Preparation and in-system study of SnCl₂ precursor layers: towards vacuum-based synthesis of Pb-free perovskites†

R. Félix,‡,‡a N. Llobera-Vila,‡a C. Hartmann,§,‡a C. Klimm,‡a M. Hartig,ab R. G. Wilksac and M. Bär†d,e

The chemical structure and topography evolution of vapor-deposited SnCl₂ thin-films on Mo-coated glass substrates was studied via a combination of electron spectroscopies and scanning electron microscopy. For this purpose, a thickness series of SnCl₂ thin-films was prepared using different evaporation times, revealing significant changes in the chemical environment of Sn and Cl along the layer profile and layer topography. The presence of O in the Mo-coated substrates can lead to oxidation in the SnCl₂ film layers. The findings in this work show the effect that substrate conditions can exert on the chemical (and electronic) properties of the deposited material layers and that need to be taken into account for device optimization.

Due to strict legal regulations concerning the handling of heavy metal Pb, its presence is regarded as a (potential) drawback for the commercial large-scale implementation of perovskites in PV technology, and thus substituting Pb by less-toxic Sn shows promise as a solution. Currently, a wider use of Sn-based perovskite absorbers in solar cell absorbers is suggested as a solution. Currently, a wider use of Sn-based perovskite absorbers in solar cell has been in general hampered by the ease of Sn to oxidize (i.e., from Sn²⁺ to Sn⁴⁺), resulting in material properties (e.g., poor conductivity, limited stability, etc.) adversely affecting solar cell performance.†6–14 In principle, a strategy to minimize this oxidation could entail a two-step perovskite conversion method, in which the Sn-containing precursor (e.g., SnCl₂) is deposited under conditions that prevent oxidation (e.g., in ultra-high vacuum (UHV)).†13,15

In this work, the first experimental results towards synthesizing Pb-free perovskite thin-films at the Energy Materials In Situ Laboratory Berlin (EMIL) are presented. It consists of a detailed X-ray photoelectron and Auger electron spectroscopy study of SnCl₂ precursor layers of different thicknesses UHV-deposited on Mo-coated glass substrates, which reveals significant changes in the chemical environment of Sn and Cl along the layer profile. These findings highlight that not only the deposition environment can impact the deposited material but that substrate conditions also play a crucial role.

Experimental

Materials and methods

Thin films of SnCl₂ were deposited on 25 × 25 mm² SGG DIAMANT® substrates coated with 200 nm films of sputtered-Mo.

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‡ These authors contributed equally to this work.
§ Although inorganic Sn compounds are considered safe for human applications, organic Sn compounds (especially mono-, di-, and tetrabutyltin and triphenyltin) are environmental pollutants posing severe dangers to aquatic ecosystems.
Prior to the SnCl₂ deposition treatments, the Mo-coated SGG substrates were cleaned by immersing them in solutions of 30% aqueous ammonium hydroxide (NH₄OH). To further remove surface adsorbates, substrates were submitted to 20 min cycles of Ar⁺-ion treatments (ion energies up to 3 keV) using a Nonsequitur Technologies 1402 ion gun attached to the UHV preparation chamber (base pressure < 5.0 × 10⁻⁹ mbar).

SnCl₂ powder 98% (Sigma-Aldrich) was used to deposit thin films by using a conventional 4-pocket evaporator (Dr Eberl MBE Komponenten Quad Cluster Source) attached to the UHV deposition chamber (base pressure < 1.0 × 10⁻⁸ mbar) directly connected to the preparation chamber where the Ar⁺-ion treatments were carried out. Eight different SnCl₂ thin-film depositions were carried out by varying the evaporation periods (i.e., between 25 s and 1600 s), using a constant crucible temperature (i.e., 112 °C). In the following, each sample will be referred to by the SnCl₂ evaporation time used to prepare it.

X-ray photoelectron spectroscopy (XPS) and X-ray-excited Auger electron spectroscopy (XAES)

The surface chemical structure of the samples was characterized via X-ray photoelectron spectroscopy (XPS) and X-ray-excited Auger electron spectroscopy (XAES), using a Scienta EW4000 electron analyser and non-monochromatized Mg Kα excitation from a PREVAC RS40B1 twin anode X-ray source. Curve fit analysis of measured detail XPS spectra were simultaneously conducted with the Fityk software. Voigt profile functions, along with linear backgrounds, were used for these fits. Spin–orbit doublets were fitted with two Voigt functions with intensity ratios set to obey the 2j + 1 multiplicity rule. The energy scale for these measurements was calibrated in accordance to ref. 22.

Scanning electron microscopy (SEM)

The thickness and morphology of the deposited SnCl₂ films were evaluated through scanning electron microscopy (SEM) measurements using a SEM Hitachi S 4100. [Due to sample surface charging effects observed for the “1600 s” sample, only its SEM – and not the XPS/XAES – characterization results are discussed in this work (i.e., the encountered surface charging distorts the XPS and XAES results yet still allows for satisfactory SEM images).]

Results and discussion

Fig. 1 shows the XPS survey spectra of a (cleaned) Mo-coated substrate and the produced SnCl₂ thin-film sample series. The survey spectrum of the substrate sample consists of signature Mo-derived lines, as well as, low-intensity O lines ascribed to remaining adsorbates. Sn- and Cl-related spectral lines are detected for all SnCl₂ evaporated samples. As expected, an increase in intensity of Sn- and Cl-related spectral lines is observed with SnCl₂ evaporation (i.e., in samples with treatments ranging from 25–400 s), along with a corresponding decrease in Mo-related spectral lines. The survey spectra of samples treated with evaporation periods of at least 600 s no longer show Mo-related spectral lines, indicating complete coverage of the Mo substrate by SnCl₂ films with a minimal thickness greater than the XPS information depth [i.e., the inelastic mean free path (IMFP) – describing the exponential decay of electrons travelling through matter – of Cl 2p/2, Mo 3d and Sn 3d/2 electrons with kinetic energies (KE) of ~1055 eV, 1026 eV, and 769 eV is approximately 2 nm in SnCl₂].

Changes in layer thickness and topography as a function of SnCl₂ evaporation time were studied through SEM. Fig. 2(a)–(h) presents 30°-tilted cross section SEM images of the investigated sample series, indicating a change of morphology of the deposited SnCl₂. The XPS information depth (ID) is taken as 3 × IMFP.

While the SEM image of the “25 s” sample appears homogeneous, starting from the “50 s” sample the formation of islands can be observed. Samples for which SnCl₂ layers have been deposited between 100–400 s (and especially for the “200 s” sample) show that the deposited SnCl₂ material grows vertically,

![Fig. 1 Mg Kα-excited XPS survey spectra of the SnCl₂ thin-film thickness series on Mo, along with identification of core level and Auger lines. Vertical offsets are added for clarity.](Image)

![Fig. 2 30°-Tilted cross section scanning electron microscope (SEM) images of SnCl₂/Mo samples with the following evaporation times: (a) 25 s, (b) 50 s, (c) 100 s, (d) 200 s, (e) 400 s, (f) 600 s, (g) 800 s, and (h) 1600 s. SEM images (a)–(g) were taken with a 30 000× magnification, whereas (h) shows a 10 000× magnification.](Image)
The apparent deposition of Cl-rich layers may arise due to Cl-termination of the SnCl₂ or diffusion of Sn into the Mo.\(^\text{26,29}\)

In fact, the relative intensity values of the Cl 2p and Mo 3d lines of the “50 s” sample \(i.e., 0.40 \pm 0.05 \) and 0.62 \(\pm 0.05\) nearly match the intensification/attenuation effects of a SnCl₂ deposition thickness equivalent to one IMFP value \(i.e., ca. 2 \text{ nm}\), indicated by the vertical dashed line in Fig. 3. This finding suggests that at least a seeding layer that homogeneously covers the substrate is formed during these evaporation times, in agreement with the SEM images of the “25 s” and “50 s” samples. Deviations from these trends are found for the values of samples with evaporation treatments between 100–400 s, with the XPS Cl 2p/Mo 3d relative intensity values of the “50 s”, “100 s” and “200 s” samples remaining statistically constant due to the large substrate/seeding layer area exposed in them (as pointed out in the SEM discussion above). With longer evaporation treatments, the XPS Sn 3d (Mo 3d) relative intensity of samples starts to increase (attenuate) in a more-linear-than-exponential way, in agreement with the observed island lateral (rather than vertical) growth for these evaporation times. The XPS and SEM results indicate that the deposition of SnCl₂ layers on Mo-coated substrates follows a Stranski–Krastanov (SK) growth mode:\(^\text{26}\) the formation of a seeding layer \(i.e., 25 \text{ s and 50 s evaporation treatments}\) with subsequent island formation \(i.e., 100–600 \text{ s evaporation treatments}\), ultimately fusing into a film \(i.e., 800 \text{ s and 1600 s evaporation treatments}\).

To gain insight into the chemical structure of the deposited SnCl₂ films, the XPS Sn 3d and Cl 2p energy regions of the sample series were investigated. In Fig. 4, the detail XPS spectra of the (a) Sn 3d and (b) Cl 2p energy regions of the “25 s” and “800 s” samples are shown, normalized to maximum intensity. To better illustrate changes in spectral width, the binding energy (BE) scales of the spectra were shifted so that the maxima overlap to the one of the “800 s” spectra. The peak widths of the spectra of the “25 s” sample are significantly larger than for the spectra of the “800 s” sample, indicating differences in chemical environment at the start and end of the SnCl₂ deposition of the investigated sample series. For the “800 s” sample additional spectral intensity between 494 and 493 eV can be observed for the Sn 3d line, which will be discussed below.

![Fig. 3](image1.png)

**Fig. 3** Relative intensities of Sn 3d, Cl 2p, and Mo 3d lines as a function of SnCl₂ evaporation time in the sample series. The solid lines show intensity evolutions expected of a homogeneous layer-by-layer deposition of SnCl₂ as a function of its effective thickness (in multiples of IMFP values). The vertical dashed line indicates a SnCl₂ effective thickness equal to one IMFP value \(i.e., ca. 2 \text{ nm}\).

![Fig. 4](image2.png)

**Fig. 4** Detail XPS spectra of the (a) Sn 3dₓᵧ and (b) Cl 2p energy regions of the “25 s” and “800 s” samples. Spectra are normalized to maximum intensity for shape comparison. The binding energy scale of the “25 s” spectrum was shifted to overlap the spectra maxima. The (outer) intersections of the horizontal black lines with the spectra were used for the full width at half maximum (FWHM) evaluation. (c) FWHM values of the Sn 3d and Cl 2p lines as a function of SnCl₂ evaporation time in the sample series.

Note that in Fig. 3 after a SnCl₂ effective thickness \(\geq 1 \text{ IMFP}\) values the increase/decrease of the signal trend lines plateau due to the information depth limit of XPS. For this reason, evaporation times showing saturated relative intensity values \(i.e., 600 \text{ s and 800 s}\) cannot be used to directly determine the (effective) thickness of the deposited SnCl₂ film \(i.e., the “800 s” sample does not have a thickness of 15 IMFP values or ca. 34 nm).
as a result of the X-ray irradiation; it has recently been shown that the levels of X-ray exposure used in the current study can lead to strong reduction of MoO3 thin films in UHV. The third peak contribution (i.e., SnIII) is located at a BE of (493.7 ± 0.1) eV, ascribed to metallic Sn. The Sn 3d3/2 spectrum of the “25 s” sample was the only one in the series to not exhibit a SnIII contribution (i.e., presence of metallic Sn, Sn0), the reason for which will be discussed below. The presence of a small Sn0 in all investigated samples (except in the “25 s” sample) seems to be an inherent product of the evaporation process. The BE values of the Sn 3d3/2 peak contributions are presented as a function of evaporation time in the ESI† (cf. Fig. S4† for more details).

Similarly, the curve fit analysis results of the doublet-separated Cl 2p line, part of which (i.e., for the “25 s”, “200 s” and “800 s” spectra) is shown in Fig. 5(b), reveal the presence of two peak doublets. The ESI† shows the complete set of the curve fit analysis of the Cl 2p spectra (cf. Fig. S3† for more details). The BE of the Cl 2p3/2 peak of the principal doublet (i.e., CI) is located at (198.6 ± 0.1) eV, a value corresponding to Sn–Cl bonds. The BE for the Cl 2p3/2 peak of the significantly less intense secondary doublet (i.e., CIH) is located at (199.4 ± 0.1) eV. This chemical shift towards higher BE values is in line with a higher oxidation state of CI, as is reported for compounds with increasing CI–O bonds. The appearance of additional O-related chemical shifts [i.e., Sn–O (SnIII) and CI–O (ClH) bonds] in the spectra of samples produced by short evaporation treatment times suggests that O remaining on the (cleaned) Mo-coated substrate readily reacts with the deposited thinner films. In that respect, it can also be expected that O at or near the interface region reacts with (i.e., oxidizes) the potentially formed Sn0, which would explain the absence of this contribution in the Sn 3d3/2 spectrum of the “25 s” sample. With longer evaporation times, either the deposition front moves away from the O source (i.e., the Mo surface/interface) or the O is depleted, resulting in the deposition of a more homogeneous SnCl2 material.

As a next step in the identification of the chemical structure of the deposited thin films, an analysis of the Sn M4,5N4,5N4,5 (MNN) XAES spectra of the investigated sample series is conducted. Fig. 6(a) shows the Sn MNN XAES spectra of the sample series, normalized to maximum intensity. The XAES spectrum of the “25 s” sample shows the broadest shape line, indicating a superposition of several Sn MNN lines originating from various Sn species, consistent with the broadening observed in the Sn 3d line of the “25 s” sample. Longer evaporation treatments, up to 600 s, decreases the shape line width (i.e., the spectral features become sharper) and remains unchanged for higher treatment times. To identify the different Sn chemical environments, changes in the shape of the Sn MNN XAES line with evaporation time are analyzed. In Fig. 6(b), the Sn MNN XAES lines measured on the “25 s”, “200 s” and “600 s” samples are reproduced as a sum of (i.e., suitably scaled and energetically shifted) “800 s” Sn MNN XAES spectrum duplicates. [The Sn MNN spectrum of the “800 s” sample was used as a reference spectrum owing to the fact that it has the narrowest shape line of the sample series and is therefore taken as the closest representation of a single Sn species spectrum. The ESI† shows
the complete set of results of the curve fit analysis of the Sn MNN line (cf. Fig. S57 for more details).] In total, four different species are needed to obtain suitable fits for the complete set of Sn MNN spectra of the investigated sample series. As shown in Fig. 6(b), the Sn MNN XAES line for the principle spectral component (i.e., Snii) is located at a KE of (433.8 ± 0.1) eV, a KE value that falls within the range reported for SnII.35 The second spectral component (i.e., Sniii) is located at a KE of (435.2 ± 0.1) eV; although this KE value range does not correspond to Sn reference compounds reported in literature. It is close to KE values corresponding to SnO bonds.31 The third spectral component (i.e., Snvi) is located at a KE of (437.2 ± 0.1) eV, ascribed to metallic Sn.36,31,34 The fourth spectral component (i.e., Snvi) is only detected in the spectrum of the “25 s” sample and is located at a KE of (435.2 ± 0.1) eV, a value that falls between KE value ranges reported for SnO bonds and SnII in literature.31,33,34 In the ESI, the KE values of the Sn MNN line contributions are presented as a function of evaporation time (cf. Fig. Sf† for more details).

Fig. 6(c) shows the evolution of the spectral fractions of the contributions of the XPS Sn 3d3/2 and the XAES Sn MNN electron lines. Similar relative intensities are found for the following XPS-XAES line pairs: Snvi–Sniii; Snii–Sniii; and Snvi–Snvi, suggesting common chemical environment origins. The Sniv spectral component found for the curve fit analysis of the Sn MNN line of the “25 s” sample, at first, appears to not (similarly) pair with an XPS Sn 3d3/2 contribution (i.e., 3 XPS contributions vs. 4 XAES contributions). However, due to the more distinctive shape of the Sn MNN spectrum and the absence of broadening related to the non-monochromatized X-ray source, it is easier to identify components related to chemical shifts. In this case, it is likely that the Sn chemical species, from which the Sniv component originates, cannot be separately resolved in the XPS Sn 3d3/2 spectrum. The fact that adding the spectral factors of the Snii and Snvi contributions [i.e., (0.23 ± 0.05) + (0.11 ± 0.05) = 0.34 ± 0.07] agrees (within experimental uncertainty) with the spectral factor of Snii [i.e., 0.29 ± 0.05] is consistent with this case. Thus, we tentatively pair the Sniv spectral component with that which overlaps with Snii. Furthermore, Fig. 6(c) highlights the change from a rather heterogeneous chemical structure of the deposited SnCl2 thin films in the region near the interface to an increasingly homogeneous structure in the thicker films represented by the long evaporation treatment samples.

Finally, combining the binding energies of the Sn 3d3/2 XPS and the kinetic energies of the Sn MNN XAES spectra of the different contributions allows for the analysis of modified Auger parameters [α* = BEXPS + KEAES] of Sn-related emission lines, a more refined evaluation of changes in the chemical structure of the sample series.32,33 This analysis reveals the presence of four Sn chemical environments in the investigated sample series. Using the XPS-XAES line pairs described above [i.e., (a) Sni–Snii; (b) Snii–Sniii; (c) Sni–Snii; and (d) Sniii–Sniii], the following α* value sets can be computed: (a) [928.2 ± 0.2] eV, (b) [929.2 ± 0.2] eV, (c) [930.4 ± 0.2] eV, and (d) [930.8 ± 0.2] eV. These results are illustrated for the whole sample series in Fig. 7 in a Wagner plot format. [In the ESI, modified Sn α* of the samples are presented as a function of evaporation time (cf. Fig. S7† for more details).] By comparing these computed values to Sn α* values reported in literature for reference compounds (illustrated as shaded areas in Fig. 7), it is possible to unambiguously identify two of the Sn environments detected in the sample series: (a) SnCl2 [i.e., 928.0 ± 0.2] eV and (d) Sn0 [i.e., 930.8 ± 0.2].35,36,39,40 The identification of the species represented by Sn α* value sets (b) [i.e., Snii–Sniii] and (c) [i.e., Snii–Sniii] is not as straightforward; however, the existing results can be used to discuss some plausible scenarios. For Sn α* value set (b), no matching value (i.e., 929.2 ± 0.2 eV) is found in literature; however, as illustrated in Fig. 7, adding extreme BE and KE values reported for SnO can match Sn α* value set (b), suggesting the formation of a Sn–O bond environment. The relative intensities of the Snii, Sniii, and Clii lines compared to the overall Sn or Cl content of the sample show a similar trend throughout the entire sample series (cf. ESI; Fig. S8† for more details). This may indicate that these lines are derived from a common origin. Together, these observations point towards the presence of a SnClOx type compound near the interface, responsible for Sn α* value set (b). Regarding the Sn α* value (c), its position is very close to Sn α* values reported for SnII [i.e., (930.4 ± 0.2) eV to Sn0.1].
the Mo-coated substrate. It is possible that the detected (potential) appearance of Sn(Cl,O)\textsuperscript{+2} avoiding the presence/formation of detrimental Sn\textsuperscript{4+} states. However, the oxidation state of Sn in the formed tin oxide is still show any indication of a presence of Sn\textsuperscript{0} due to O leaching from deposited thin-

Because Sn\textsubscript{iv} lies between KE values reported for Sn\textsuperscript{0} (oxidation state: 0) and SnO (oxidation state: +2), it is expected that the oxidation state of Sn in the compound related to Sn \( \alpha^* \) value (c) (i.e., Sn\textsubscript{iv}–Sn\textsubscript{v}) lies between 0 and +2 (i.e., an “intermediate” oxidation state). Earlier it was discussed that the “25 s” sample (i.e., the only sample in the series yielding a Sn\textsubscript{iv} signal) does not show any indication of a presence of Sn\textsuperscript{0} due to O leaching from the Mo-coated substrate. It is possible that the detected “intermediate” oxidation Sn species is formed as the O depletes (e.g., Sn\textsubscript{ox} where \( x < 1 \)) or due to charge transfer between the deposited thin-film and the substrate’s Mo (or even as a result of Sn diffusing into the Mo substrate).\textsuperscript{28,29}

The findings presented in this work highlight the effect that substrate conditions can exert on the chemical (and electronic) properties of the deposited material layers and have to be considered when optimizing the material as a precursor for Pb-free HOIP devices. The presence of O in the Mo-coated substrates may partly oxidize SnCl\textsubscript{2} [resulting in the (potential) appearance of Sn(Cl,O)\textsubscript{x} phases near the interface]. However, the oxidation state of Sn in the formed tin oxide is still +2 avoiding the presence/formation of detrimental Sn\textsuperscript{4+} states. For perovskites using SnCl\textsubscript{2} as an inorganic precursor deposited on the TiO\textsubscript{2} substrate (e.g., in a two-step deposition method), similar results can be expected, which could lead to differences in morphology and crystallization of the deposited perovskite. Furthermore, it needs to be considered that metallic Sn is present in the deposited precursor film, which (if left unreacted) will act as deep defect and recombination center. However, it is highly probable that the small detected metallic Sn composition will readily react with the organic precursor (e.g., MAI) in the perovskite conversion step (i.e., second step of the two-step method),\textsuperscript{24} as evidenced by the absence of metallic Sn in the “25 s” sample. In the case of a (future) study of a fully-prepared Pb-free perovskite, additional structural information will be crucial to identify high-quality (i.e., single-phase) material.

### Conclusions

The combined XPS/XAES and SEM characterization of a sample series of SnCl\textsubscript{2} thin-films vapor deposited in UHV on Mo-coated substrates reveals the formation of up to four different Sn chemical environments and a Stranski–Krastanov type growth. The presence of O residues on the Mo-coated substrates likely acts as O source to oxidize SnCl\textsubscript{2} and form Sn(Cl,O)\textsubscript{x} phases near the interface. Metallic Sn is also found to be present in all evaporation treatments. Similar results are expected for the deposition of SnCl\textsubscript{2} on other O-containing substrate materials (e.g., TiO\textsubscript{2}) and thus need to be taken into account for precursor material optimization towards vacuum-based synthesis of Pb-free perovskites.

### Conflicts of interest

There are no conflicts to declare.

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### Notes and references