

Deposition of In_2S_3 on $\text{Cu}(\text{In}, \text{Ga})(\text{S}, \text{Se})_2$ thin film solar cell absorbers by spray ion layer gas reaction: Evidence of strong interfacial diffusion

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Recently, Cd-free $\text{Cu}(\text{In}, \text{Ga})(\text{S}, \text{Se})_2$ -based “CIGSSe” thin film solar cells with a nominal In_2S_3 buffer layer deposited by the spray ion layer gas reaction technique resulted in photovoltaic performances comparable to that of CdS buffered references. In the past it was argued that diffusion processes across the In_2S_3 /CIGSSe interface play a significant role for the device quality. Investigating the interface formation by using x-ray photoelectron spectroscopy, the authors were able to confirm a strong interfacial diffusion involving Cu and Na from the CIGSSe. © 2007 American Institute of Physics. [DOI: 10.1063/1.2717534]

$\text{Cu}(\text{In}_{(1-x)}\text{Ga}_x)(\text{S}_Y\text{Se}_{(1-Y)})_2$ (“CIGSSe”) thin film solar cells promise to be the next generation of photovoltaic cells, superseding the more expensive current state-of-the-art Si-based solar cell technology. Corresponding n^+ -ZnO/ i -ZnO/CdS/CIGSSe/Mo/glass devices have already reached power conversion efficiencies close to 20%.¹ However, because of economic and ecological reasons there is a strong impetus to replace not only the CdS layer by a nontoxic, more transparent alternative buffer but also the conventionally used chemical bath deposition (CBD) by a technique which is capable of in-line processing. In_2S_3 layers deposited by physical vapor deposition² (PVD), sputtering,³ or atomic layer deposition^{4,5} (ALD) are among the promising alternatives. Recently, nominal In_2S_3 buffers were also prepared by the spray ion layer gas reaction⁶ (Spray-ILGAR). The resulting CIGSSe-based solar cells yield comparable efficiencies⁶ and stabilities⁷ as corresponding CBD-CdS buffered references.

Despite the fact that for ALD- In_2S_3 the highest growth rate is reported for process temperatures between 160 and 180 °C,⁸ different optimization experiments^{4,9} show that for the best photovoltaic performance it is necessary to prepare the ALD- In_2S_3 buffer at much higher temperatures (210–220 °C). This might be an indication that the thermal input during interface formation between buffer and absorber plays an important role for the performance of respective solar cells. In fact, based on x-ray photoelectron^{4,10} (XPS), secondary ion mass,^{3,9} or sputtered neutral mass spectroscopy⁹ depth profiles, several groups have found that there is a thermally driven diffusion of copper and also of sodium (stemming from the soda-lime glass) from the CIGSSe substrate into the In_2S_3 buffer layer. This was also recently confirmed by microstructural studies of the In_2S_3 /chalcopyrite interface by transmission electron micrographs and related energy dispersive x-ray analysis.¹¹ Similar

diffusion processes were also reported for PVD- In_2S_3 .^{2,12} The optimal process temperature for the preparation of Spray-ILGAR In_2S_3 buffers with respect to the performance of corresponding solar cells is comparable⁶ (200–250 °C) to that for optimal ALD- In_2S_3 buffers. Hence, in this letter we will investigate whether across the Spray-ILGAR In_2S_3 /CIGSSe ALD- In_2S_3 interface such diffusion processes also take place. However, in contrast to the destructive sputter depth profiling experiments mentioned above, whose results critically depend on the exact knowledge of the sputter and ionization cross sections, respectively, we use a different approach. The Spray-ILGAR In_2S_3 /CIGSSe interface formation is investigated by monitoring the surface composition of a set of CIGSSe samples with differently thick nominal In_2S_3 cover layers with XPS and thus is not necessarily the equivalent to a depth profile.

All experiments were based on industrial-grade CIGSSe/Mo/glass absorber substrates from the pilot line of Shell Solar GmbH (now AVANCIS GmbH & Co. KG). The CIGSSe is formed by rapid thermal annealing of stacked elemental layers on Mo-coated soda-lime glass in a sulfur containing atmosphere.¹³ For the preparation of the nominal In_2S_3 layers, we used the Spray-ILGAR technique,^{6,14} where a precursor solution is sprayed onto the heated absorber substrates followed by conversion of the solid film to a chalcogenide by a reactive gas. In the present study, the spray solution used is InCl_3 dissolved in ethanol and the reactive gas is H_2S . A more detailed description can be found elsewhere.^{6,7,14} Because of the cyclical nature of the Spray-ILGAR process, the thickness of the buffer layer can simply be adjusted by varying the number of spray cycles. A set of samples where this number has been varied between 0 (bare, uncovered CIGSSe absorber), 1, 2, 3, 4, and 6 was investigated. The process temperature for all samples was 250 °C, for which the growth rate was determined to be ~ 3.3 nm/cycle.⁶ After preparation, the ($1/2 \times 1$ in.²) samples were sealed in a polyethylene bag filled with N_2 . The sample transfer was performed as quickly as possible in order to limit the exposure time to ambient air. Then, the samples were transferred into

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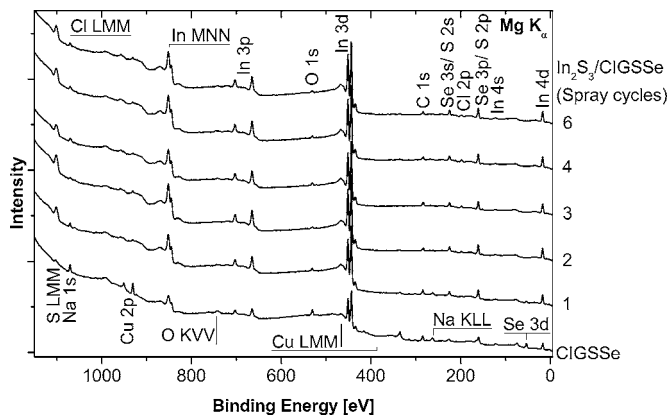


FIG. 1. XPS survey spectra of differently thick In_2S_3 layers deposited on CIGSSe absorbers by a varying number of spray cycles.

the analysis chamber of a combined ultrahigh vacuum preparation and spectroscopy system (“CISSY,” see Ref. ¹⁵ for more details) at a base pressure of $<1 \times 10^{-9}$ mbar via an attached N_2 filled glovebox. The samples were characterized by XPS using $\text{Mg } K\alpha$ (1253.6 eV) and $\text{Al } K\alpha$ (1486.6 eV) excitations and a CLAM4 electron spectrometer from Thermo VG Scientific (calibrated according to Ref. ¹⁶).

Figure 1 shows the XPS survey spectra of the investigated samples. For the uncovered CIGSSe absorber the spectrum is dominated by features, which can be ascribed to Cu, In, S, and Se. Interestingly, no Ga-related XPS or Auger peaks can be observed, confirming the earlier reported accumulation of Ga exclusively at the Mo back contact.¹⁷ As expected, distinct spectral features attributed to Na can also be identified. The small features attributed to O and C (which are ascribed to a minor surface contamination layer) are indicative for a rather clean sample surface. Thus, the impact of the signal attenuation induced by this surface contamination layer, which is more pronounced for low kinetic energy photoemission lines (e.g., $\text{Cu } 2p$), on the comparison of different photoemission lines is considered to be minimal. With increasing number of spray cycles and thus increasing In_2S_3 layer thickness, the XPS and Auger signals ascribed to S and In become more intense. Close inspection of the survey spectra reveals a small but distinct additional feature attributable to the most prominent Cl photoemission line ($\text{Cl } 2p$ at a binding energy E_B of 199 eV), which increases in intensity with the number of spray cycles. This might be due to an incomplete conversion of the precursor to the sulfide, which has been previously studied.¹⁴ The detail spectra in Fig. 2(a) reveal that the intensity of the CIGSSe related Na 1s, Cu 2p

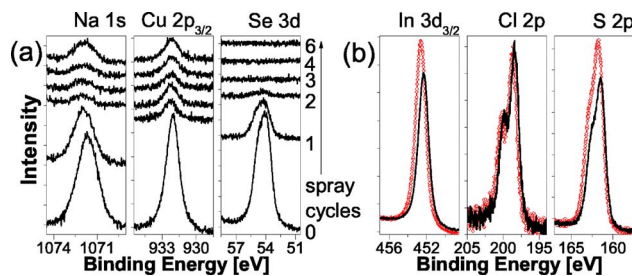


FIG. 2. (Color online) (a). Na 1s, Cu $2p_{3/2}$, and Se 3d XPS detail spectra of the investigated sample series. (b). In $3d_{3/2}$, Cl 2p, and S 2p XPS detail spectra of a four-cycle In_2S_3 layer deposited on CIGSSe (black line) and Mo (red open circles).

and Se 3d photoemission lines decreases, but despite the largest photoelectrons’ inelastic mean free path only the Se 3d signal vanishes after three spray cycles. Assuming that the Se 3d signal represents the CIGSSe surface (note that the S:Se ratio is not altered significantly by applying H_2S at 250 °C to the bare CIGSSe), this finding points to an outdiffusion of Na and Cu from the CIGSSe absorber during the ILGAR process and their subsequent incorporation into the In_2S_3 layer. However, for the sake of clarity this material is still referred to as In_2S_3 in this letter. The disappearance of the Se 3d photoemission line on the other hand is indicative of a complete coverage of the CIGSSe by the three cycle In_2S_3 layer with a minimum thickness which corresponds to the XPS information depth (for Se 3d excited with $\text{Mg } K\alpha$ this is approximately 7.5 nm). Note that all shown detail spectra were recorded using $\text{Mg } K\alpha$ excitation except that of the Na 1s photoemission line in Fig. 2(a). Here, Al $K\alpha$ excitation was used in order to prevent the overlap with the Cl LMM Auger peak (see Fig. 1). In addition to the $\text{In}_2\text{S}_3/\text{CIGSSe}$ test structures an In_2S_3 reference sample was prepared on a Mo/glass substrate using four spray cycles. The respective In $3d_{3/2}$, Cl 2p, and S 2p detail spectra are compared to those of the corresponding $\text{In}_2\text{S}_3/\text{CIGSSe}$ sample in Fig. 2(b). While the intensity of the Cl 2p spectra is independent of the substrate, indicating a comparable layer thickness, we find increased In $3d_{3/2}$ and S 2p intensities for the $\text{In}_2\text{S}_3/\text{Mo}$ sample. The shift of all photoemission lines of the Mo sample to higher E_B by approximately 0.3 eV can be explained by a different interface induced band bending caused by the deposition of In_2S_3 on either CIGSSe or Mo. The increased In- and S-related XPS intensities of the $\text{In}_2\text{S}_3/\text{Mo}$ sample confirms the interpretation from above that the In_2S_3 layer deposited on CIGSSe is not exclusively composed of In and S but rather contains additional ingredients on cation as well as anion sites. In order to shed light on the suspected diffusion process, the XPS data were quantified. As generally known the photoemission signal intensity is directly proportional to the elemental concentration c , the ionization cross section σ , the inelastic mean free path λ , and the transmission of the electron analyzer T . Thus in order to obtain c , the intensity of the XPS line was determined by fitting the photoemission peak using a Voigt function and a linear background. Note that doublets were fitted with two Voigt functions with intensity ratios set according to their spin-orbit splitting. Then we followed two approaches to estimate c . First we assumed that for photoelectrons with a kinetic energy, $E_K > 30\text{eV}$ $\lambda \propto E_K^{1/2}$ and $T \propto E_K^{-1/2}$, and hence we corrected the peak intensities only for σ (taken from Ref. ¹⁸) to determine c . In our second approach, we additionally considered λ and T . λ was calculated by the TPP2M formula¹⁹ for a pure In_2S_3 layer using the QUASES code written by Tougaard.²⁰ T of the used electron analyzer was determined by measuring the Au 4f photoemission line at a (in terms of excitation energy) tuneable light source. In order to account for the uncertainty in these quantification approaches, in the following always their average together with the standard deviation from the mean value is given. Note that the resulting very defensively designed error margins certainly also include possible deviations from the calculated composition due to differently pronounced attenuation of the photoemission lines by the surface contamination layer (see above). The resulting picture is shown in Fig. 3(a), where the samples’ surface composition is shown for each spray cycle.

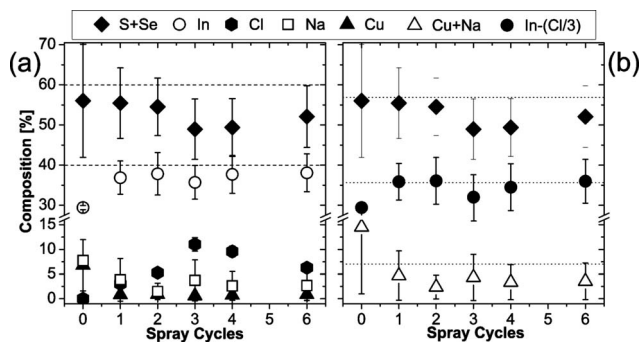


FIG. 3. Surface composition of the investigated sample series as determined from the collected XPS data. The dashed lines in (a) indicate the S and In content of a pure In_2S_3 layer and the dotted lines in (b) represent the 1:5:8 composition of a possible $(\text{Cu}_{1-x}\text{Na}_x)\text{In}_5\text{S}_8$ phase.

Note that according to the $\text{CuIn}(\text{S},\text{Se})_2$ composition of the absorber's surface the presented surface content of S and Se is combined. However, keep in mind that $[\text{Se}]=0$ after three spray cycles. Despite the partially extensive error bars, some conclusions can nevertheless be drawn from Fig. 3(a). The surface of the CIGSSe ("0 spray cycles") is Cu poor. In addition, it can be observed that the Cl content increases with the number of spray cycles and reaches a maximum of $(11 \pm 2)\%$ at three cycles. This can be understood by the thicker growing buffer layer, causing the Cl content to increase until the layer thickness is in the range of the XPS information depth. Furthermore, as already expected from Fig. 2(a), the amount of Cu and Na decreases with increasing number of spray cycles, levels off after three cycles, and is still significant after six cycles ($[\text{Cu}]=(1 \pm 1)\%$ and $[\text{Na}]=(3 \pm 3)\%$). A further indication of additional buffer constituents other than In and S is found in the S(+Se) content of the samples prepared by three cycles or more. It does not comply (even within the defensively designed error bars) with the assumption of the formation of a pure In_2S_3 for which the respective S content is indicated by the upper dashed line in Fig. 3(a). In order to evaluate whether our data support the formation of a $(\text{Cu}_{1-x}\text{Na}_x)\text{In}_5\text{S}_8$ phase as suggested by Barreau *et al.*²¹ for ALD- and PVD- In_2S_3 deposited on CIGSSe absorbers, the constituents of the Spray-ILGAR buffer are combined, respectively, assuming a mixed composition of $(\text{Cu}_{1-x}\text{Na}_x)\text{In}_5\text{S}_8$ and remainders of unconverted precursor (InCl_3). Thus, Cu+Na, S(+Se), and (in order to correct the In for the Cl content) In-(Cl/3) amounts are presented in Fig. 3(b). Based on the (within the error bars) good agreement of the measured composition for samples deposited by three or more spray cycles with the indicated 1:5:8 composition [dotted lines in Fig. 3(b)], one could speculate that indeed a $(\text{Cu}_{1-x}\text{Na}_x)\text{In}_5\text{S}_8$ phase is formed. However, a mixture of different phases or even the formation of NaCl (favored by the affinity of Na to Cl) cannot be excluded.

In summary, we conclude that similar to the ALD and PVD depositions of In_2S_3 on CIGSSe also during the Spray-ILGAR process distinct interfacial diffusion processes take place, which in particular involve Cu and Na. In addition, we find Cl from unconverted precursor in the deposited nominal In_2S_3 . Further work is needed to shed more light on the actual buffer composition, especially concerning the role of Cl.

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