Supporting Information:

Correlative and in situ microscopy investigation of phase transformation, crystal growth and degradation of antimony sulfide thin films

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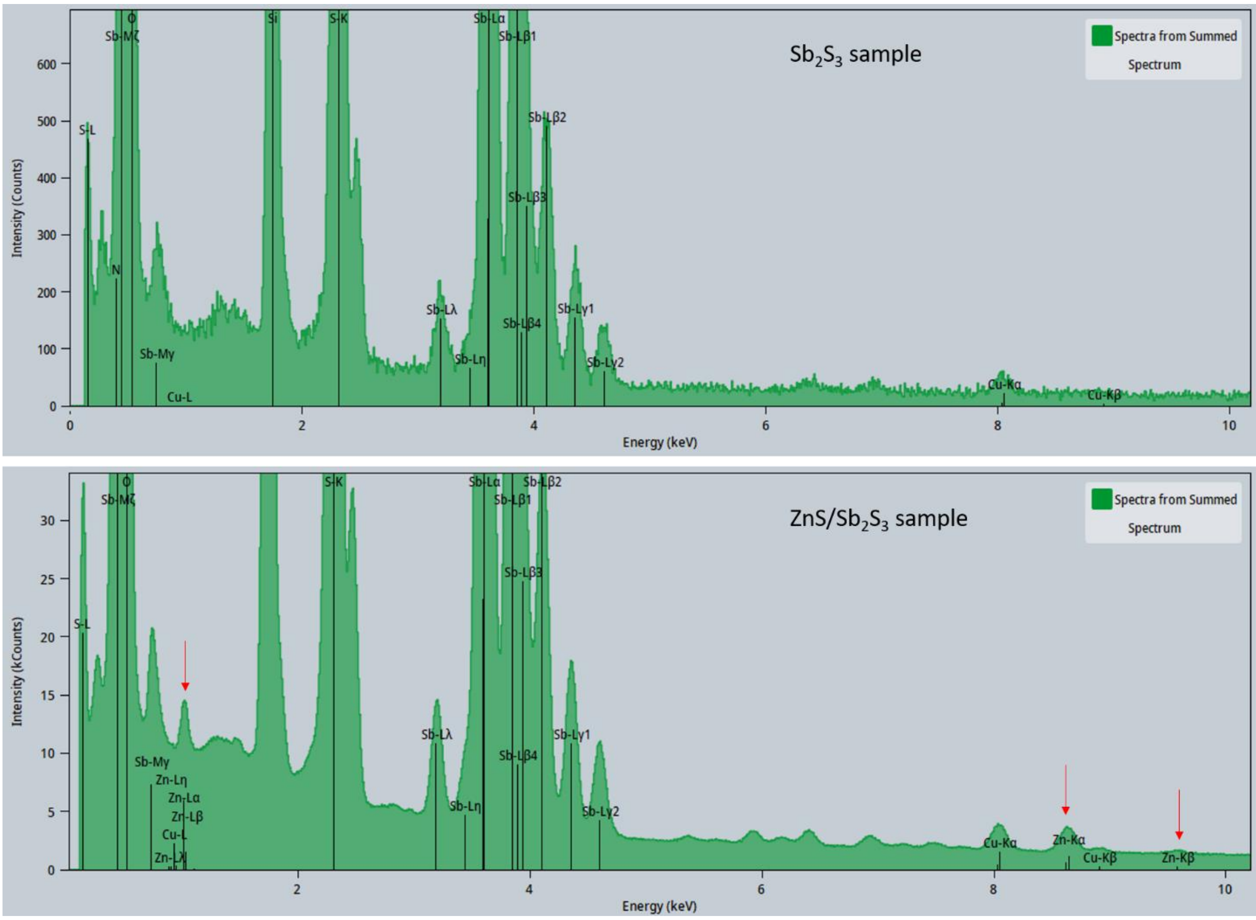
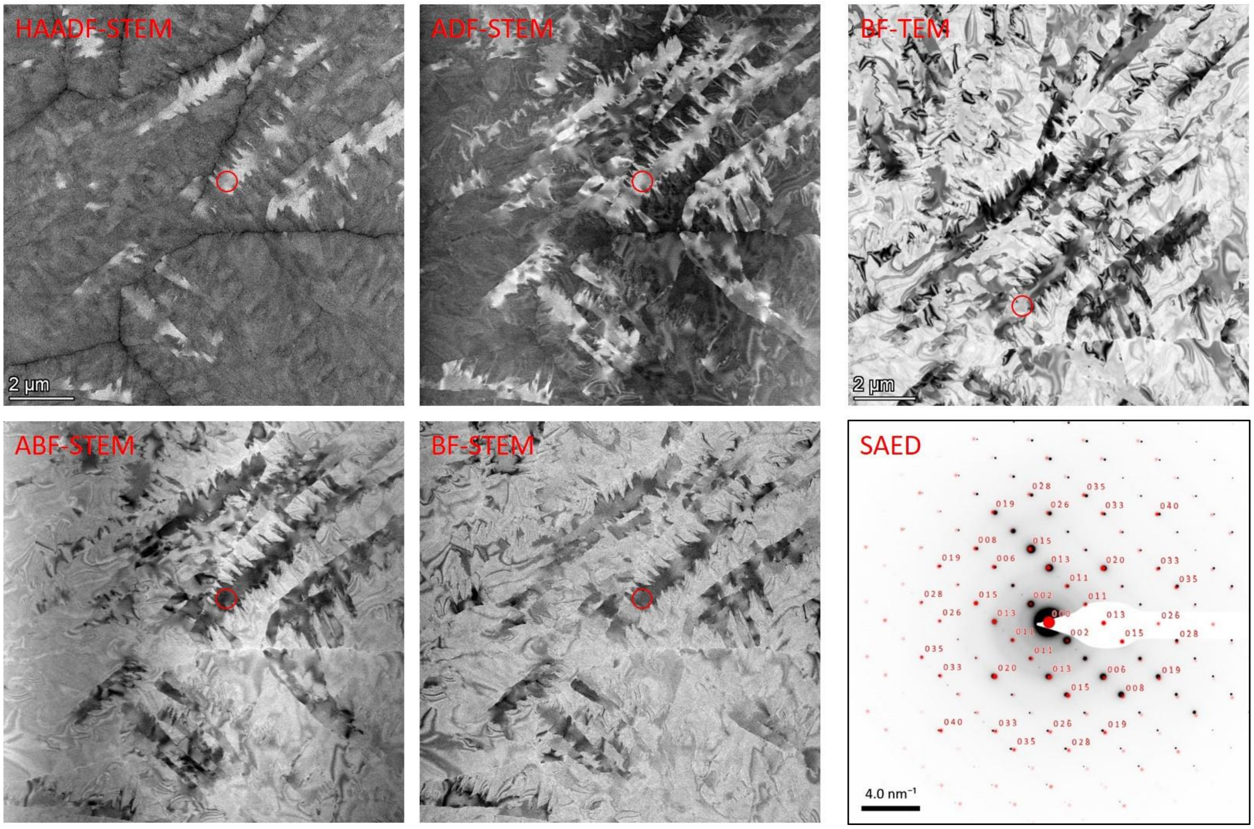
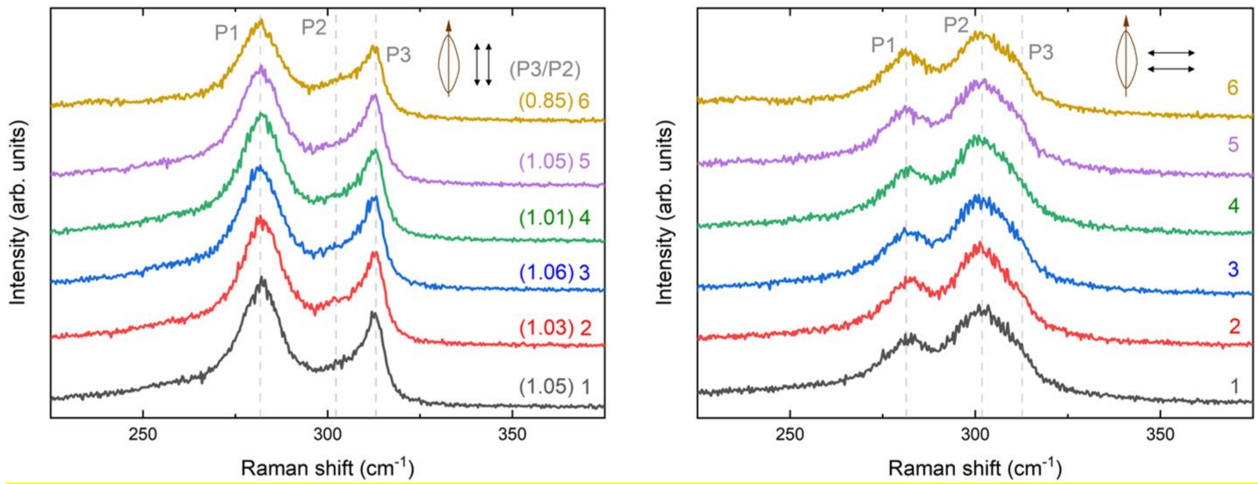


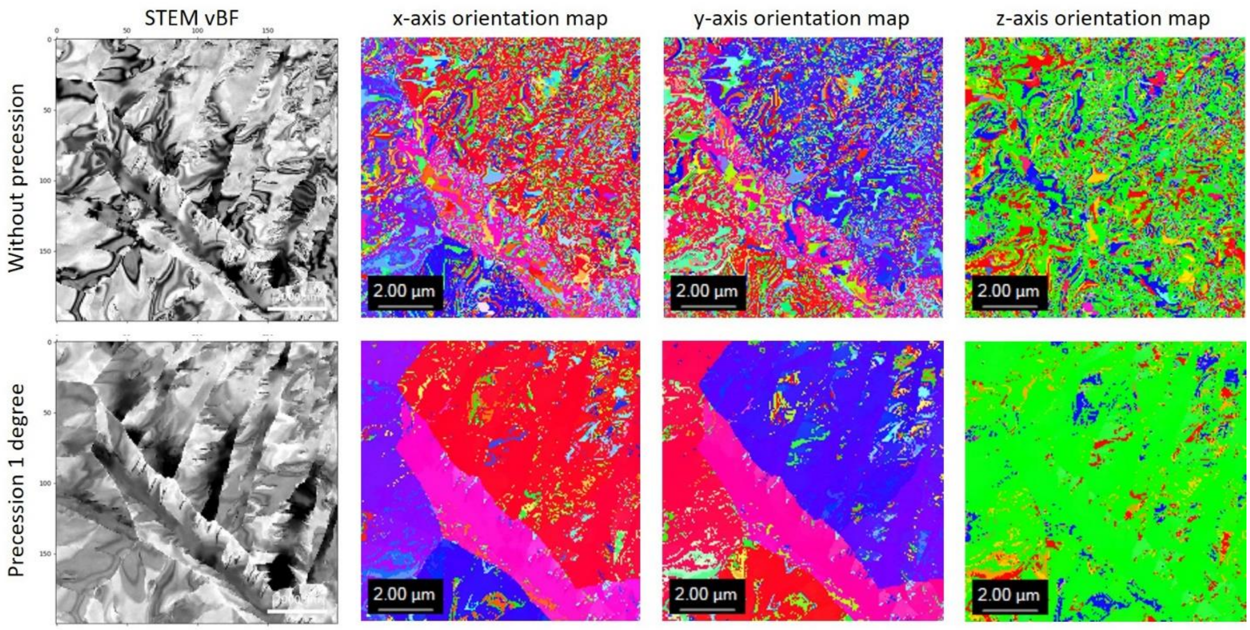
Supporting Figure S1. EDXS of Sb_2S_3 thin film and ZnS/Sb_2S_3 film. The Zn signal peaks are indicate by the red arrows.



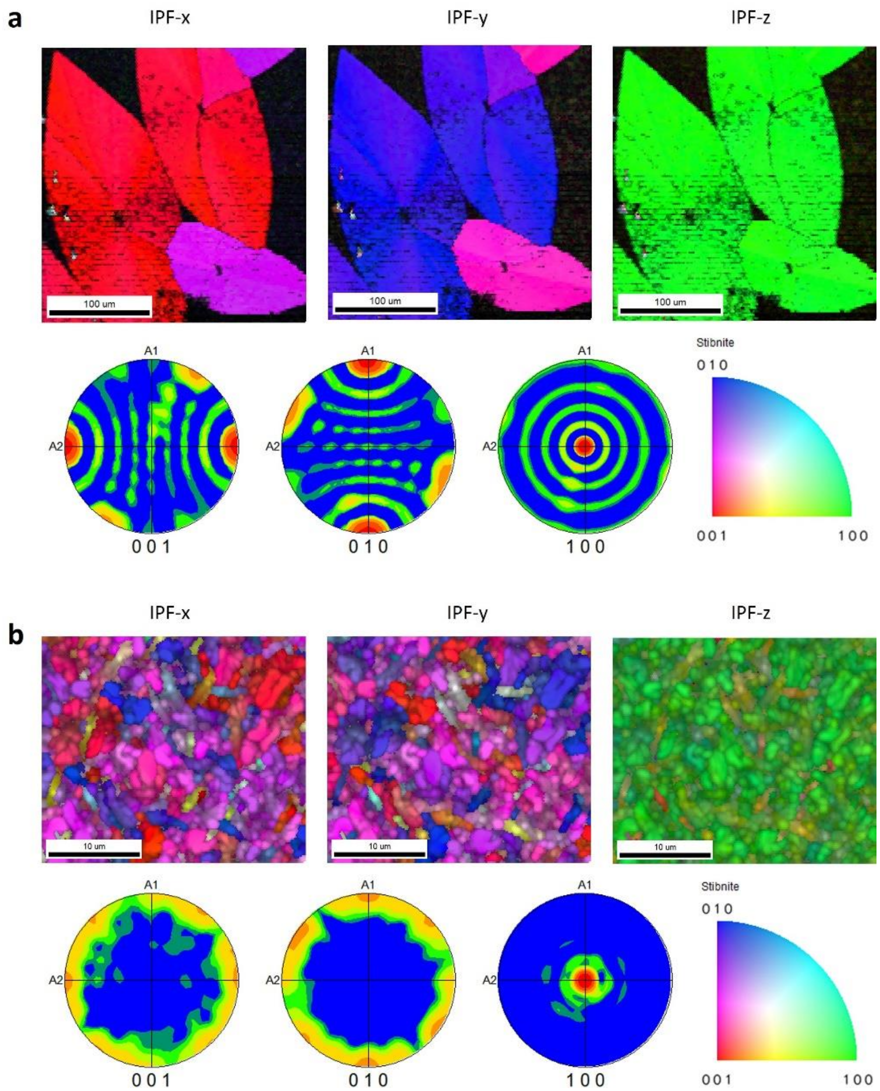
Supporting Figure S2. Simultaneously acquired STEM images and the subsequently acquired BF-TEM and SAED from the same sample region (from the Sb_2S_3 sample without ZnS). The red circle indicate where the SAED was acquired.



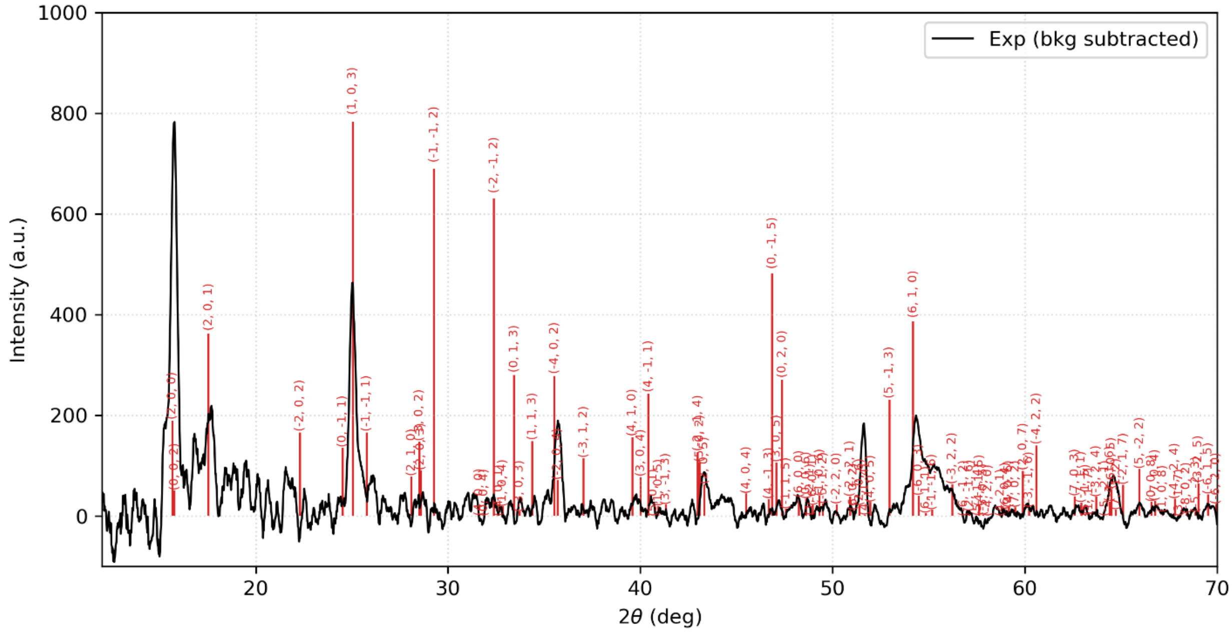
Supporting Figure S3 Raman spectroscopy analysis of the Sb_2S_3 samples. Raman spectra of Sb_2S_3 thin film at spots (numbering as in Fig. 3b of the main text) with different in-plane-rotation with the [010] in-plane orientation axis of the Sb_2S_3 leaf being parallel (a), and perpendicular (b) to the polarization of the laser and the scattered light. The numbers in brackets indicate the intensity ratio of the peaks P3/P2.



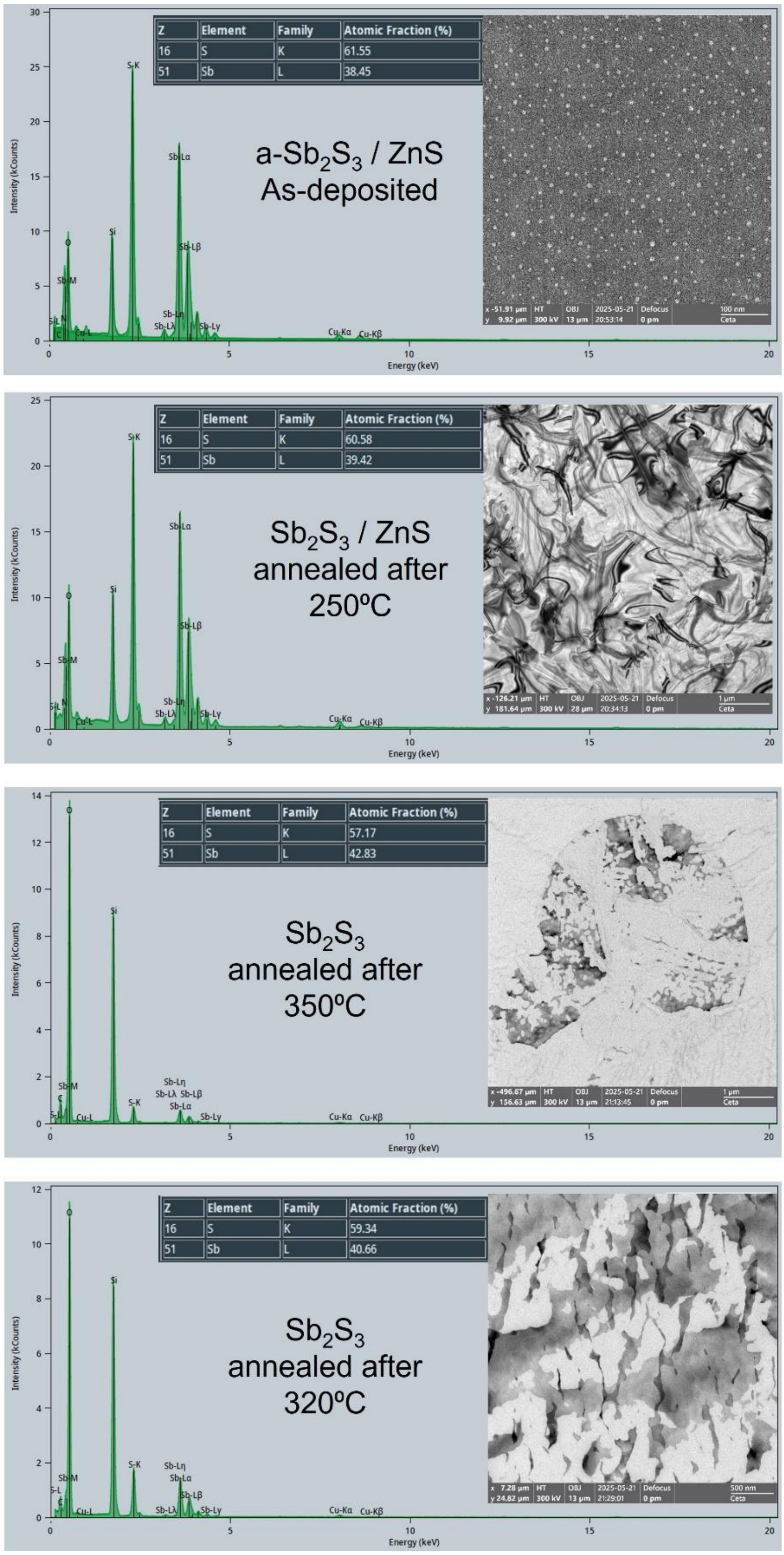
Supporting Figure S4. Orientation mapping results with and without beam presession.



Supporting Figure S5. Orientation mapping results from EBSD data, represented using inverse pole figures (IPFs) and pole figures (PF) from (**a**) the annealed Sb_2S_3 sample and (**b**) the annealed Sb_2S_3/ZnS sample.



Supporting Figure S6. XRD data (grazing incidence geometry and 2-theta scan) of the TEM grid shown in Fig. 1f, which is formed after *in situ* TEM observations summarized in Fig. 5c and also documented in supplementary video 3, and further correlatively studied in Fig. 3c and Fig. 4b and c. The simulated powder diffraction peaks (using JEMS software) are overlayed. Despite being very noisy (due to small size of the TEM grid for GIXRD) the experimental data qualitatively reveal the overall [100] texture, as the (200), (103) and (402) peaks are particularly strong. This is in good agreement with the quantitative texture analysis in Fig. 3c and Fig. S5 using EBSD.



Supporting Figure S7. EDXS of samples as-deposited, and those annealed under different temperatures. The Stoichiometry remained almost the same when transforming from amorphous to crystal at mild temperature just above the phase transition temperature. Higher temperature caused loss of sulfur as evident from the quantified atomic ratio of S and Sb, indicate preferential sublimation of S in the thin film during degradation. EDXS were carried out in TEM mode, with illumination area of ~3 – 4 µm in diameter, 2 – 3 nA probe current. Quantification in Thermo Fischer Scientific Velox software with same parameters (fitting, background subtraction and absorption correction) for all samples.

The following Supporting Video files are provided in public data repository with accession:

DOI: 10.5281/zenodo.15536234

Supplementary video file 1: "1520 STEM HAADF-DF-I-DF-O-BF ADF.mrc" STEM-ADF movie showing phase transformation of Sb_2S_3 during an *in situ* observation at temperature between 240 and 245ºC. Data acquired at 628 ms/frame. The temperature reached 240ºC at frame #960, and very slowly raised to 250ºC at frame #1130 and hold to the last frame #1682.

Supplementary video file 2: "1545 STEM HAADF-DF-I-DF-O-BF ADF.mrc" STEM-ADF movie showing degradation of Sb_2S_3 during an *in situ* observation at a temperature of 350ºC. Data acquired at 492 ms/frame. The temperature reached 290ºC at frame #60, raised to 350ºC at frame #200 and hold there until the end of movie.

Supplementary video file 3: "1038 STEM HAADF-DF4-DF2-BF DF4.mrc" STEM-ADF movie showing nucleation and growth of Sb_2S_3 from the a-Sb_2S_3/ZnS sample during an *in situ* observation when the temperature was kept at 250ºC. Data acquired at 400 ms/frame.