Electronic Supplementary Material (ESI) for Materials Advances.
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Supplementary Information

Synthesis and characterization of Cu_3SbS_4 semiconducting thin films grown by co-sputtering metal precursors and subsequent sulfurization

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1. Schematic representation of two-stage growth process:

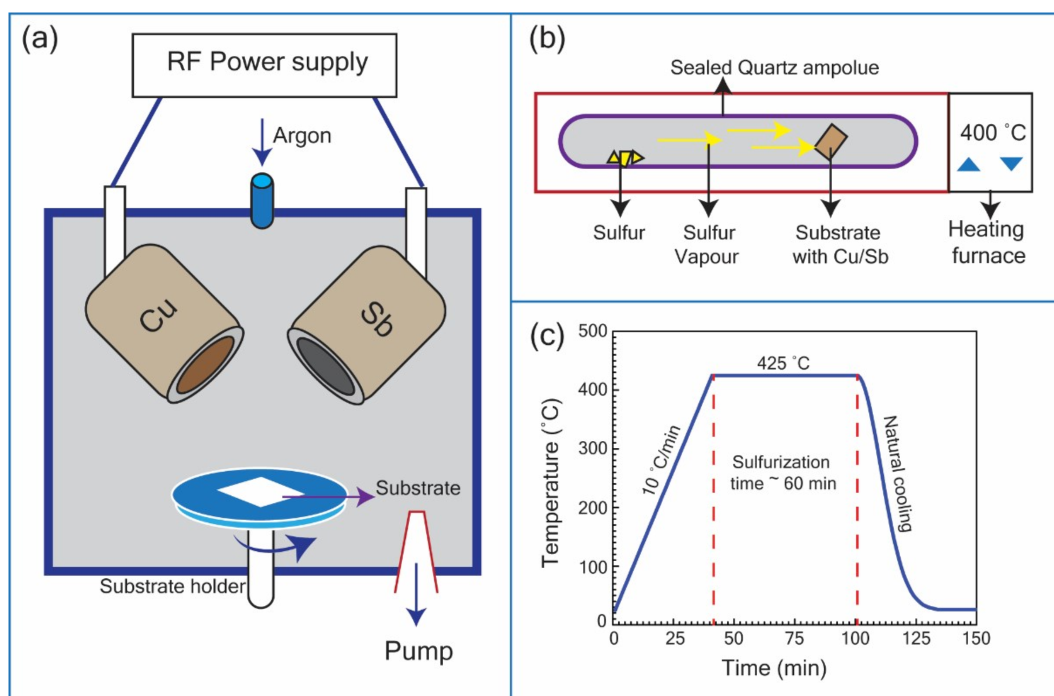

Fig. SI 1: (a) Schematic illustration of co-sputtering Cu and Sb metal precursor by RF magnetron sputtering (b) Sulfurization process (c) typical temperature profile of the sulfurization process.

2. **Influence of Cu/Sb metal precursor ratio and sulfurization time on the composition of Cu-Sb-S thin films.**

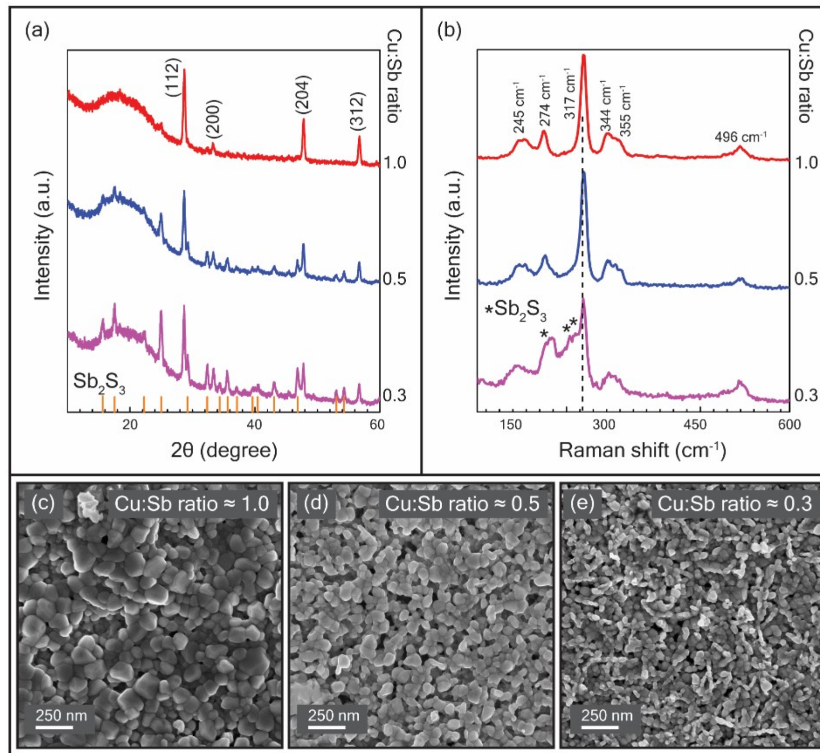

Fig. SI 2 (a) GIXRD pattern (b) Raman spectra and [(d), (e), (f]) Surface morphology of Cu_3SbS_4 thin films sulfurized with Cu/Sb ~ 0.1, 0.5 and 0.3 respectively

RF sputtering power (W)		Sputtered film composition (at. %)			After sulfurization (at. %)			Identified phases
[Cu]	[Sb]	[Cu]	[Sb]	~[Cu]/[Sb]	[Cu]	[Sb]	[S]	
50	35	48.7	51.3	1	34.3	12.8	52.9	Phase-pure Cu_3SbS_4
50	40	32.5	67.5	0.5	29.4	18.5	52.1	Cu_3SbS_4, Sb_2S_3
50	50	23.4	76.6	0.3	19.5	25.8	54.7	Cu_3SbS_4, Sb_2S_3

Table. SI 1: EDS composition analysis of sputtered and sulfurized samples with different [Cu]/[Sb] ratio

The influence of Cu/Sb metal precursor ratio on the sulfurized films are evaluated by co-sputtering precursors with different Cu/Sb ratio (0.1, 0.5, 0.3). Variation in Cu/Sb ratio was achieved by varying the RF sputtering power of [Sb] metal from 35 W to 50 W. Fig. SI.1 shows the GIXRD pattern, Raman spectroscopy, and surface morphology of the sputtered films. Increase in Sb content on the co-sputtered films promotes the growth of binary Sb_2S_3 phase. The surface morphology of the samples also indicated that phase-pure Cu_3SbS_4 with fully coalesced and uniform surface morphology can be obtained for Cu/Sb ~ 1. The EDS analysis tabulated in SI. Table 1 also corroborates with XRD results. Similarly, the sulfurization time was optimized by sulfurizing the thin films with 1:1 Cu:Sb metal ratio for 30,60, 90 minutes. The structural properties of the sulfurized thin films for different dwell time is shown in Fig. SI 2. For samples sulfurized for 30 minutes shows the presence CuS impurity phase. Similarly, for samples sulfurized for longer time i.e. 90 minutes a reduction in crystallite size was observed. From the results it was concluded that for the sulfurization time of 60 minutes was optimum for obtaining phase-pure Cu_3SbS_4 thin films.

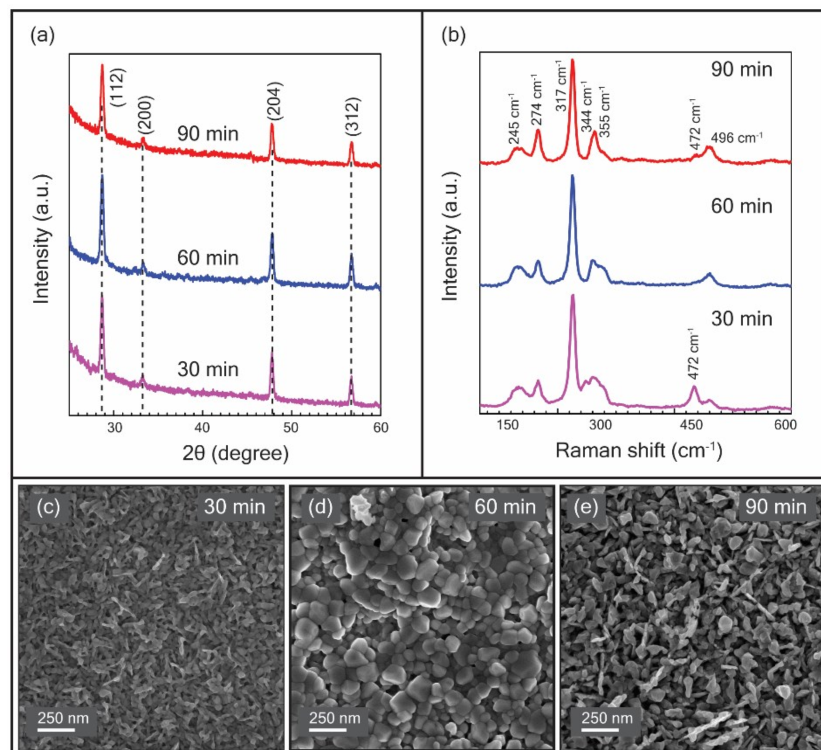

Fig. SI 3: (a) GIXRD pattern (b) Raman spectra and [(d), (e), (f]) Surface morphology of Cu_3SbS_4 thin films sulfurized with different sulfurization times.

3. **Spectroscopic Ellipsometry (SE) data of optimized Cu_3SbS_4 thin films**

The experimental and fitted data for Δ and Ψ as a function of energy, measured for different angle of incidence are shown in Fig. SI 3.

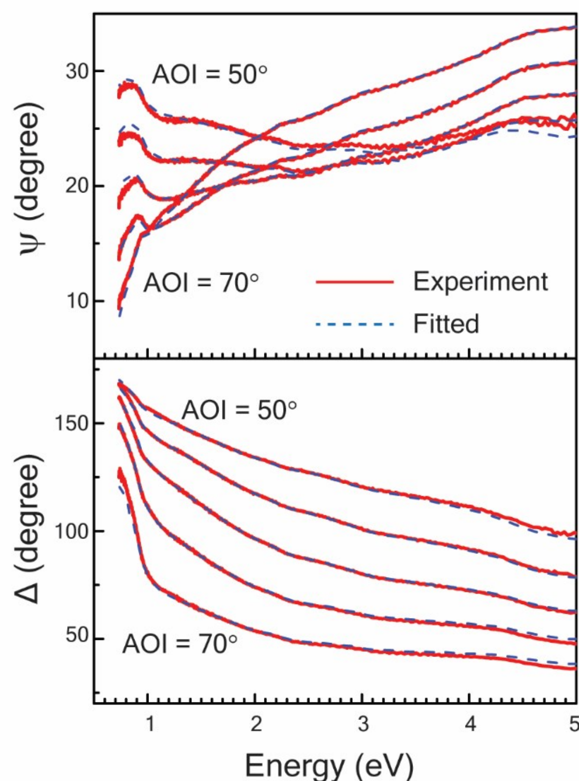

Fig. SI 4: Spectral magnitude (Ψ) and phase (Δ), measured by variable angle spectroscopic ellipsometry at 50°-70° on the Cu_3SbS_4 thin films grown at a temperature of 425 ℃. Solid colored lines: measured spectra. Dashed lines: fitted spectra.

4. **Tauc plot calculated from transmission and reflectance spectra for Cu_3SbS_4 thin films sulfurized at different temperatures.**

The optical absorption coefficient (α_λ) is calculated from transmission and reflectance spectra measured by UV-VIS-NIR spectroscopy. Fig. SI 5 shows the direct optical bandgap of the thin films sulfurized at different temperatures. The values of these films are found to be in the range of 0.88 – 0.9 eV. The slight variation in the bandgap of these films might be due to the change in composition or crystallinity influenced by sulfurization temperature.

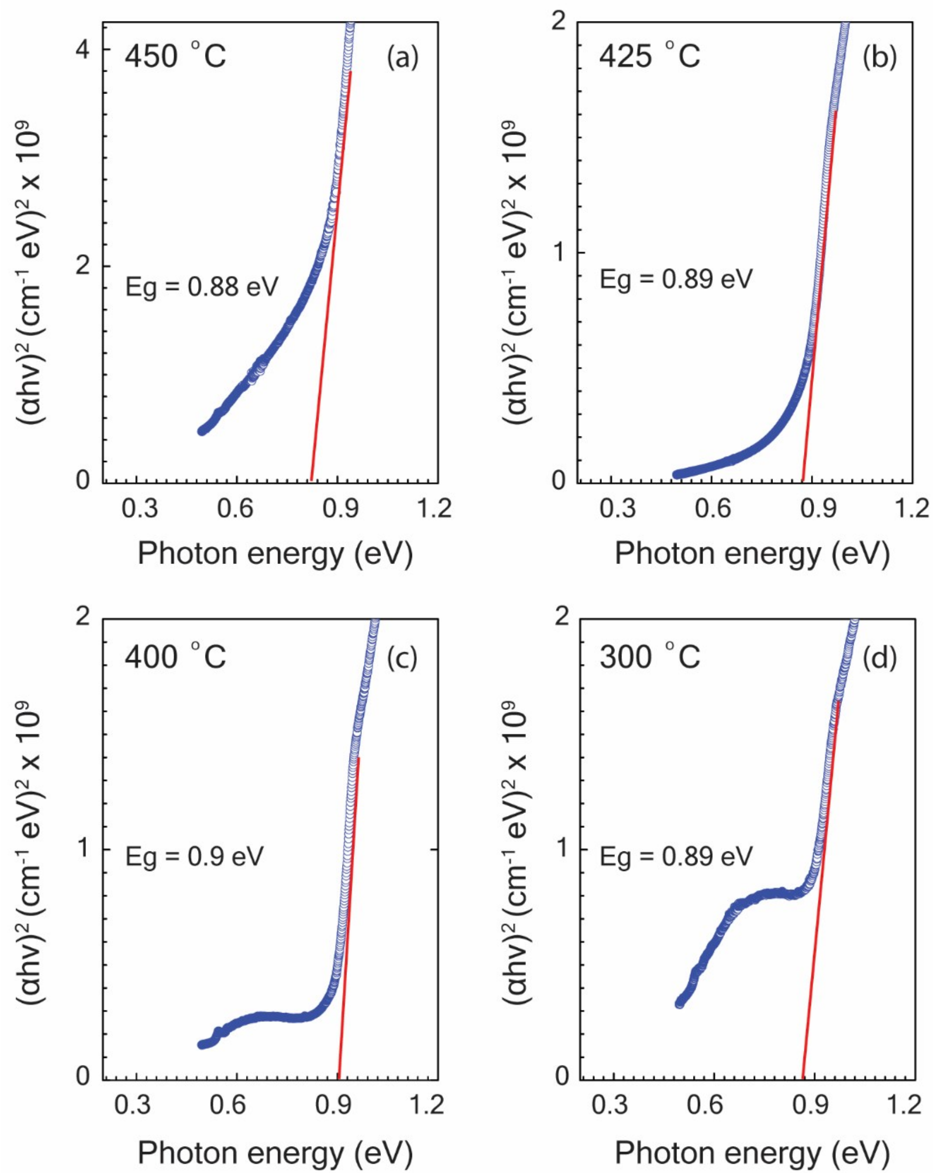

Fig. SI 5: $(\alpha h\upsilon)^2$ versus hυ plots of Cu_3SbS_4 thin films prepared by sulfurizing at temperatures (a) 450 ℃ (b) 425 ℃ (c) 400 ℃ (d) 300 ℃.