

## Supplementary Information

### Light-induced degradation of methylammonium tin iodide absorber layers

Joana Ferreira Machado,<sup>a</sup> Jeremy Hieulle,<sup>a</sup> Aline Vanderhaegen,<sup>a</sup> and Alex Redinger<sup>a</sup>

<sup>a</sup> *Department of Physics and Materials Science, University of Luxembourg, Luxembourg City L-1511, Luxembourg. E-mail: alex.redinger@uni.lu*

#### 1 Work Function Distribution

Figure S1 shows the work function distribution of the pristine MASnI<sub>3</sub>.

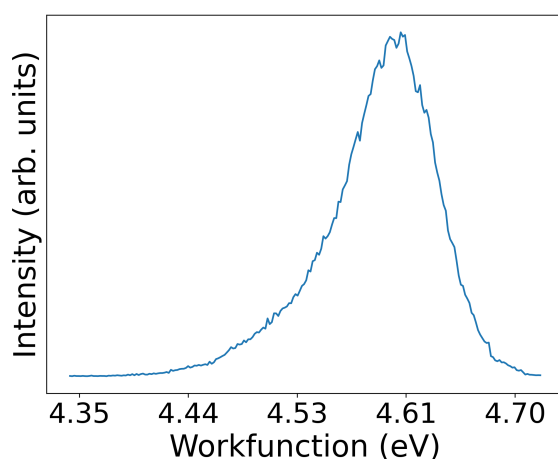


Figure S1: Work function distribution of pristine MASnI<sub>3</sub>

#### 2 Satellite peak occurrence

In Figure S2 the spectrum of pristine SnI<sub>2</sub> is plotted twice. In both plots, the Sn(2+) oxidation state is filled in yellow. Nevertheless, in the top, the satellite peaks (filled in gray) are taken into account in the fitting, whereas in the bottom plot the satellite peaks are ignored. As a consequence, the quantity of Sn(0) is different although the same data is used, more specifically, the top plot shows 1.6% of Sn(0) and the bottom plot shows 3.8% of Sn(0).

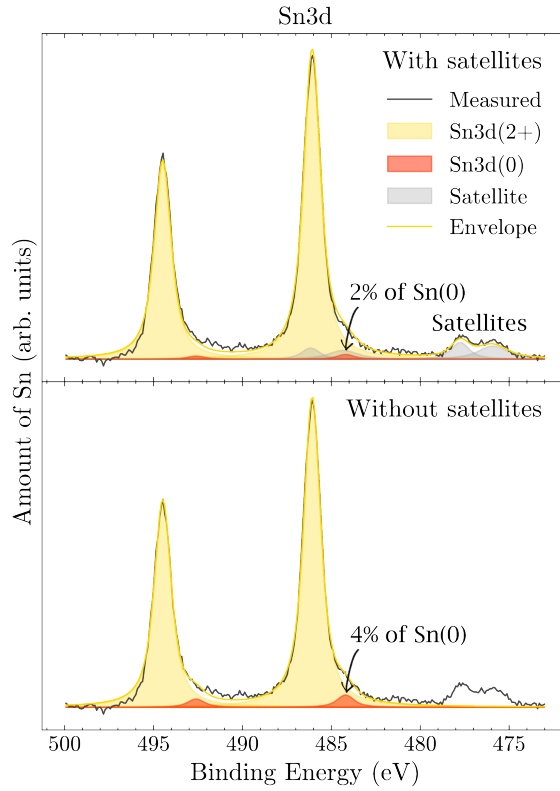


Figure S2: Figure showing XPS peak model when considering satellite peaks (top) and when not considering satellite peaks (bottom)

### 3 XRD of $\text{SnI}_2$ and $\text{MASnI}_3$

XRD measurements were performed using the Bruker D8 Cu  $K\alpha$  diffractometer in a  $\theta$ - $2\theta$  Bragg-Brentano configuration. The X-ray source had a voltage of 40 mA and 40 kV. The samples were exposed to air for the duration of the measurement. All measurements took less than 40 minutes. The samples were not used after the XRD measurement, as they were exposed to air.

Figure S3 shows the XRD measurement of the deposited  $\text{MASnI}_3$  and  $\text{SnI}_2$  films. The measurement of  $\text{MASnI}_3$  shows a secondary phase of  $\text{SnI}_2$ . Nevertheless  $\text{MASnI}_3$  peaks position are in agreement with the literature [1,2]. However, the XRD reflexes are rather low in intensity. This could be due to slow crystallization kinetics, as reported by [3] for the case of Sn-containing halide perovskites. On the other hand, the measurements were performed in air and, consequently, degradation effects cannot be excluded. Therefore, XRD measurements have to be analyzed with caution. In the present case, a perovskite phase was confirmed which was the sole reason for the measurement.

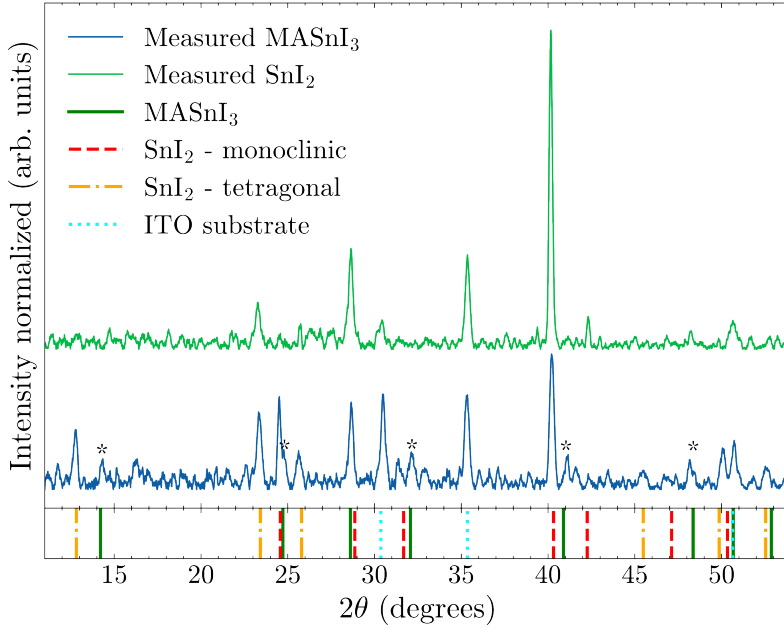


Figure S3: XRD measurement of PVD deposited  $\text{SnI}_2$  and  $\text{MASnI}_3$  films. Intensity normalized for  $\theta = 35.36^\circ$ . The  $\text{MASnI}_3$  peaks are marked with a \* for better visibility. The reference spectra were extracted from literature [4–6].

## 4 Derivation of the bi-layer model

Suppose that  $\text{MASnI}_3$  is fully covered by a thin layer of  $\text{SnI}_2$ . In this case, the XPS signal of Sn and I would have a contribution from both the bulk and the surface. Because the oxidation states of Sn and I in the bulk and at the surface are the same, it is impossible to disentangle them by just looking at the scan. However, by applying a bi-layer model to the calculated ratios, one can estimate the thickness  $d$  of the  $\text{SnI}_2$  layer. According to Hofmann and Siegfried the corrected measured intensity is given by [7]

$$I_{\text{Sn}} = I_{\text{Sn}}^s \left[ 1 - \exp\left(\frac{-d}{\lambda_{\text{Sn}} \cos \theta}\right) \right] + I_{\text{Sn}}^b \exp\left(\frac{-d}{\lambda_{\text{Sn}} \cos \theta}\right). \quad (1)$$

Where,  $I_{\text{Sn}}^s$  and  $I_{\text{Sn}}^b$  are the mole fraction of Sn on the surface and in the bulk, respectively,  $\theta$  is the angle between the sample's surface normal and the analyzer lenses and  $\lambda_{\text{Sn}}$  is the inelastic mean free path (IMFP) of Sn in the surface material ( $\text{SnI}_2$  in this case). Note in the original work by Hofmann and Siegfried,  $\lambda_{\text{Sn}}$  stands for the attenuation length, which takes into account the elastic and inelastic scattering. By neglecting the elastic scattering, an error of 10%-15% is introduced. Equation 1 is made up of two terms: surface contribution and bulk contribution. Similarly, for any other element  $x$  in the bulk,

$$I_x = I_x^s \left[ 1 - \exp\left(\frac{-d}{\lambda_x \cos \theta}\right) \right] + I_x^b \exp\left(\frac{-d}{\lambda_x \cos \theta}\right).$$

The ratio  $I_x/I_{\text{Sn}}$  between two elements, for  $\theta = 0$  is given by,

$$R_{x,\text{Sn}} = \frac{I_x}{I_{\text{Sn}}} = \frac{I_x^s (1 - e^{-d/\lambda_x}) + I_x^b \cdot e^{-d/\lambda_x}}{I_{\text{Sn}}^s (1 - e^{-d/\lambda_{\text{Sn}}}) + I_{\text{Sn}}^b \cdot e^{-d/\lambda_{\text{Sn}}}}. \quad (2)$$

Due to the lack of reference materials, it is difficult to estimate the mole fractions of I and Sn in the bulk. Nevertheless, the expected values for the ratios between

different mole fractions are known and depend on the chemical formula of the material. The ratio of the volume density of Sn in the bulk and in the surface, is given by the ratio between the amount of Sn at the surface and the amount of Sn in the bulk, which is

$$\rho_{Sn} = \frac{I_{Sn}^s}{I_{Sn}^b} \Rightarrow I_{Sn}^s = \rho_{Sn} I_{Sn}^b \quad (3)$$

Additionally, we can define  $R_{surf}$  and  $R_{bulk}$  as the ratio between the amount of  $x$  and Sn on the surface and in the bulk, respectively. Then,

$$R_{surf} = \frac{I_x^s}{I_{Sn}^s} \Rightarrow I_x^s = R_{surf} I_{Sn}^s = R_{surf} \cdot \rho_{Sn} I_{Sn}^b \quad (4)$$

and

$$R_{bulk} = \frac{I_x^b}{I_{Sn}^b} \Rightarrow I_x^b = R_{bulk} I_{Sn}^b. \quad (5)$$

Replacing the mole fractions in Eq. 2, by the results from Eq. 3, 4 and 5 implies,

$$R_{x,Sn} = \frac{R_{surf} \cdot \rho_{Sn} I_{Sn}^b (1 - e^{-d/\lambda_x}) + R_{bulk} I_{Sn}^b \cdot e^{-d/\lambda_x}}{\rho_{Sn} I_{Sn}^b (1 - e^{-d/\lambda_{Sn}}) + I_{Sn}^b e^{-d/\lambda_{Sn}}}$$

Simplifying  $I_{Sn}^b$ ,

$$R_{x,Sn} = \frac{R_{surf} \rho_{Sn} (1 - e^{-d/\lambda_x}) + R_{bulk} \cdot e^{-d/\lambda_x}}{\rho_{Sn} (1 - e^{-d/\lambda_{Sn}}) + e^{-d/\lambda_{Sn}}}. \quad (6)$$

Equation 6, can be developed further for each element in  $MASnI_3$ . In this case, since the surface layer is composed of  $SnI_2$  and the bulk is composed of  $MASnI_3$ , for iodide the  $R_{surf} = 2$  and  $R_{bulk} = 3$  and

$$R_{I,Sn} = \frac{2\rho_{Sn} (1 - e^{-d/\lambda_I}) + 3e^{-d/\lambda_I}}{\rho_{Sn} (1 - e^{-d/\lambda_{Sn}}) + e^{-d/\lambda_{Sn}}}. \quad (7)$$

Following the same reasoning for carbon and nitrogen, for these elements  $R_{surf} = 0$  and  $R_{bulk} = 1$ , which implies

$$R_{C,Sn} = \frac{e^{-d/\lambda_C}}{\rho_{Sn} (1 - e^{-d/\lambda_{Sn}}) + e^{-d/\lambda_{Sn}}}.$$

and

$$R_{N,Sn} = \frac{e^{-d/\lambda_N}}{\rho_{Sn} (1 - e^{-d/\lambda_{Sn}}) + e^{-d/\lambda_{Sn}}}.$$

This ratio  $\rho_{Sn}$  must be calculated from the tabulated values for the crystalline structure of  $SnI_2$  and  $MASnI_3$  or be deduced by fitting the measured data. In the main article,  $\rho_{Sn}$  was deduced from the fitting, but in the next section the calculation with tabulated values is explained.

## 5 Estimation of $\rho_{Sn}$

Let  $\rho_{Sn}^s$  be the volume density of Sn atoms in the surface material, which is given by,

$$\rho_{Sn}^s = \frac{N_{Sn}^s}{V_{Sn}^s}$$

Where  $N_{Sn}^s$  is the number of Sn atoms per unit cell and  $V_{Sn}^s$  is the volume of the unit cell in the surface material. Assuming that the mole fraction of tin  $I_{Sn}^s$  is proportional to  $\rho_{Sn}^s$ , then

$$I_{Sn}^s = \alpha \cdot \rho_{Sn}^s = \alpha \cdot \frac{N_{Sn}^s}{V_{Sn}^s}$$

where  $\alpha$  is the proportionality factor. Given that the surface material is  $\text{SnI}_2$  and the XRD showed monoclinic  $\text{SnI}_2$ , then from the chemical structure  $N_{Sn}^s = 6$  and from the XRD database [5]  $V_{Sn}^s = 349.03 \text{ \AA}^3$ .

Similarly for the bulk material,

$$I_{Sn}^b = \alpha \cdot \rho_{Sn}^b = \alpha \cdot \frac{N_{Sn}^b}{V_{Sn}^b}$$

The bulk material is  $\text{MASnI}_3$  in the cubic crystalline structure, therefore  $N_{Sn}^b = 1$  and from the XRD database [4]  $V_{Sn}^b = 242.69 \text{ \AA}^3$ .

Finally, from equation 3,

$$\rho_{Sn} = \frac{I_{Sn}^s}{I_{Sn}^b} = \frac{\rho_{Sn}^s}{\rho_{Sn}^b} = \frac{N_{Sn}^s V_{Sn}^b}{V_{Sn}^s N_{Sn}^b} = 4.2. \quad (8)$$

## 6 AFM measurement of $\text{MASnI}_3$

Figure S4 shows the AFM measurement of the sample before and after 61 h of illumination. It is visible that light exposure do not induce a significant change in topography.

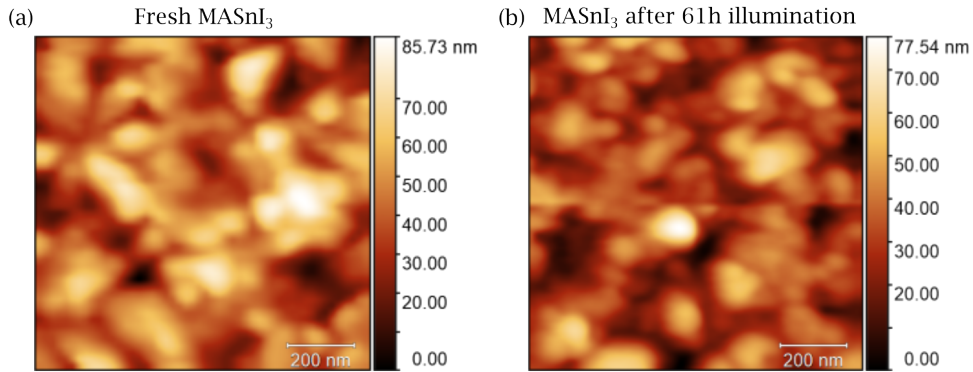


Figure S4: AFM measurement of  $\text{MASnI}_3$  (a) before and (b) after illuminating for 61 h.

## References

- [1] Y. Q. Huang, J. Su, Q. F. Li, D. Wang, L. H. Xu, and Y. Bai, “Structure, optical and electrical properties of  $\text{CH}_3\text{NH}_3\text{SnI}_3$  single crystal,” *Physica B: Condensed Matter*, vol. 563, no. March, pp. 107–112, 2019.
- [2] “Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties,” *Inorganic Chemistry*, vol. 52, no. 15, pp. 9019–9038, 2013.
- [3] D. Di Girolamo, E. Blundo, G. Folpini, C. Ponti, G. Li, M. H. Aldamasy, Z. Iqbal, J. Pascual, G. Nasti, M. Li, R. Avolio, O. Russina, A. Latini, F. Alharthi, M. Felici, A. Petrozza, A. Polimeni, and A. Abate, “Energy Distribution in Tin Halide Perovskite,” *Solar RRL*, vol. 6, no. 8, 2022.
- [4] K. Yamada, K. Nakada, Y. Takeuchi, K. Nawa, and Y. Yamane, “Tunable perovskite semiconductor  $\text{CH}_3\text{NH}_3\text{SnX}_3$  (X: Cl, Br, or I) characterized by X-ray and DTA,” *Bulletin of the Chemical Society of Japan*, vol. 84, no. 9, pp. 926–932, 2011.
- [5] R. A. Howie, W. Moser, and I. C. Trevena, “The crystal structure of tin(II) iodide,” *Acta Crystallographica Section B Structural Crystallography and Crystal Chemistry*, vol. 28, no. 10, pp. 2965–2971, 1972.
- [6] G. Gospodinov, 2004. Dept. of Inorganic Chemistry, Bourgas Prof. Assen Zlatarov Univ., Bulgaria. Private Communication.
- [7] S. Hofmann, *Auger- and X-Ray Photoelectron Spectroscopy in Materials Science: A User-Oriented Guide*. 2013.