Supplementary information

Sample characterization

Tin sulfide thin films with different stoichiometry were grown by co-evaporation of the elements (Sn and S) on heated glass substrates. Both the substrate and the tin source temperatures were fixed at 250 °C and 890 °C, respectively, while the sulfur source temperature was varied in the 100 - 160 °C range. The deposition time was 40 minutes, which corresponds to thin films with thickness between 100 and 200 nm.

The crystalline structure of the samples was analyzed by X-ray diffraction (XRD) using the nickel-filtered Kα1 emission line of copper (λ = 1.54056 Å), in a Philips X'pert instrument with Bragg-Brentano θ − 2θ configuration. Crystalline phases were identified by comparison of the measured diffraction peaks with the standard Powder Diffraction Files (PDF). The identification is summarized in Figure 1, where it can be seen that the crystalline structure changes as a function of the sulfur source temperature. Orthorhombic SnS (PDF no. 39-0354) is obtained at T_S = 100 °C and hexagonal SnS_2 (PDF no. 23-0677) at T_S = 160 °C.

Optical measurements were performed with a double beam spectrophotometer Perkin-Elmer Lambda 9, having an integrating sphere to measure the total transmittance (*T*) and reflectance (*R*). The optical absorbance is determined as $A = -\log [T/(1-R)]$, which is represented in Figure 2 as a function of the radiation energy for the crystalline phases identified in figure 1. A fast increment in the absorbance is observed above the respective band gap value, i.e. E_g ~ 1.6 eV for SnS and ~ 2.2 eV for SnS_2.

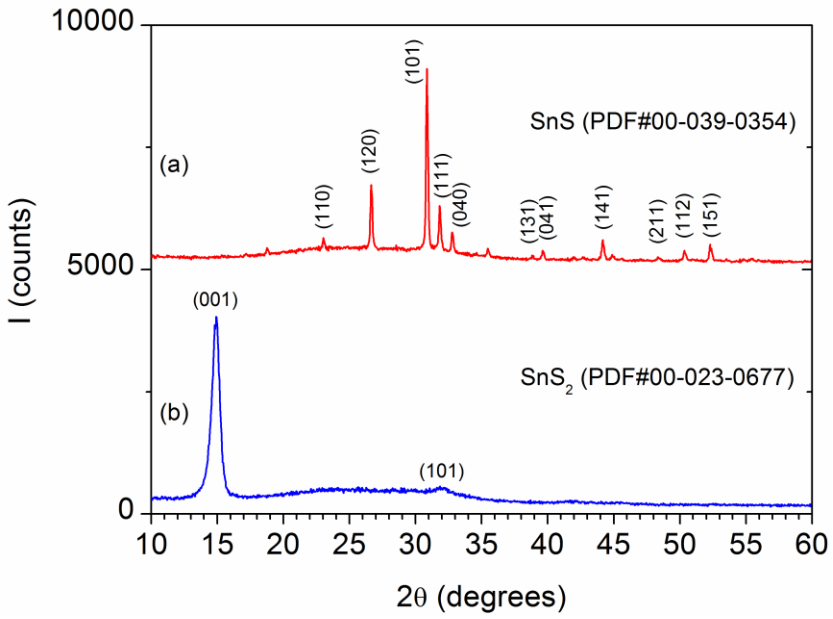

Figure S1. XRD patterns corresponding to the tin sulfide thin films grown at different sulfur source temperatures: a) T_S = 100 °C, b) T_S = 160 °C

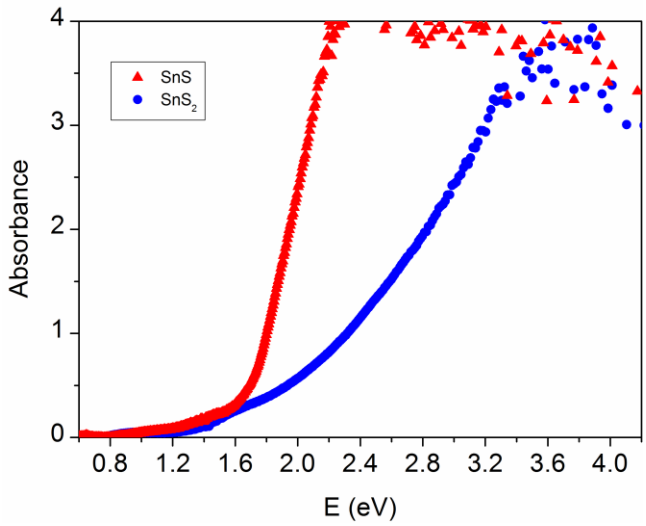

Figure S2. Optical absorbance corresponding to the tin sulfide thin films grown at different sulfur source temperatures, named for the crystalline phase identified in figure 1.

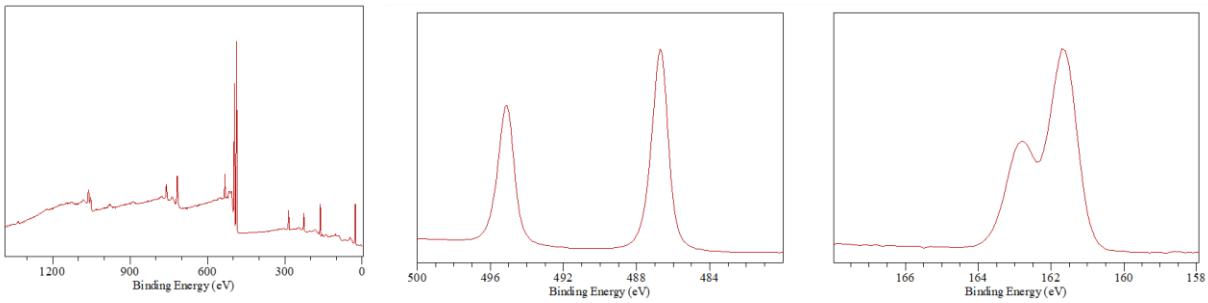

Figure S3. XPS of SnS_2. From left to right, wide, Sn 3d and S2p characteristic scans. Wide scan shows minimal carbon and oxygen surface contamination.

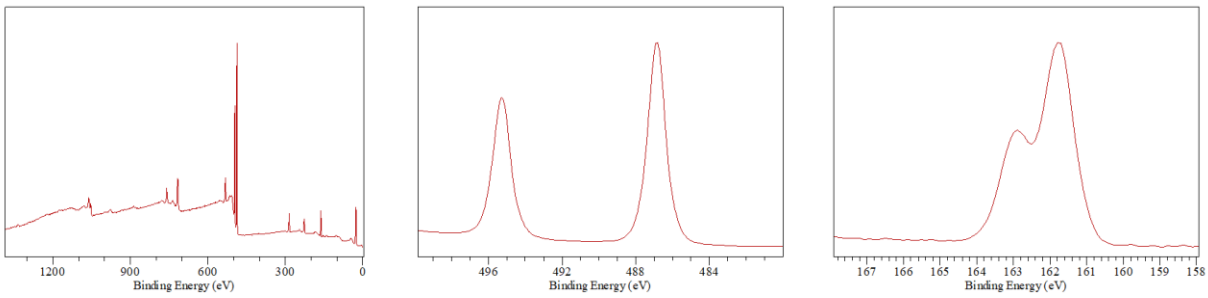

Figure S4. XPS of SnS. From left to right, wide, Sn 3d and S2p characteristic scans. Wide scan shows minimal carbon and oxygen surface contamination.

Table S1.

System	*Code*	*A*	*B*	*C*	α	β	γ	$E_{gap,DFT}$	$E_{gap,exp}$ *(single crystal)*	$E_{gap,exp}$ *(our thin films)*
SnS	VASP	0.40	0.44	1.14	90.00	90.00	90.00	1.26	1.10	1.6
SnS	CP2k	0.41	0.42	1.29	90.47	90.00	90.00	1.46	-	
SnS_2	VASP	0.36	0.37	0.70	90.00	90.00	119.57	2.23	2.20	2.2
SnS_2	CP2k	0.38	0.38	0.67	89.97	90.00	120.33	2.20	-	

Table S1. Lattice parameters (*A*, *B*, *C* in nm) and angles (α, β, and γ in degrees) and electronic band gaps ($E_{gap,DFT}$ in eV) of the optimized structures for SnS and SnS_2. Experimental electronic gaps ($E_{gap,exp}$) are also shown for comparison.

Snapshot x-ray absorption spectra:

Figure S5:

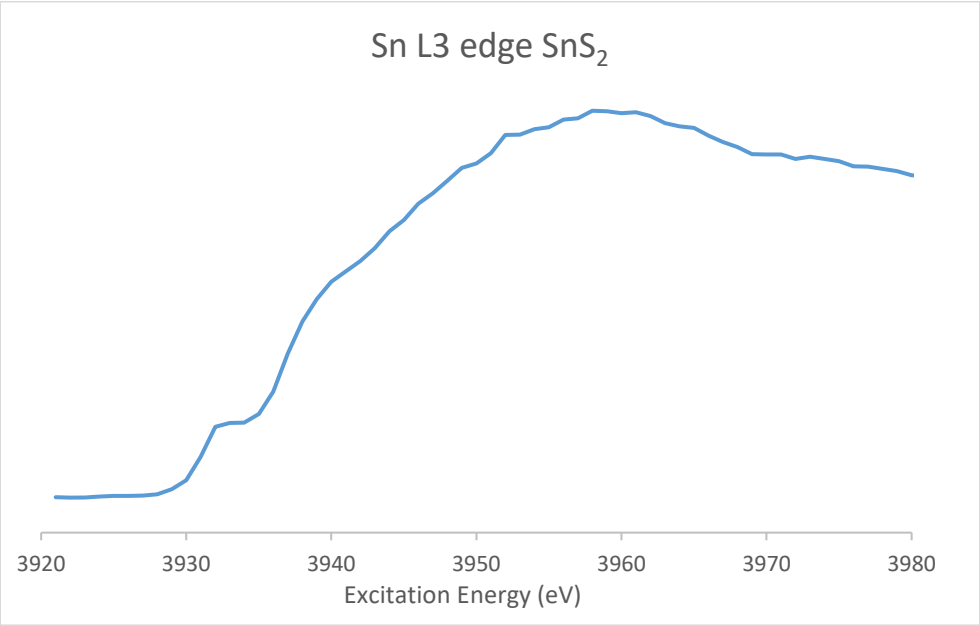

Figure S6:

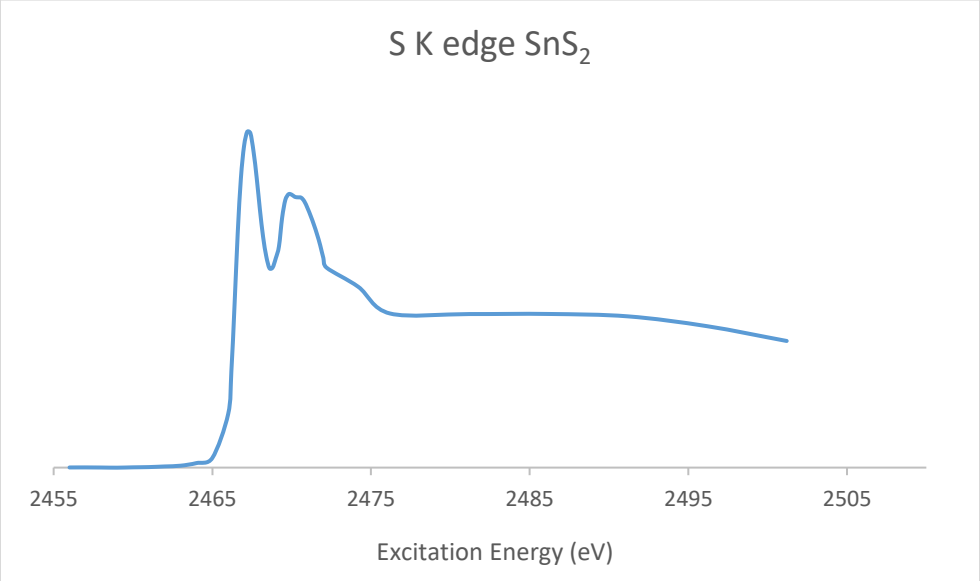

Figure S7:

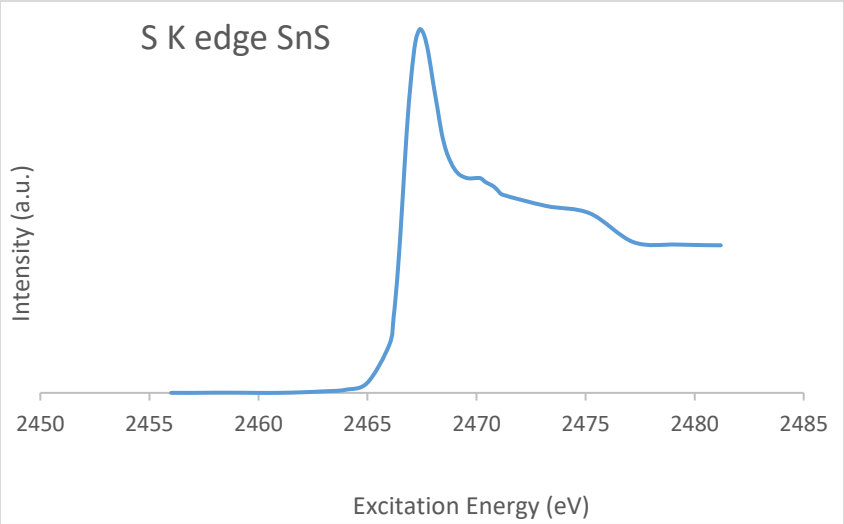

Figure S8:

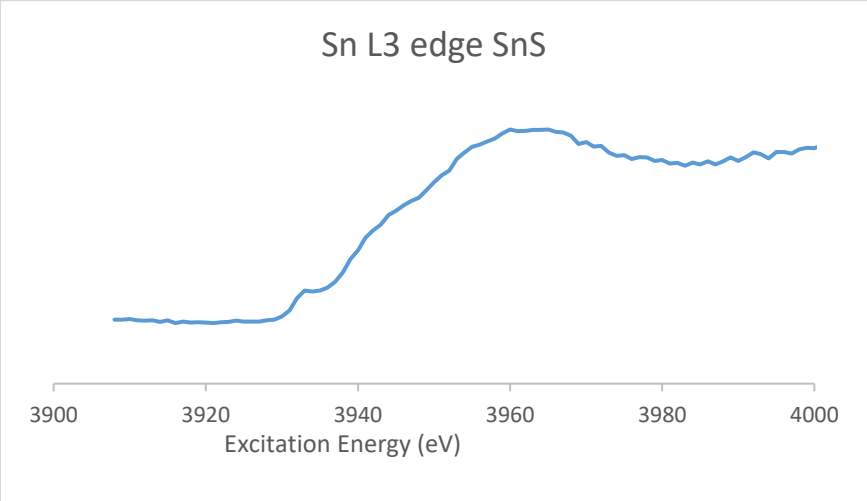

Figure S9. DFT electron density of virtual states projected on the p_x, p_y, and p_z S orbitals with the Fermi level set to zero.

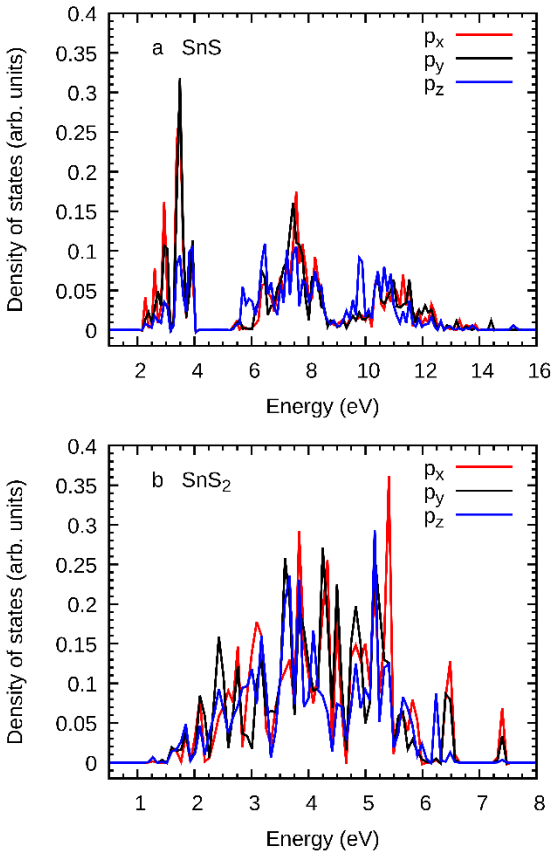

Table S2: SnS, orbital contribution to the wavefunction by atoms in the system.

ions 1, 2, 3 and 4 are Sn
ions 5, 6, 7 and 8 are S
(LUMO)

ion	s	py	pz	px	dxy	dyz	dz2	dxz	x2-y2	tot
1	0.009	0.005	0.014	0.074	0.004	0.000	0.002	0.001	0.001	0.109
2	0.009	0.005	0.014	0.074	0.004	0.000	0.002	0.001	0.001	0.109
3	0.009	0.005	0.014	0.074	0.004	0.000	0.002	0.001	0.001	0.109
4	0.009	0.005	0.014	0.074	0.004	0.000	0.002	0.001	0.001	0.109
5	0.024	0.005	0.005	0.001	0.000	0.000	0.000	0.000	0.000	0.036
6	0.024	0.005	0.005	0.001	0.000	0.000	0.000	0.000	0.000	0.036
7	0.024	0.005	0.005	0.001	0.000	0.000	0.000	0.000	0.000	0.036
8	0.024	0.005	0.005	0.001	0.000	0.000	0.000	0.000	0.000	0.036
tot	0.133	0.039	0.076	0.300	0.015	0.000	0.008	0.003	0.002	0.577

(LUMO+1)

ion	s	py	pz	px	dxy	dyz	dz2	dxz	x2-y2	tot
1	0.031	0.033	0.056	0.010	0.001	0.001	0.002	0.000	0.001	0.134
2	0.005	0.005	0.009	0.061	0.006	0.000	0.000	0.002	0.000	0.089
3	0.005	0.005	0.009	0.061	0.006	0.000	0.000	0.002	0.000	0.089
4	0.031	0.033	0.056	0.010	0.001	0.001	0.002	0.000	0.001	0.134
5	0.030	0.011	0.007	0.002	0.000	0.000	0.000	0.000	0.000	0.049
6	0.005	0.002	0.001	0.009	0.000	0.000	0.000	0.000	0.000	0.017
7	0.005	0.002	0.001	0.009	0.000	0.000	0.000	0.000	0.000	0.017
8	0.030	0.011	0.007	0.002	0.000	0.000	0.000	0.000	0.000	0.049
tot	0.141	0.102	0.146	0.164	0.013	0.001	0.004	0.004	0.002	0.579

(LUMO+2)

ion	s	py	pz	px	dxy	dyz	dz2	dxz	x2-y2	tot
1	0.041	0.004	0.015	0.048	0.002	0.000	0.000	0.002	0.001	0.112
2	0.052	0.005	0.019	0.037	0.002	0.000	0.000	0.001	0.001	0.117
3	0.052	0.005	0.019	0.037	0.002	0.000	0.000	0.001	0.001	0.117
4	0.041	0.004	0.015	0.048	0.002	0.000	0.000	0.002	0.001	0.112
5	0.016	0.001	0.004	0.032	0.000	0.000	0.000	0.000	0.000	0.053
6	0.020	0.001	0.006	0.025	0.000	0.000	0.000	0.000	0.000	0.052
7	0.020	0.001	0.006	0.025	0.000	0.000	0.000	0.000	0.000	0.052
8	0.016	0.001	0.004	0.032	0.000	0.000	0.000	0.000	0.000	0.053
tot	0.256	0.021	0.089	0.283	0.008	0.000	0.000	0.006	0.004	0.667

(LUMO+3)

ion	s	py	pz	px	dxy	dyz	dz2	dxz	x2-y2	tot
1	0.052	0.005	0.019	0.037	0.002	0.000	0.000	0.001	0.001	0.117
2	0.041	0.004	0.015	0.048	0.002	0.000	0.000	0.002	0.001	0.112
3	0.041	0.004	0.015	0.048	0.002	0.000	0.000	0.002	0.001	0.112
4	0.052	0.005	0.019	0.037	0.002	0.000	0.000	0.001	0.001	0.117
5	0.020	0.001	0.006	0.025	0.000	0.000	0.000	0.000	0.000	0.052
6	0.016	0.001	0.004	0.032	0.000	0.000	0.000	0.000	0.000	0.053

7	0.016	0.001	0.004	0.032	0.000	0.000	0.000	0.000	0.000	0.053
8	0.020	0.001	0.006	0.025	0.000	0.000	0.000	0.000	0.000	0.052
tot	0.256	0.021	0.089	0.283	0.008	0.000	0.000	0.006	0.004	0.667

(LUMO+4)

ion	s	py	pz	px	dxy	dyz	dz2	dxz	x2-y2	tot
1	0.000	0.001	0.008	0.074	0.008	0.001	0.006	0.000	0.000	0.099
2	0.000	0.001	0.008	0.074	0.008	0.001	0.006	0.000	0.000	0.099
3	0.000	0.001	0.008	0.074	0.008	0.001	0.006	0.000	0.000	0.099
4	0.000	0.001	0.008	0.074	0.008	0.001	0.006	0.000	0.000	0.099
5	0.009	0.003	0.015	0.017	0.000	0.000	0.000	0.000	0.000	0.043
6	0.009	0.003	0.015	0.017	0.000	0.000	0.000	0.000	0.000	0.043
7	0.009	0.003	0.015	0.017	0.000	0.000	0.000	0.000	0.000	0.043
8	0.009	0.003	0.015	0.017	0.000	0.000	0.000	0.000	0.000	0.043
tot	0.036	0.017	0.090	0.364	0.033	0.002	0.025	0.002	0.001	0.569

Table S3: SnS_2, orbital contribution to the wavefunction by atoms in the system.
ion 1 is Sn
ions 2 and 3 are S

(LUMO)

ion	s	py	pz	px	dxy	dyz	dz2	dxz	x2-y2	tot
1	0.316	0.000	0.000	0.000	0.018	0.003	0.001	0.007	0.006	0.351
2	0.008	0.028	0.009	0.083	0.000	0.000	0.000	0.000	0.000	0.127
3	0.008	0.028	0.009	0.083	0.000	0.000	0.000	0.000	0.000	0.127
tot	0.332	0.055	0.017	0.166	0.018	0.003	0.001	0.007	0.006	0.606

(LUMO+1)

ion	s	py	pz	px	dxy	dyz	dz2	dxz	x2-y2	tot
1	0.000	0.005	0.383	0.000	0.000	0.000	0.000	0.000	0.000	0.388
2	0.067	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.069
3	0.067	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.069
tot	0.134	0.006	0.386	0.000	0.000	0.000	0.000	0.000	0.000	0.526

(LUMO+2)

ion	s	py	pz	px	dxy	dyz	dz2	dxz	x2-y2	tot
1	0.003	0.328	0.074	0.000	0.000	0.002	0.003	0.000	0.003	0.413
2	0.024	0.048	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.073
3	0.024	0.048	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.073
tot	0.052	0.423	0.076	0.000	0.000	0.002	0.003	0.000	0.003	0.559

(LUMO+3)

ion	s	py	pz	px	dxy	dyz	dz2	dxz	x2-y2	tot
1	0.000	0.000	0.000	0.561	0.000	0.000	0.000	0.000	0.000	0.561
2	0.000	0.000	0.000	0.042	0.000	0.000	0.000	0.000	0.000	0.042
3	0.000	0.000	0.000	0.042	0.000	0.000	0.000	0.000	0.000	0.042
tot	0.000	0.000	0.000	0.645	0.000	0.000	0.000	0.000	0.000	0.645

(LUMO+4)

ion	s	py	pz	px	dxy	dyz	dz2	dxz	x2-y2	tot
1	0.012	0.017	0.063	0.032	0.029	0.011	0.059	0.037	0.009	0.269
2	0.003	0.004	0.048	0.017	0.000	0.000	0.000	0.000	0.000	0.072
3	0.003	0.004	0.048	0.017	0.000	0.000	0.000	0.000	0.000	0.072
tot	0.018	0.026	0.159	0.066	0.029	0.011	0.059	0.037	0.009	0.413