the peak intensities and the attenuation behavior of the absorber peaks determines a deposition of 0.5 – 1 monolayer of Cd.

A reliable chemical identification of the adsorbed Cd-containing compound is very difficult, because the variations in Cd XPS and Auger line positions between different compounds can be very small. In the present case, a formation of CdS or CdSe appears equally feasible. To resolve this problem, we have performed XES measurements that give detailed information about the local chemical bonding of the sulfur atoms [3]. Fig. 2 a) and b) show the spectra of an untreated and a Cd^{2+} treated absorber using a Cd^{2+} concentration of 1.5 mM (normalized to their maximum). Because XES as a "photon-in-photon-out" technique is much less surface sensitive than XPS and XAES, we have to create a difference spectrum (Fig. 3 c) to get information about changes at the absorber surface induced by the Cd^{2+} treatment. In this spectrum we observe several important features, which can be compared with the CdS reference spectrum in Fig. 2 e). First, a double peak structure (2) is found,
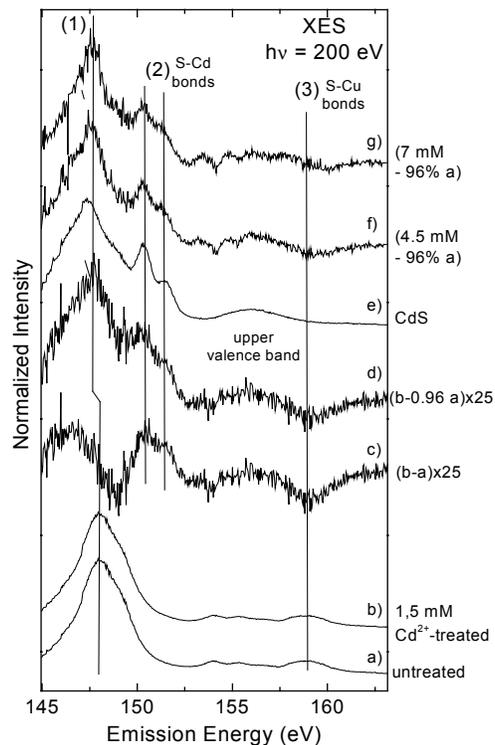
which can be assigned to Cd 4d electrons decaying into S 2p holes, giving a first evidence for Cd-S bonds at the absorber surface. This is corroborated by the broader structure on the right hand side of these peaks, which can be assigned to transitions from the upper valence band of CdS. Based on these findings, we have subtracted a properly scaled spectrum a) from b), resulting in spectrum d), which very closely resembles the CdS spectrum. Apart from the features described above, we also find a shift of the peak with highest overall intensity, which is associated with S 3s electrons decaying into S 2p holes. This shift is ascribed to a chemical shift of the S 2p core level. Therefore, about 4 % of the S XES spectrum of the Cd^{2+} treated absorber can be attributed to S atoms bonded to Cd, which corresponds to approximately one monolayer of CdS in accordance with the quantitative evaluation of the XPS results given above. An additional finding in the XES spectra is a dip in the spectral region of electrons originating from Cu 3d levels decaying into S 2p holes (3). This indicates that S-Cu bonds are broken during the Cd^{2+} treatment.

For Cd^{2+} concentrations above 1.5 mM, a drastic change occurs. We observe (Fig. 1) an abrupt increase of the amount of deposited Cd and, in parallel, a shift of the Cd $M_4N_{45}N_{45}$ line position to lower kinetic energies. The new chemical species can be identified as $Cd(OH)_2$ in accordance with the fact that we now also find a strongly increased O 1s signal. In the S XES spectra for this higher Cd^{2+} concentration regime, we also find Cd-S bonds as is shown in Fig. 2 f) and g). The two spectra are obtained with the same factors (a 4 % fraction of the CdS spectrum) as spectrum d). This is a clear indication that the deposition of $Cd(OH)_2$ takes place on top of the CdS monolayer.

We now can interpret the findings discussed above in the following way. The Cd^{2+} treatment leads to a deposition of Cd on the absorber surface. First these Cd atoms are bound to S atoms from the absorber (the SO_4^{2-} in the solution is much too stable to act as a sulfur source) and the reaction stops when a homogeneous coverage of the absorber surface is reached (i.e., one monolayer). Therefore, the amount of Cd on the absorber surface stays constant until we reach the "high concentration regime", in which an additional $Cd(OH)_2$ deposition on top of the CdS layer occurs. Since record CdS-free CISSe solar cells are generally prepared in the low concentration regime, it is evidently the CdS/CISSe interface formation which is responsible for the empirical success of the Cd^{2+}-treatment. In particular the positive impact of the CdS/CISSe interface on the electronic structure is expected to play an important role for the optimization of next-generation, nominally CdS-free thin film solar cells on the basis of CISSe.

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