Supplementary Information

Electron-Beam Induced Transformation of Layered Tin Dichalcogenides

E. Sutter,[1,*] Y. Huang,[2] H.-P. Komsa,[3] M. Ghorbani-Asl,[4] A.V. Krasheninnikov,[3,4] and P. Sutter[5,*]

[1]Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, Lincoln, NE 68588, USA

[2]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

[3]Department of Applied Physics, Aalto University, P.O. Box 11100, FI-00076 Aalto, Finland

[4]Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, 01314 Dresden, Germany

[5]Department of Electrical and Computer Engineering, University of Nebraska-Lincoln, Lincoln, NE 68588, USA

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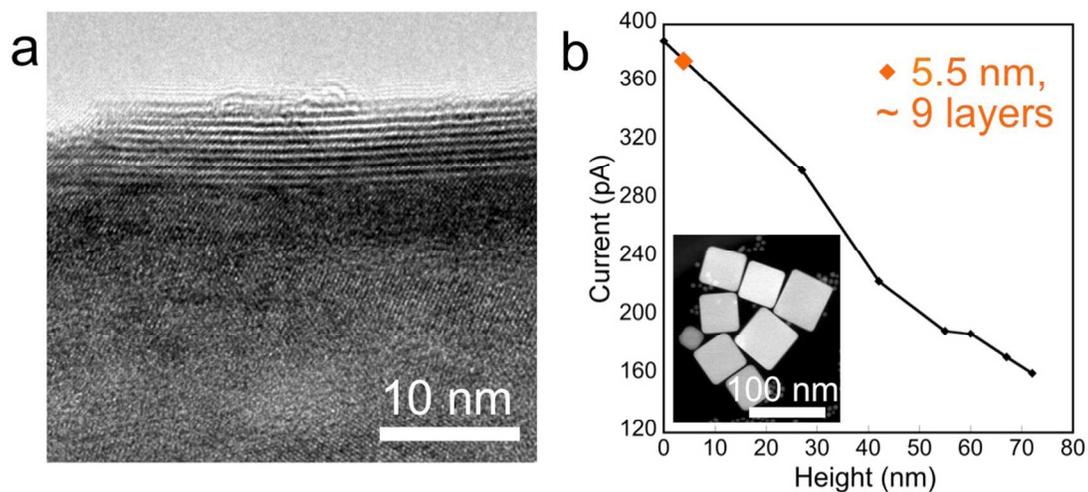
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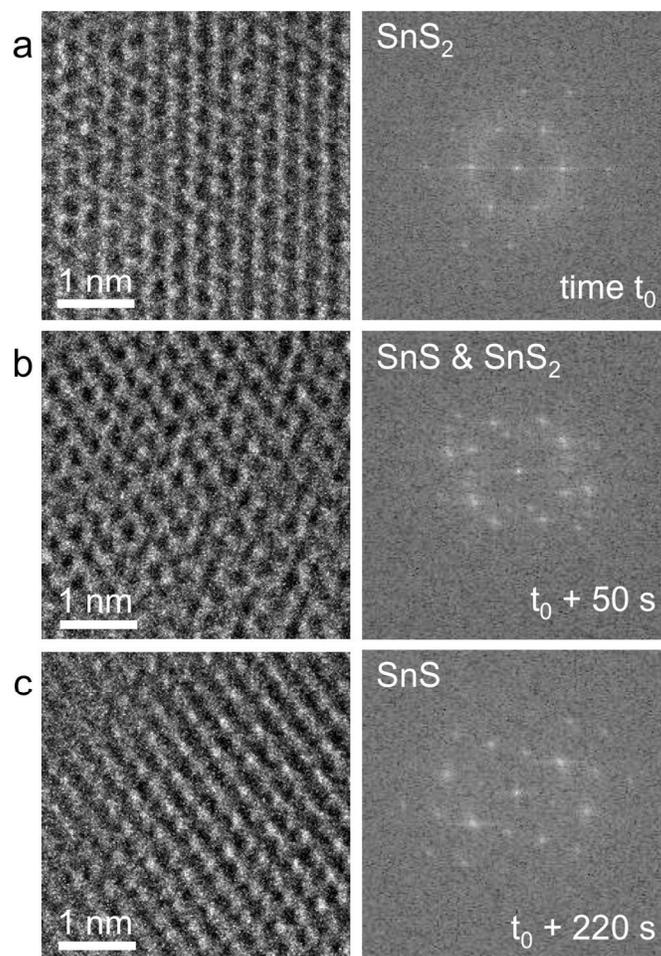
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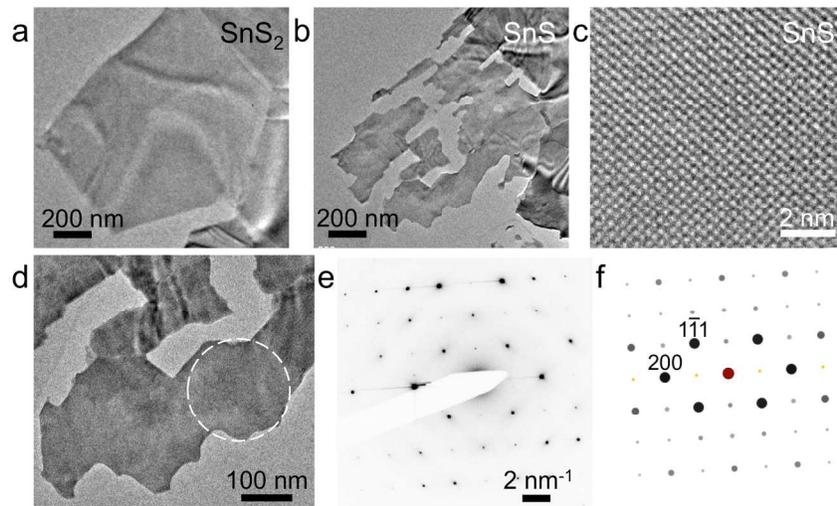
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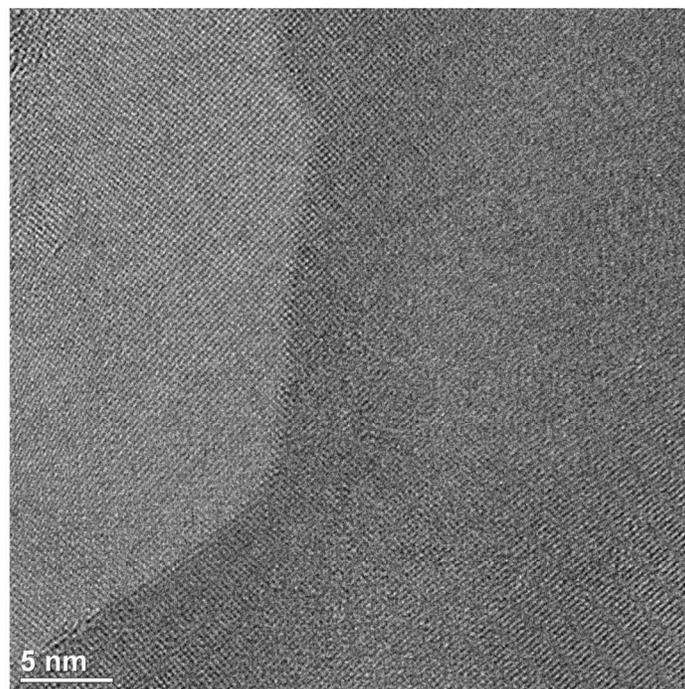
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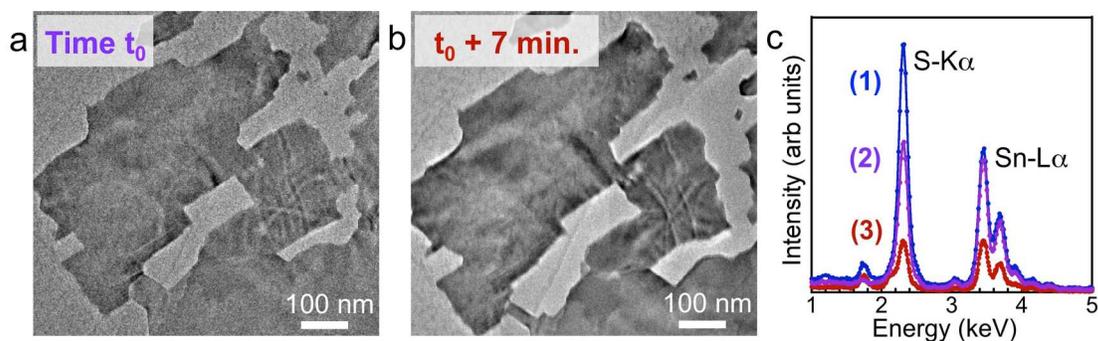
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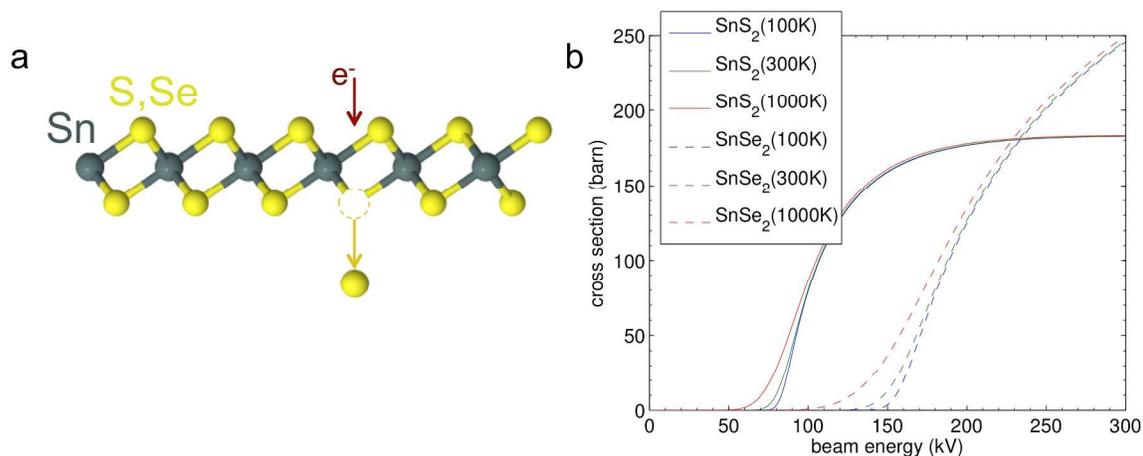

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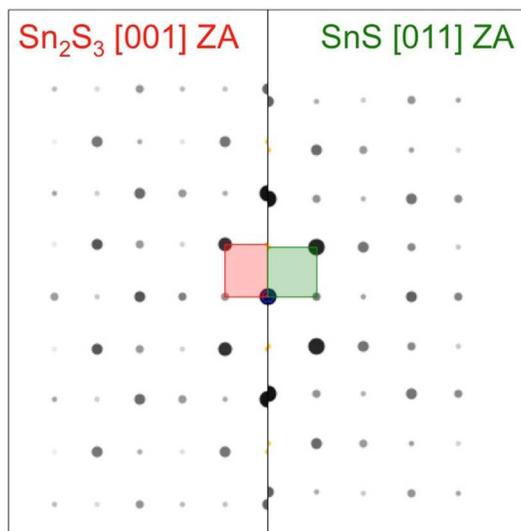
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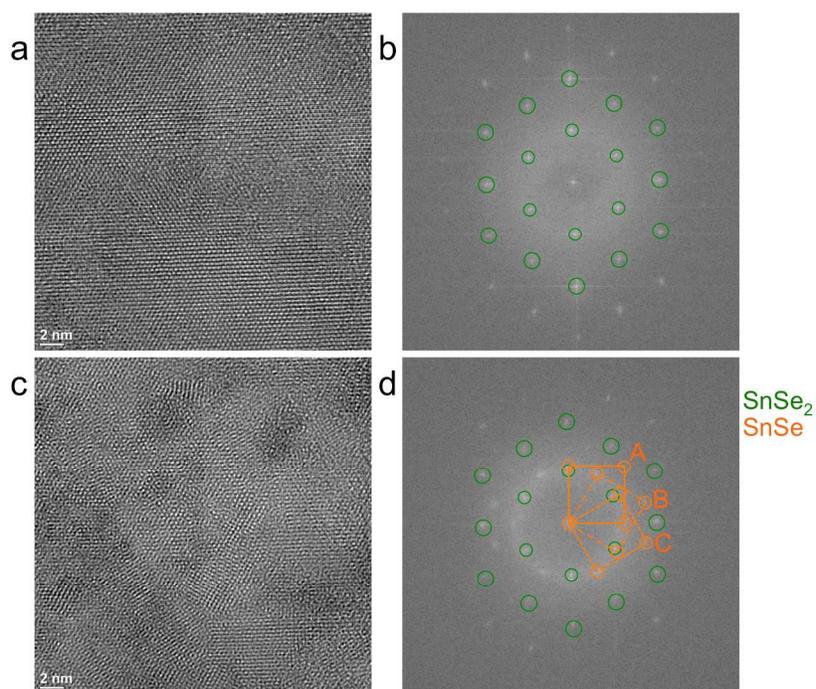
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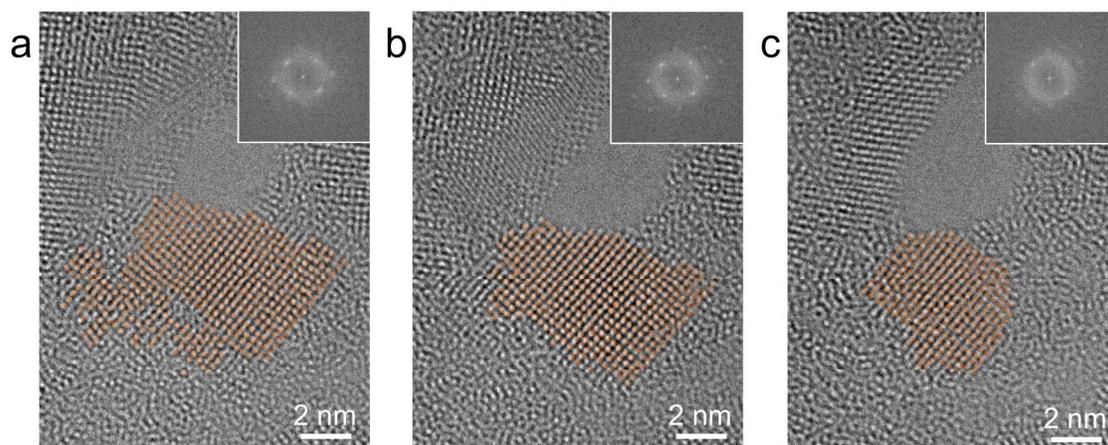
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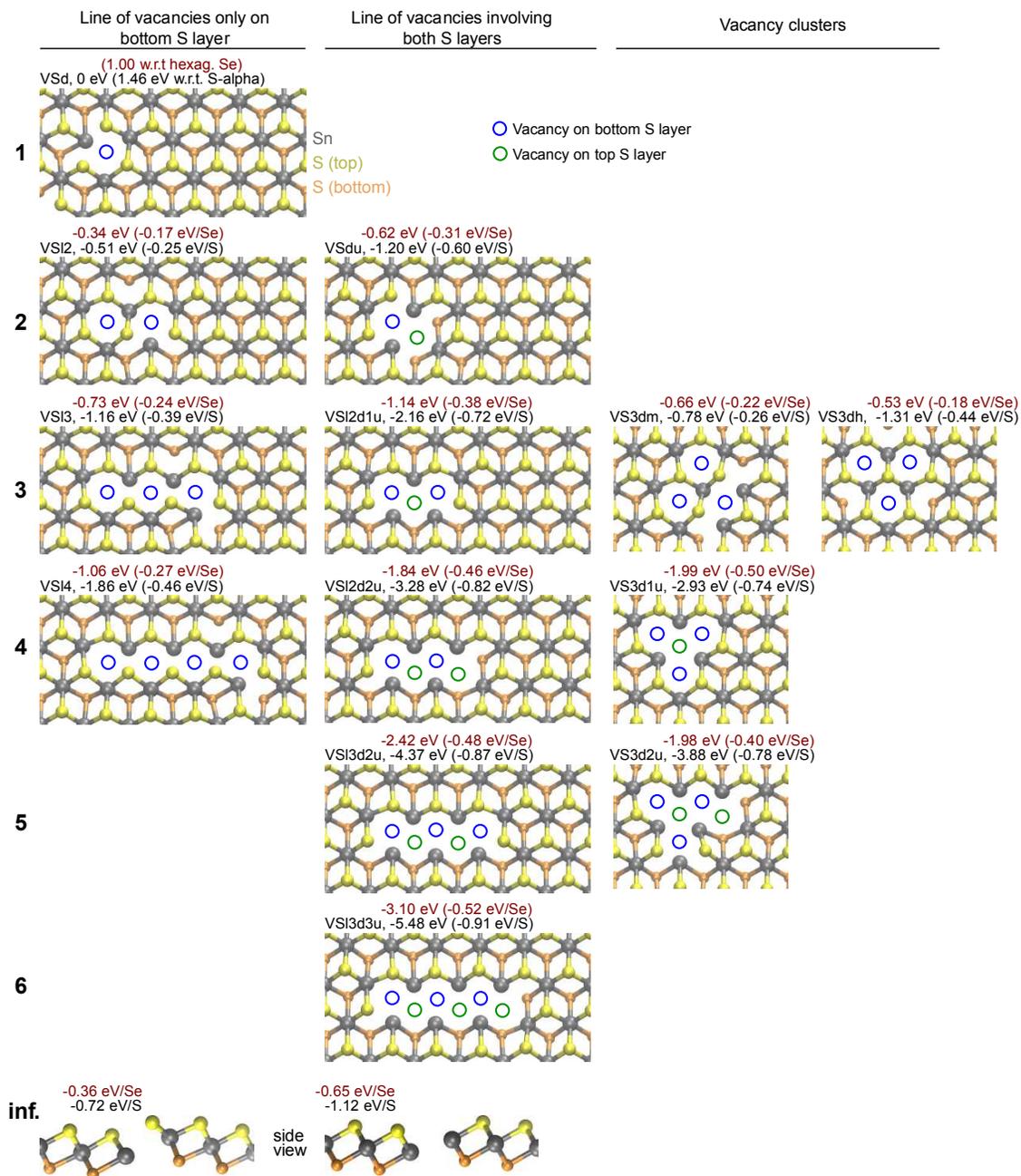
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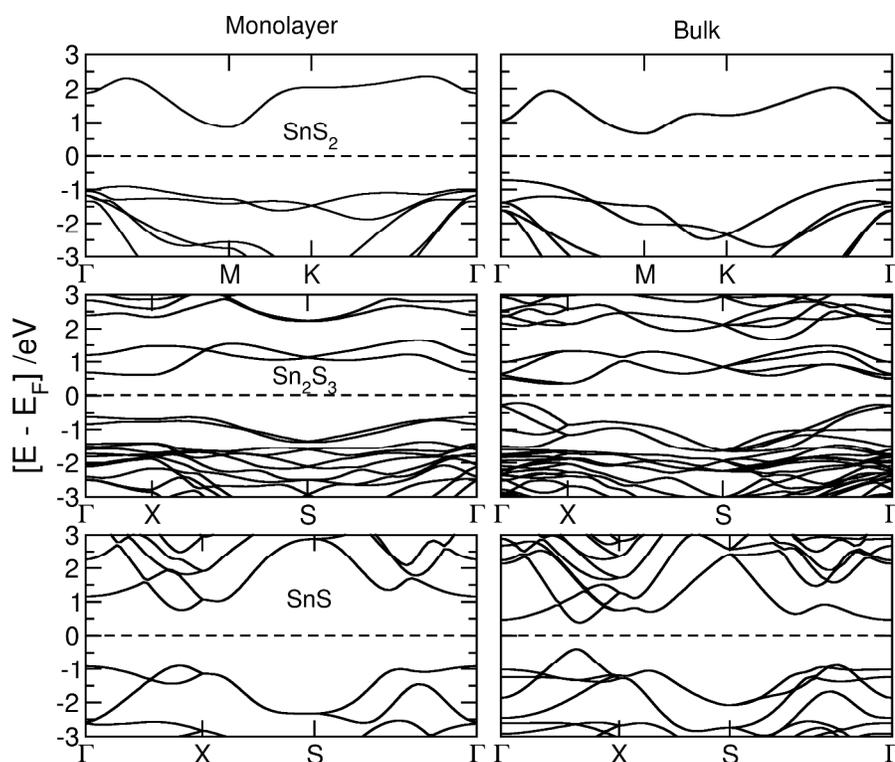
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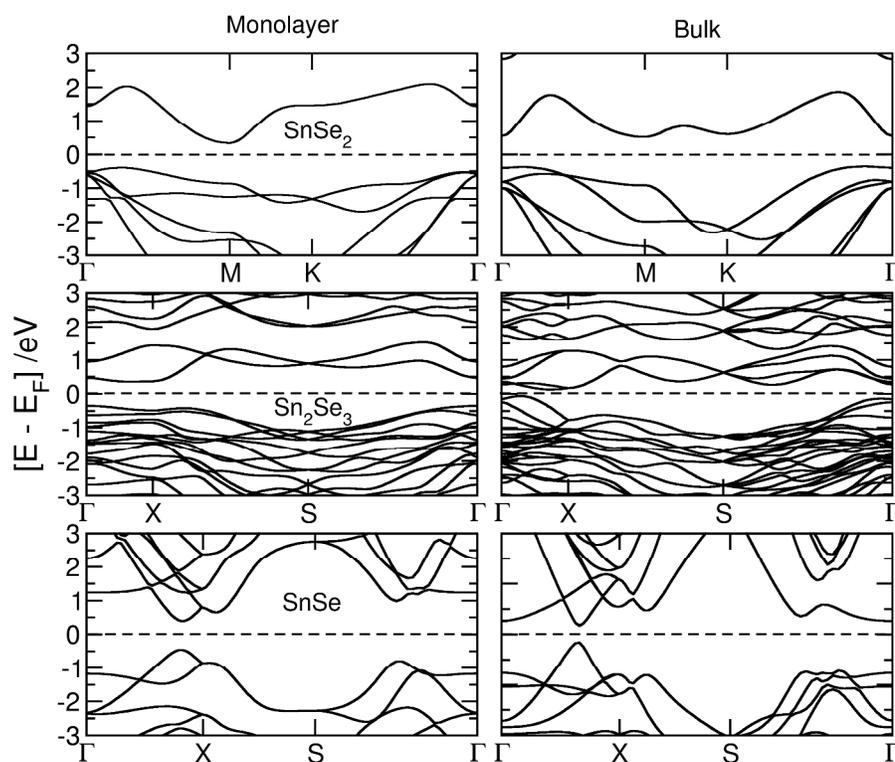
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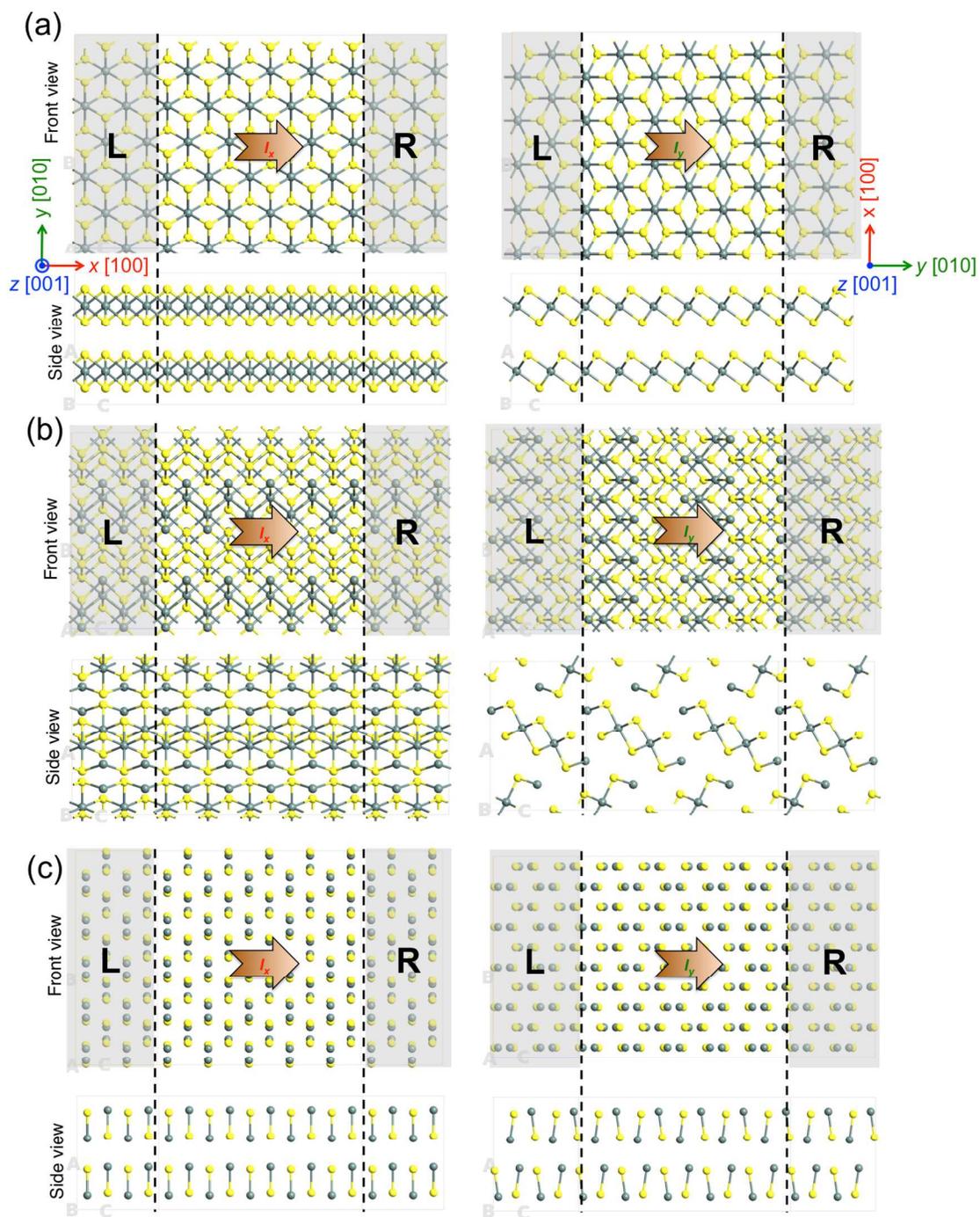
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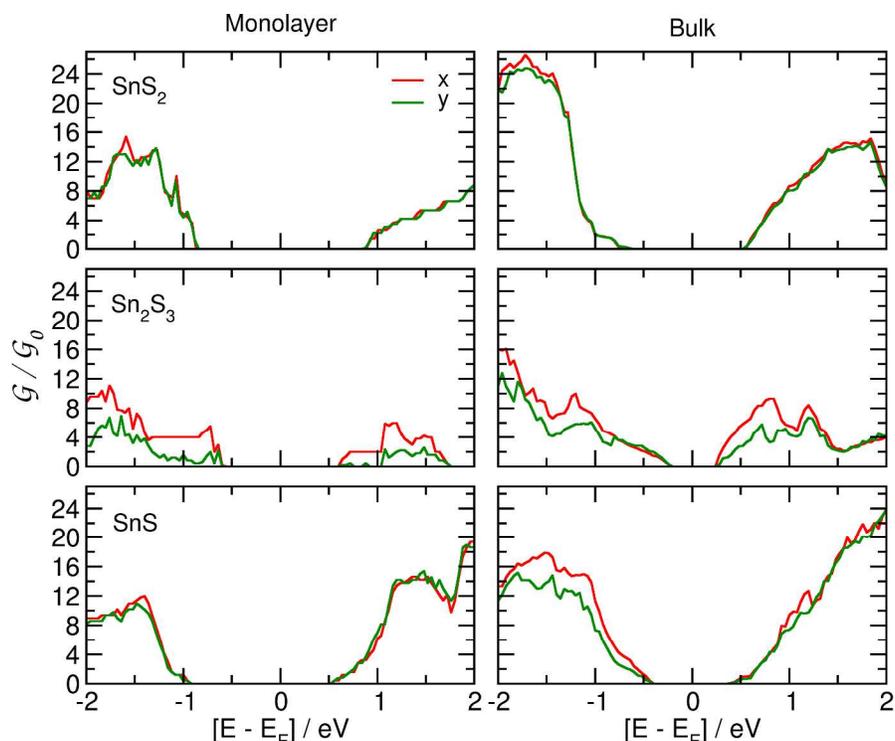
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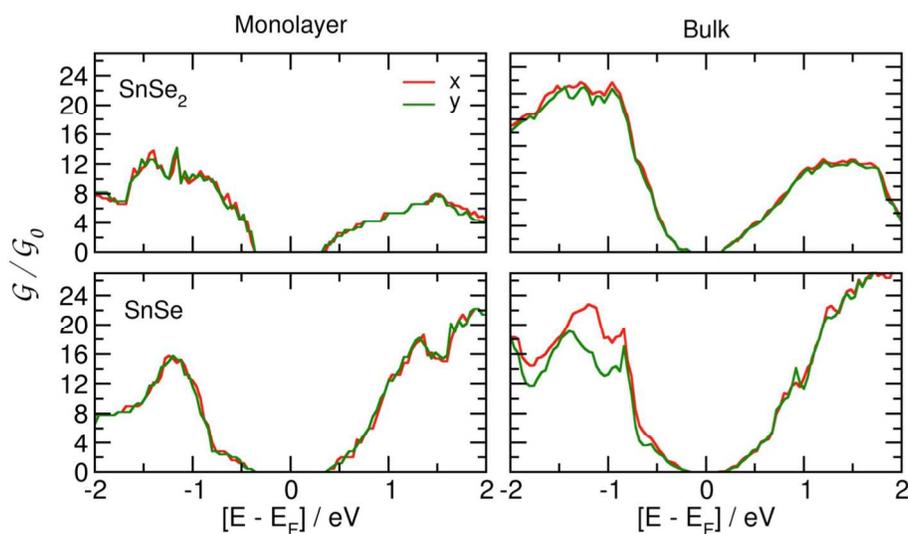
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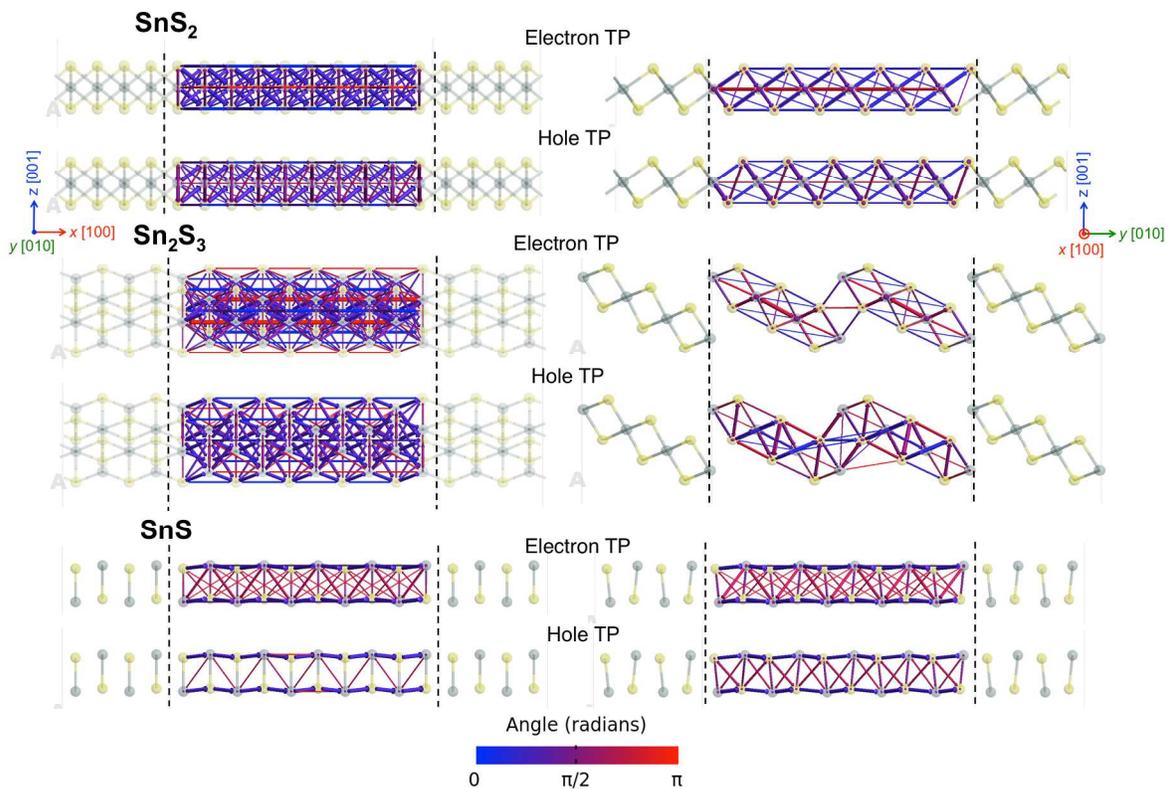
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2. Supplementary Tables

Table S1. Formation enthalpy at 0 K and without ZPE for bulk systems. Energies are per formula unit, first line eV, second line kJ/mol, Experimental values (Exp.) in kJ/mol, and $\Delta E = E(Sn_2S_3) - (E(SnS) + E(SnS_2))$.

	SnS	Sn_2S_3	SnS_2	ΔE
LDA	-1.01	-2.34	-1.32	-0.00
	-98	-225	-127	
PBE	-0.82	-1.80	-1.00	0.03
	-80	-173	-96	
PBE-D2	-1.17	-2.54	-1.38	0.01
	-113	-245	-133	
revB86b	-1.10	-2.49	-1.36	-0.02
	-107	-240	-132	
Exp.	-100 to -108	-249 to -297	-148 to -182	< 0
	SnSe	Sn_2Se_3	$SnSe_2$	ΔE
LDA	-0.89	-1.92	-1.05	0.03
	-86	-185	-101	
PBE	-0.89	-1.93	-1.06	0.03
	-86	-186	-102	
PBE-D2	-1.10	-2.29	-1.25	0.05
	-106	-221	-121	
revB86b	-0.98	-2.04	-1.08	0.01
	-94	-197	-104	
Exp.				> 0

Table S2. Lattice parameters for bulk systems (in Å).

	SnS	Sn_2S_3	SnS_2
LDA	10.97, 3.96, 4.16	8.59, 3.76, 13.59	3.63, 5.70
PBE	11.42, 4.02, 4.42	9.27, 3.80, 14.41	3.70, 7.08
PBE-D2	11.38, 4.01, 4.27	8.84, 3.78, 13.98	3.69, 5.89
revB86b	11.28, 4.02, 4.30	8.85, 3.80, 13.96	3.68, 5.88
Expt.	11.32, 4.05, 4.24	8.87, 3.75, 14.02	3.64, 5.89
	SnSe	Sn_2Se_3	$SnSe_2$
LDA	11.31, 4.12, 4.30	8.91, 3.94, 14.16	3.80, 5.90
PBE	11.76, 4.21, 4.55	9.68, 3.99, 14.83	3.87, 8.22
PBE-D2	11.63, 4.20, 4.36	9.19, 3.92, 14.80	3.83, 6.16
revB86b	11.63, 4.20, 4.43	9.22, 3.99, 14.55	3.88, 6.11
Expt.	11.57, 4.19, 4.46		3.81, 6.14

Table S3. Band gaps (in eV) of monolayer and bulk SnS$_2$(Se$_2$), Sn$_2$S$_3$(Se$_3$), SnS(Se) calculated at DFT/PBE+SOC level.

Material	Monolayer	Bulk
SnS$_2$	1.75	1.37
Sn$_2$S$_3$	1.23	0.56
SnS	1.66 (d)*	0.78
SnSe$_2$	0.73	0.88
Sn$_2$Se$_3$	0.70	0.18
SnSe	0.87 (d)*	0.34

*d represents a direct band gap

Table S4. The values of electron effective masses for bulk SnS$_2$, Sn$_2$S$_3$ and SnS. Data obtained from DFT/PBE+SOC band structure calculations.

Material	$m^*_{[100]}/m_0$	$m^*_{[010]}/m_0$	$m^*_{[001]}/m_0$	$m^*_{[110]}/m_0$	$m^*_{[101]}/m_0$	$m^*_{[011]}/m_0$
SnS$_2$	0.544	0.328	1.064	0.717	1.025	0.784
Sn$_2$S$_3$	0.275	1.270	0.710	0.488	0.897	3.452
SnS	0.101	0.195	0.699	0.133	0.177	0.305

3. Supplementary Movies
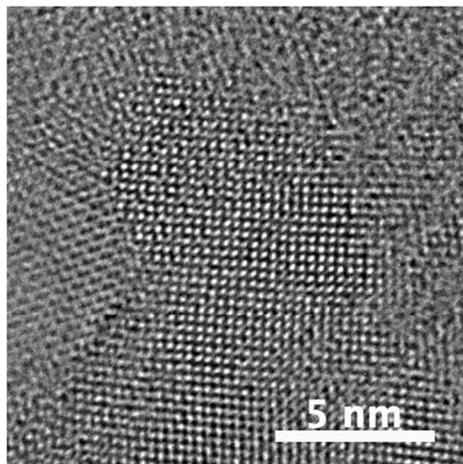
Movie S1: Time-lapse movie of the electron-beam induced transformation of few-layer SnS_2 to SnS at room temperature. Electron energy: 300 keV (FEI Titan 80-300, Orius CCD camera). Total duration: 490 sec. Spatial scale as shown in the movie. 50 frames.
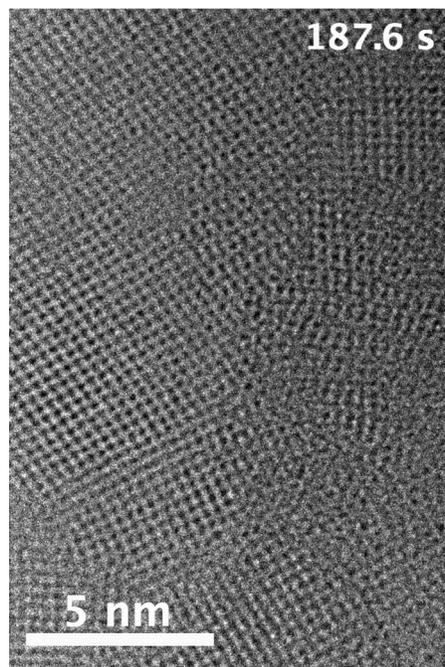
Movie S2: Time-lapse movie of the electron-beam induced transformation of few-layer SnS_2 to SnS at room temperature. Electron energy: 300 keV (FEI Titan 80-300, Gatan K2-IS DDD camera). Actual capture rate: 2.5 milliseconds per frame. The movie shows every 100th frame of the original dataset at 50% scaling. Spatial scale and timing as shown in the movie. 470 frames.

4. Computational details for electronic structure and transport calculations

The electronic structure and quantum transport calculations were performed using Atomistix ToolKit (ATK) code.[1] The calculations have been done using GGA/PBE functional[2] with double-zeta plus polarization numerical basis sets. The effect of spin-orbit coupling (SOC) was considered in all electronic structure calculations. We have used an energy cutoff of 300 Ryd and 0.0002 Ryd of tolerance for the self-consistent calculations. A 9x9x9 and 5×5×100 Monkhorst-Pack k-sampling is used for the electronic structure and transport calculations. A vacuum separation of 30 Å has been applied for simulation of monolayers, which minimizes any artificial interaction between its periodic images. The Poisson-Schrödinger equation of the system was self-consistently solved using a Fast Fourier Transform (FFT) solver. Transport calculations were performed such that the system is divided into three parts: the semi-infinite left (L) and right (R) electrode, and the finite central region (C), also called scattering region. In order to provide straightforward comparison between different orientations, we used a supercell with almost equal length and width along x and y directions for all the calculations. According to the Fisher-Lee formula,[3] the electron conductance at low temperatures can be obtained via transmission matrix (T):

$$\mathcal{G} = \mathcal{G}_0 \sum_n T_n(E) = \mathcal{G}_0 \, Trace\big[\hat{G}_C \hat{\Gamma}_R \hat{G}_C^\dagger \hat{\Gamma}_L\big],$$

where $\mathcal{G}_0$ represents quantum conductance, G_C is the Green's function of the central region and $\hat{\Gamma}_{L,R}$ are the coupling matrices of left and right electrodes.

5. Supplementary References

(1)   QuantumWise A/S. Atomistix ToolKit, 2015, www.quantumwise.com.
(2)   Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
(3)   Fisher, D. S.; Lee, P. A. *Phys. Rev. B* **1981**, *23*, 6851.