

Formation Mechanism of Voids and Pin-holes in CuSbS₂ Thin Film via Sulfurizing Co-sputtered Cu-Sb Precursor

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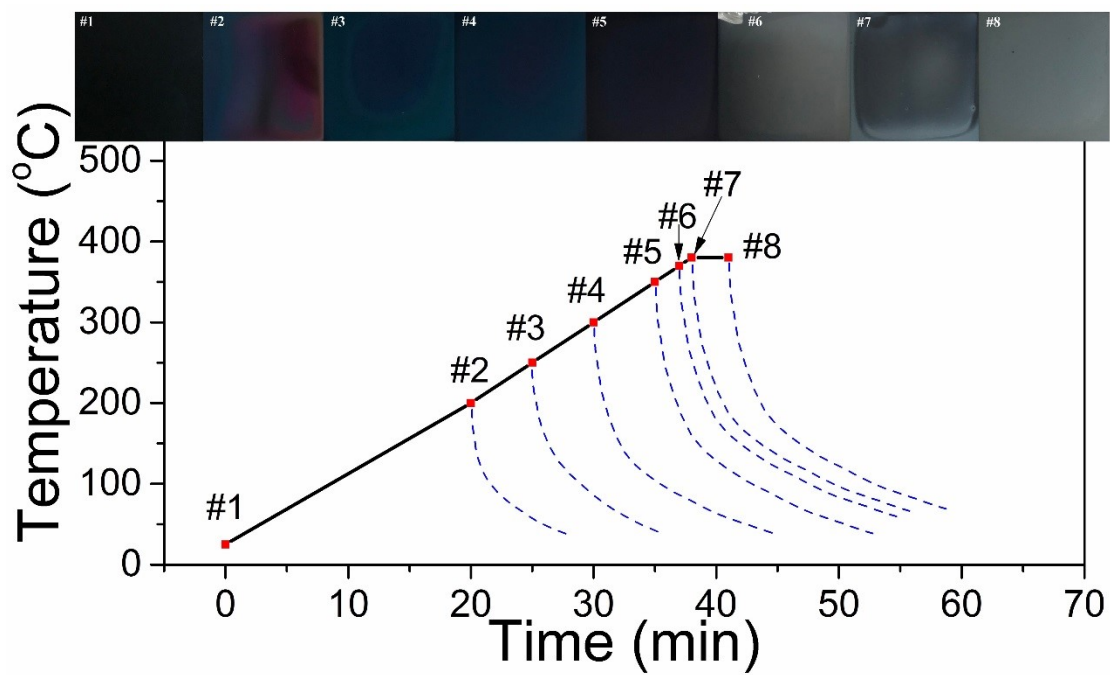


Fig S1 Temperature profiling of sulfurization process and photographs of samples as indicated on temperature profiling.

Table S1 Summary of phase evolution of Cu-Sb co-sputtering precursor after being sulfurized at a series of temperatures and times.

| Samples | Compositions | PDF Cards # |
|----------------|--------------------------------|--------------------|
| Precursor | Cu | 01-070-3038 |
| | Cu ₂ Sb | 01-085-0492 |
| | Sb | 01-085-1322 |
| 200 °C | Cu | 01-070-3038 |
| | Cu ₂ S | 00-002-1284 |
| | Cu ₂ Sb | 01-085-0492 |
| | Sb | 01-085-1322 |
| 250 °C | CuS | 00-024-0060 |
| | Sb | 01-085-1322 |
| 300 °C | CuS | 00-024-0060 |
| | Sb ₂ S ₃ | 01-075-1310 |
| | Sb | 01-085-1322 |
| 350 °C | CuS | 00-024-0060 |
| | Sb ₂ S ₃ | 01-075-1310 |
| | Sb | 01-085-1322 |
| 370 °C | CuS | 00-024-0060 |
| | CuSbS ₂ | 03-065-2416 |
| | Sb ₂ S ₃ | 01-075-1310 |
| 380 °C | CuSbS ₂ | 03-065-2416 |
| | Sb ₂ S ₃ | 01-075-1310 |
| 380 °C-3min | CuSbS ₂ | 03-065-2416 |
| | Sb ₂ S ₃ | 01-075-1310 |

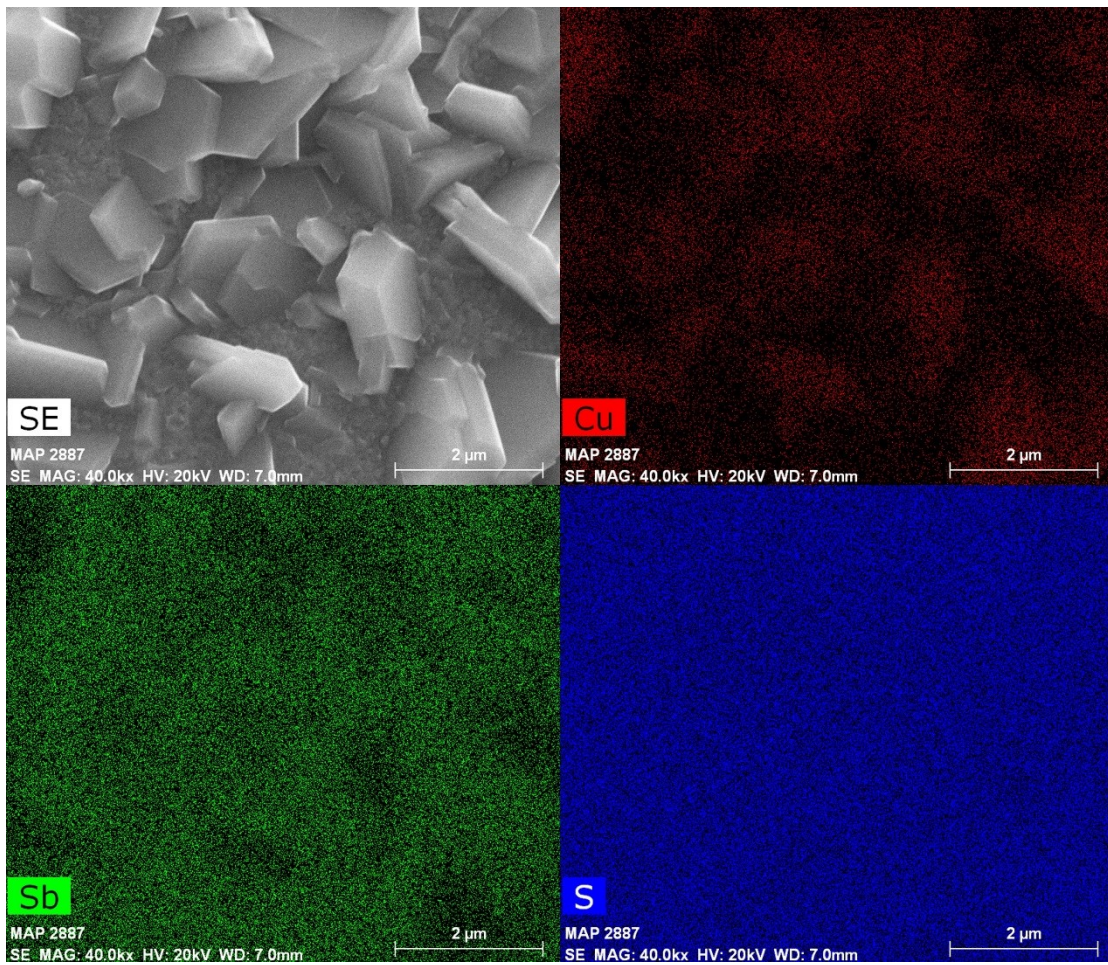


Fig S2 SEM and corresponding EDS mapping images of Cu-Sb precursor after sulfurization treatment at 350 °C followed by rapid cooling.

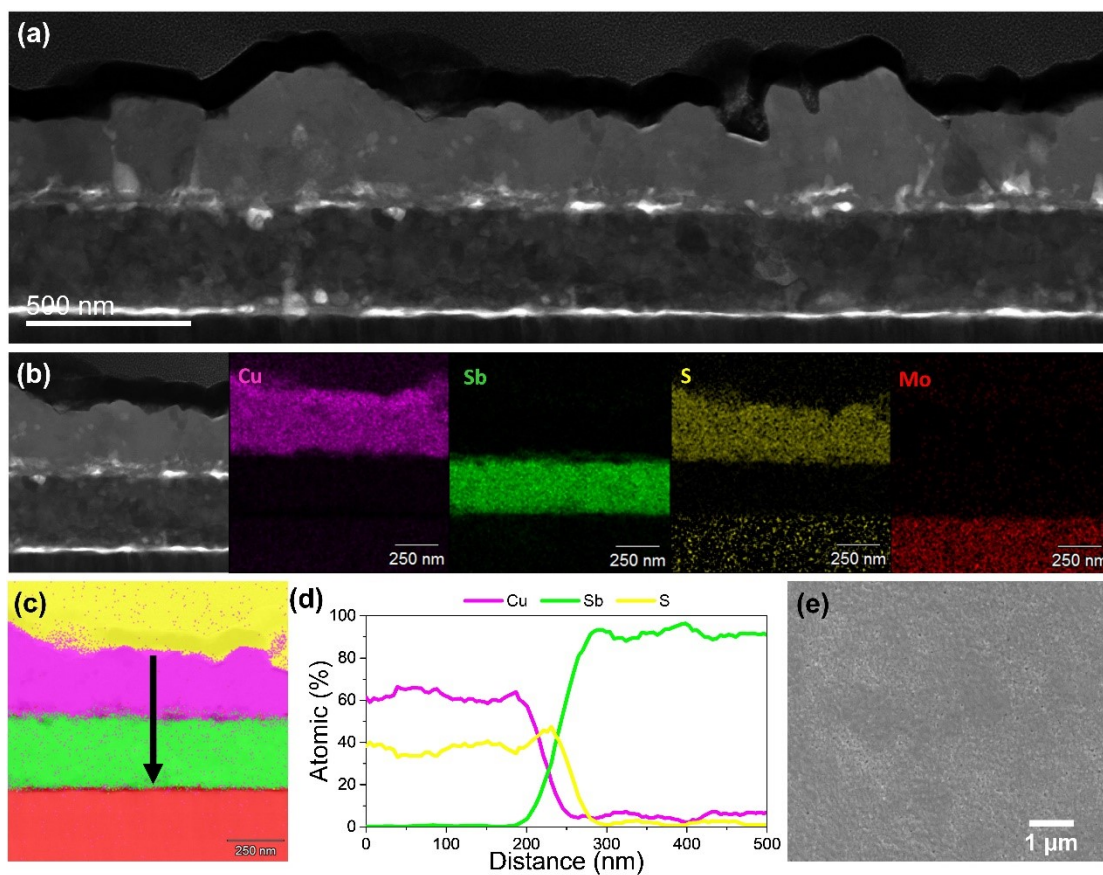
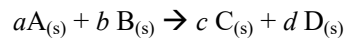


Fig S3 Microscopy analysis of Cu-Sb precursor after sulfurization treatment at 250 °C followed by rapid cooling, (a) cross-section TEM image, (b) STEM-EDS mapping, (c) phases mapping, (d) STEM-EDS line scan as arrow marked in (c), (e) SEM image of exfoliated backside surface.



Fig. S4 Schematic diagram of the thin film morphology and the corresponding Pillings-Bedworth ratio.

For a general solid reaction,



the PB_{ratio} can then be expressed as

$$PB_{\text{ratio}} = \frac{\sum_i v_i [M_i / \rho_i]_{\text{product}}}{\sum_i v_i [M_i / \rho_i]_{\text{reactant}}}$$

where i denotes the compound, v_i is the stoichiometric coefficient of i , M_i represents the molar mass of i in (g/mol), and ρ_i is the density of i in (g/cm³).

Table S2 Densities and molar masses for the various elements and compounds, as well as the Pillings-Bedworth ratios calculated for the given reactions.

| | ρ (g/cm ³) | M (g/mol) | Reaction | PB-ratio |
|--------------------------------|-----------------------------|-----------|--|----------|
| Cu | 8.96 | 63.546 | | |
| Sb | 6.697 | 121.76 | | |
| S | 2.07 | 32.066 | | |
| Cu ₂ S | 5.6 | 159.158 | $2\text{Cu} + \text{S}(\text{g}) \rightarrow \text{Cu}_2\text{S}$ | 2.00 |
| CuS | 4.76 | 95.611 | $\text{Cu} + \text{S}(\text{g}) \rightarrow \text{CuS}$ | 2.83 |
| Sb ₂ S ₃ | 4.562 | 339.715 | $2\text{Sb} + 3\text{S}(\text{g}) \rightarrow \text{Sb}_2\text{S}_3$ | 2.05 |
| CuSbS ₂ | 4.87 | 249.43 | $2\text{CuS} + \text{Sb}_2\text{S}_3 \rightarrow 2\text{CuSbS}_2 + \text{S}(\text{g})$ | 0.89 |
| | | | $2\text{Cu} + \text{Sb}_2\text{S}_3 \rightarrow 2\text{CuSbS}_2$ | 1.16 |
| | | | $\text{Cu}_2\text{S} + \text{Sb}_2\text{S}_3 \rightarrow 2\text{CuSbS}_2$ | 1 |

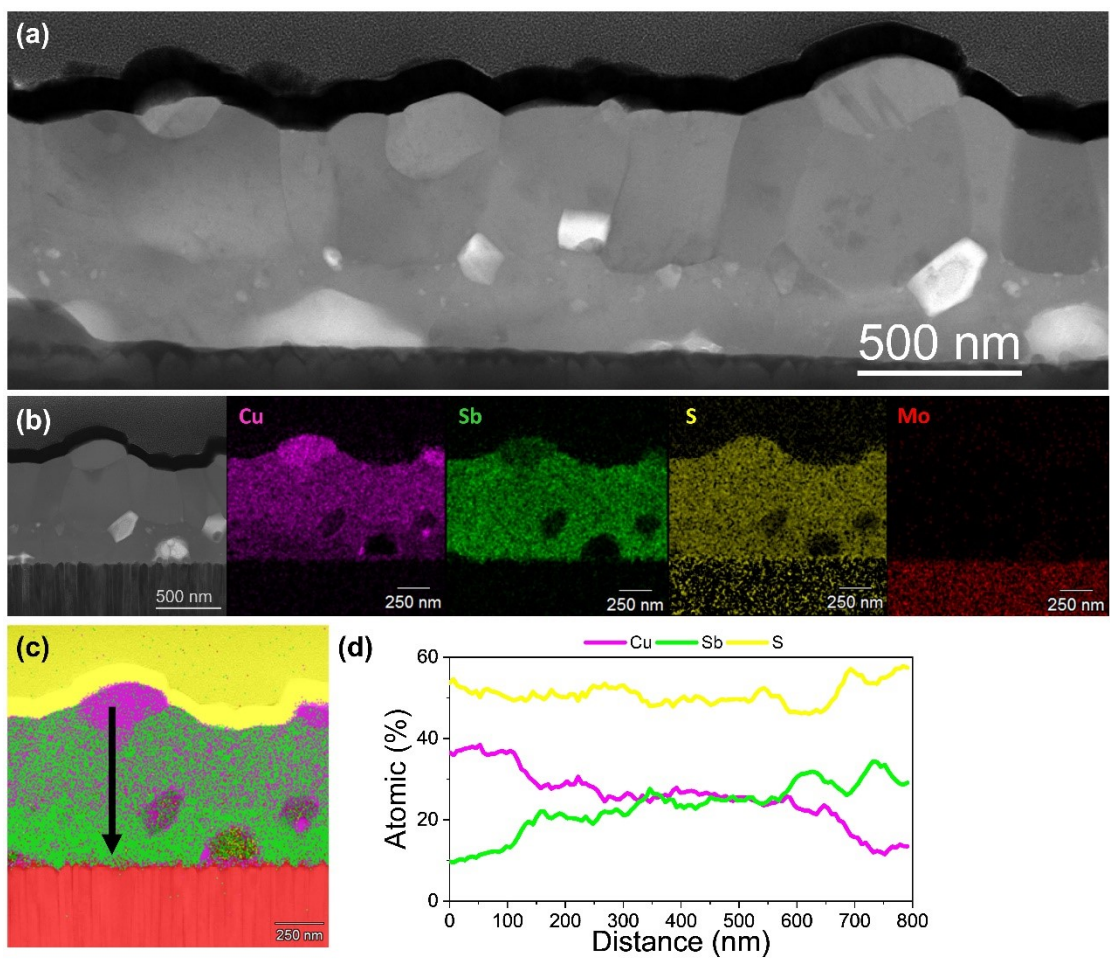


Fig S5 Microscopy analysis of Cu-Sb precursor after sulfurization treatment at 380 °C followed by rapid cooling, (a) cross-section TEM image, (b) STEM-EDS mapping, (c) phases mapping, (d) STEM-EDS line scan as arrow marked in (c).

Table S3 Composition changes of CuSbS₂ thin films subjected to different sulfurization treatments measured by ICP.

| Sample ID | Cu/Sb | Sb loss (%) |
|--------------------|--------------|--------------------|
| precursor | 0.889 | N/A |
| 350 °C | 0.896 | 0.713 |
| 380 °C | 0.904 | 1.630 |
| 380 °C-3min | 0.906 | 1.796 |