Supporting Information

Table SI 1. Details of all samples used for calibration and as references. Abbreviations used: ARMI: Analytical Reference Materials International; MBH: MBH Analytical Limited; IFW: Institute for Solid State and Materials Research Dresden; HZB: Helmholtz-Zentrum Berlin.

Sample	Origin	Usage	Composition (m%)	Density (g cm^{-3})	Additional Information
IARM 85B	ARMI	Calibration	Cu: 69.18; Ni: 29.60; Mn: 0.53; Zn: 0.12; Co: 0.034; Sn: 0.014; C: 0.011; S: 0.010; P: 0.007; Pb: 0.005; Al, Si, Sb: <0.01	8.88	Composition certified by Analytical Reference Materials International. Certificate No. 85B-04011994-ARM-F. Density was directly determined by scaling and measured the volume of the cylindrical sample.
IARM 86B	ARMI	Calibration	Cu: 84.7; Pb: 5.49; Sn: 4.58; Zn: 4.18; Ni: 0.78; Sb: 0.092; P: 0.071; S: 0.03; Fe: 0.029; Al, Mn, Si: <0.01	8.88	Composition certified by Analytical Reference Materials International. Certificate No. 86B-04011994-ARM-F. Density was directly determined by scaling and measured the volume of the cylindrical sample.
PB14	MBH	Calibration	Cu: 91.0; Sn: 8.38; Bi: 0.16; Ni: 0.92; S: 0.086; Sb: 0.061; Pb: 0.051; P: 0.032; Zn: 0.029; As: 0.021; Fe: 0.005; Si : <0.005; Mn: <0.002; Mg: <0.001	8.85	Composition certified by MBH Analytical Ltd. Certificate No. 32X PB14 (Batch B). Density was directly determined by scaling and measured the volume of the cylindrical sample.
Cu:NaCl 1	Sintered at IFW	Calibration	Cu: 99.9; Cl: 0.06; Na: 0.02	8.84	Composition given as it was weighted in during the sintering process. Density was directly determined by scaling and measured the volume of the cylindrical sample.
Cu:NaCl 2	Sintered at IFW	Calibration	Cu: 99.5; Cl: 0.30; Na: 0.10	8.71	Composition given as it was weighted in during the sintering process. Density was directly determined by scaling and measured the volume of the cylindrical sample.
Cu:NaCl 3	Sintered at IFW	Calibration	Cu: 99.0; Cl: 0.61; Na: 0.20	8.57	Composition given as it was weighted in during the sintering process. Density was directly determined by scaling and measured the volume of the cylindrical sample.
Cu	Thin film grown at HZB	Calibration	Cu: 100.0	-	Composition measured in-house using XRF. Density was not needed since the sample is only used for background-determination in the S- and Na-calibration.
In_2Se_3	Thin film grown at HZB	Calibration	In: 49.3; Se: 50.7	-	Composition measured in-house using XRF. Density was not needed since the sample is only used for background-determination in the Cu-calibration.
CISe	Thin film grown at HZB	Calibration	Cu: 17.8; In: 34.5; Se: 47.8	-	Composition measured in-house using XRF. Density was not needed since the sample is only used for background-determination in the Ga-calibration.
CGSe	Thin film grown at HZB	Calibration	Cu: 20.1; Ga: 24.8; Se: 50.7	-	Composition measured in-house using XRF. Density was not needed since the sample is only used for background-determination in the In-calibration.
$CuInS_2$	Thin film grown at the University of Luxembourg	Calibration	Cu: 25.8; In: 29.0; S: 45,2	4.73	Composition measured in-house using XRF. Density was taken from: Sombuthawee, C.; Consall, S. B.; Hummel, F. A. Phase equilibria in the systems ZnS-MnS, ZnS-$CuInS_2$, and MnS-$CuInS_2$. *J. Solid State Chem.* **1978**, 25: 391-399.
CIGSSe:Na	EvoChem	Calibration & Reference	Cu: 21.2; In: 28.0; Ga: 6.2; Se: 40.7; S: 3.8; Na: 0.02	5.34 ± 0.01	Composition measured in-house using laser ablation inductively coupled plasma mass spectrometry measurements using a LSX213 laser system by CETAC and an ICP-MS 4500 by Hewlett Packard. Density measured at BAM using picnometry.
CIGSe	Thin films grown at HZB	Calibration & Reference	Cu: 12.8 to 19.5; In: 18.7 to 27.3; Ga: 4.9 to 10.9; Se: 49.1 to 51.3	5.21 to 5.68	Composition measured in-house using XRF. Densities determined using equation (14). In total 6 samples with different *CGI* and *GGI* have been used.

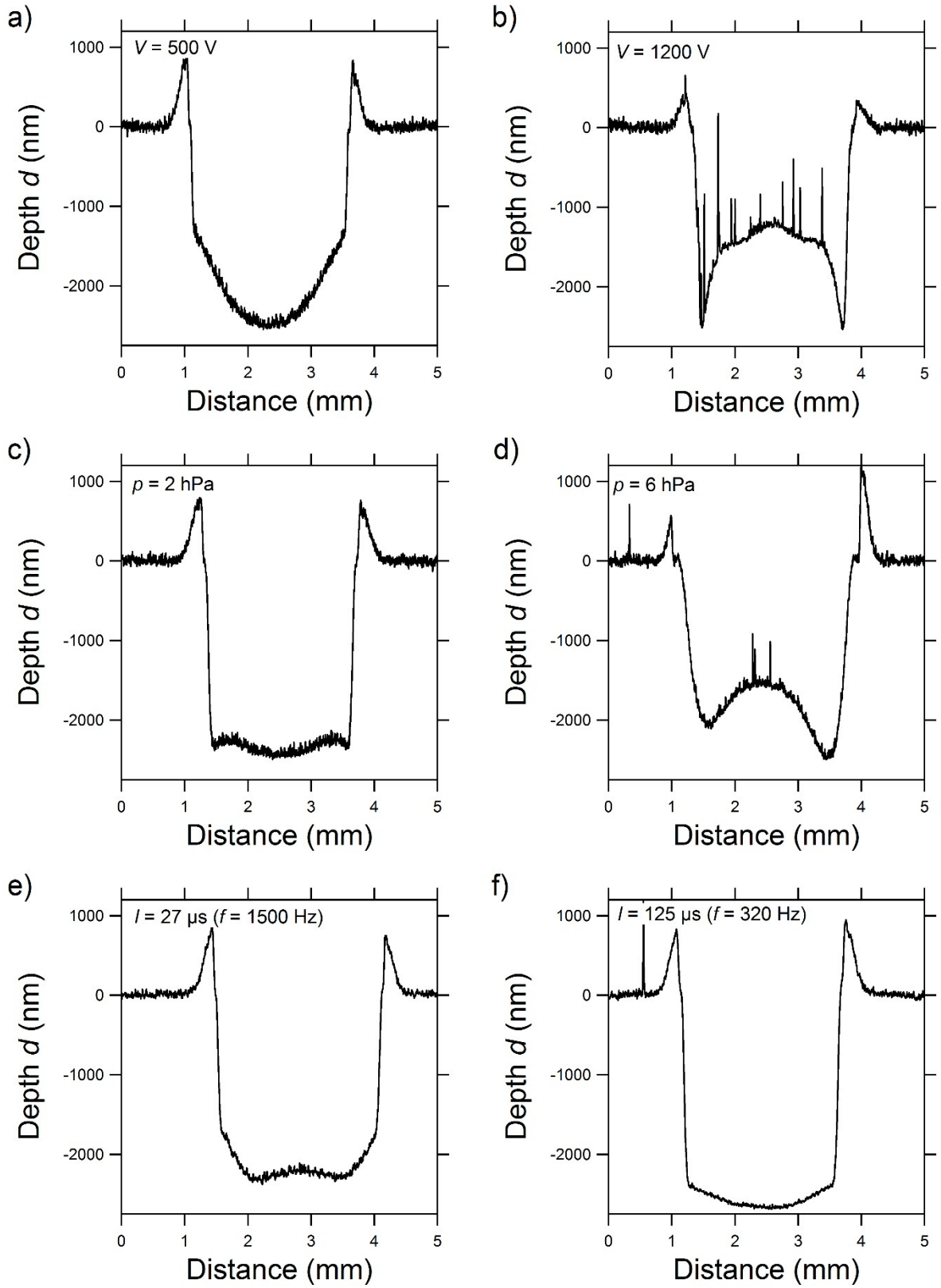

Figure SI 1. Examples of how non optimal sputtering parameters can lead to strong variations in the shape of the sputtering shape. As described in the article low voltage and pressures result in concave shapes (a, c) while high voltages and pressures lead to convex ones (b, d). Short pulse lengths on the other hand lead to convex crater shapes (e), while pulses longer than about 100 µs lead to flat or slightly concave ones (f and optimized example in the article).

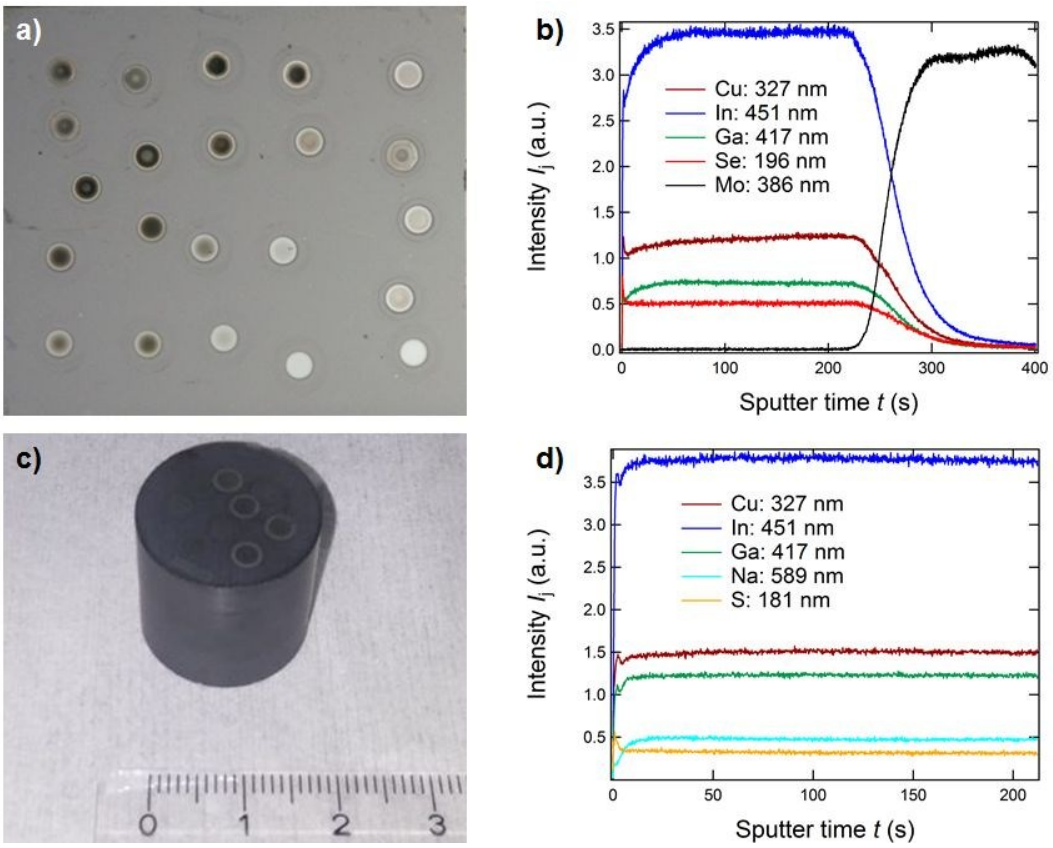

Figure SI 2. Sputtered craters on a CIGS thin film reference (a), the CIGSSe:Na reference (c) and the corresponding qualitative GD-OES depth profiles (b and d).