Supporting Information

Low-temperature Atomic Layer Deposition of $CuSbS_2$ for Thin Films Photovoltaics

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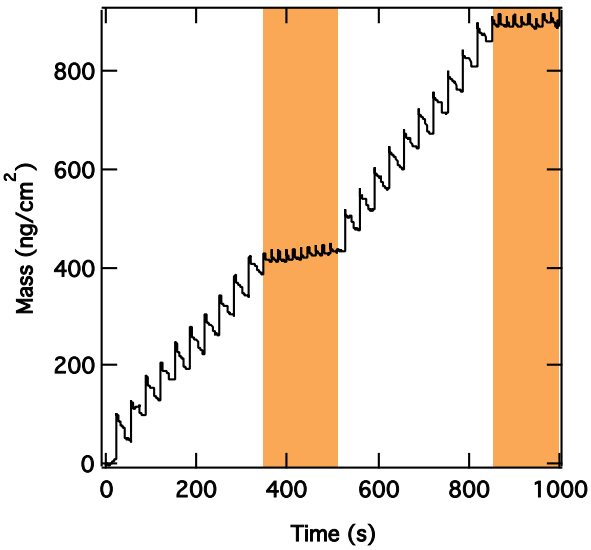

Figure S1. *In situ* QCM analysis of SbTDMA exposure to Cu_2S thin films at a deposition temperature of 150 °C. The orange shaded regions highlight 10 consecutive SbTDMA doses following Cu-S ALD cycling.

Table S1. Elemental analysis from SEM-EDS.

Deposition T (°C)	Cu-S:Sb-S cycle ratio	Post Processing	Atomic % Cu	Atomic % Sb	Atomic % S
160	1:1	n/a	49	9	42
140	1:4	n/a	44	15	41
140	1:9	n/a	38	20	42
100	1:4	n/a	27.5±0.3	24.7±0.5	47.8±0.7
100	1:4	Annealed 225 °C for 15 min	32.3±2.2	21.3±1.1	46.4±1.3
100	1:9	n/a	23.4±5.0	24.8±1.8	51.8±5.9
100	1:9	Annealed 225 °C for 15 min	21.6±3.8	23.9±1.4	54.5±4.4

The atomic % for each element does not take into account an attenuation correction factor. Assuming a film thickness of 100 nm, we would expect 2% attenuation for Cu, 3-9% attenuation for Sb, and 10% attenuation for S. Therefore, the atomic % values shown for Sb and S are likely lower than the actual amount in the film.

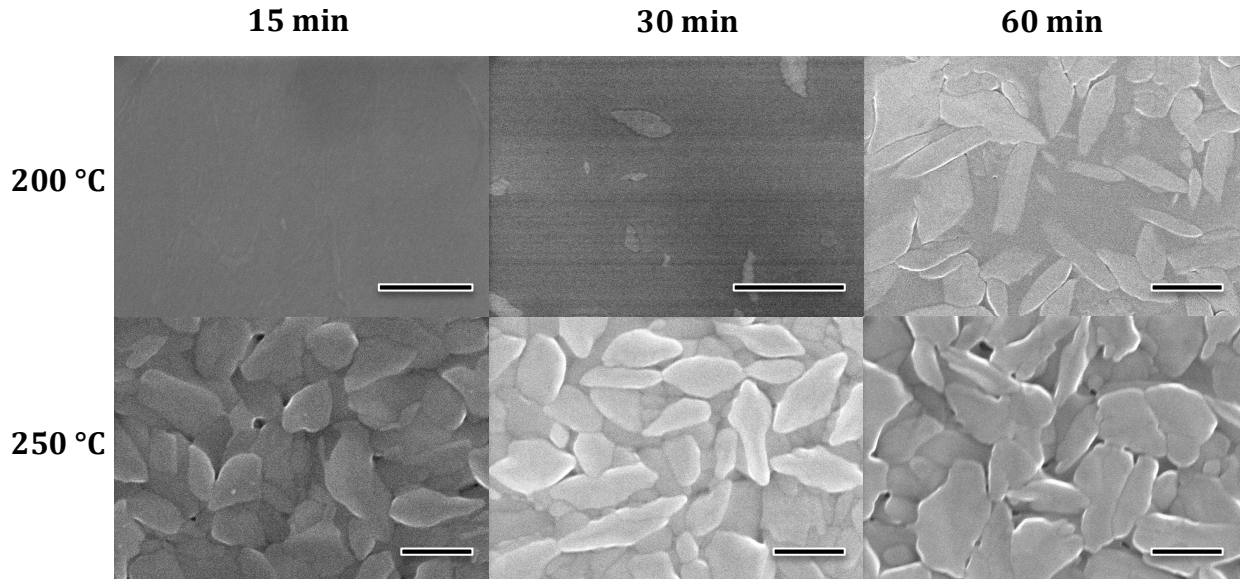

Figure S2. SEM images of $CuSbS_2$ thin films annealed at 200 or 250 °C for a period of 15, 30, or 60 minutes in the ALD chamber. (Temperatures above 250 °C were not investigated due to the temperature limitations of the gasket joining the ALD and N_2 glove box.) Crystallization, while minimal, first appeared after 30 minutes at 200 °C. With prolonged annealing at 200 °C, the film further crystallized, producing large oblong-shaped grains. At 250 °C, large grains were observed after only 15 minutes, and longer annealing times at 250 °C did not result in an increase in the grain area. In some instances, film delamination near the edges resulted when annealing at 250 °C for any period of time. The grain areas were found to be similar for the films annealed at 225 °C for 15 min (image in main text) and the films annealed at 250 °C, however, the films annealed at 225 °C did not show signs of delamination. Therefore, an annealing temperature of 225 °C was chosen for the remainder of the study. While this temperature is rather low, it is not unreasonable given the film thickness and low decomposition temperature (>400 °C) of this material.[1] In fact, Rabhi, et al. reported 130-280 nm thick $CuSbS_2$ films crystallized at 200 °C after a 2 h vacuum anneal.[2] On the other hand, when forming $CuSbS_2$ films from metal stacks followed by sulfurization, or Cu/Sb_2S_3 stacks, annealing temperatures of 300-400 °C are often reported.[3-5] However, Yang, et al. determined that $CuSbS_2$ could form at temperatures as low as 200-220 °C when starting with molecular precursors.[1]

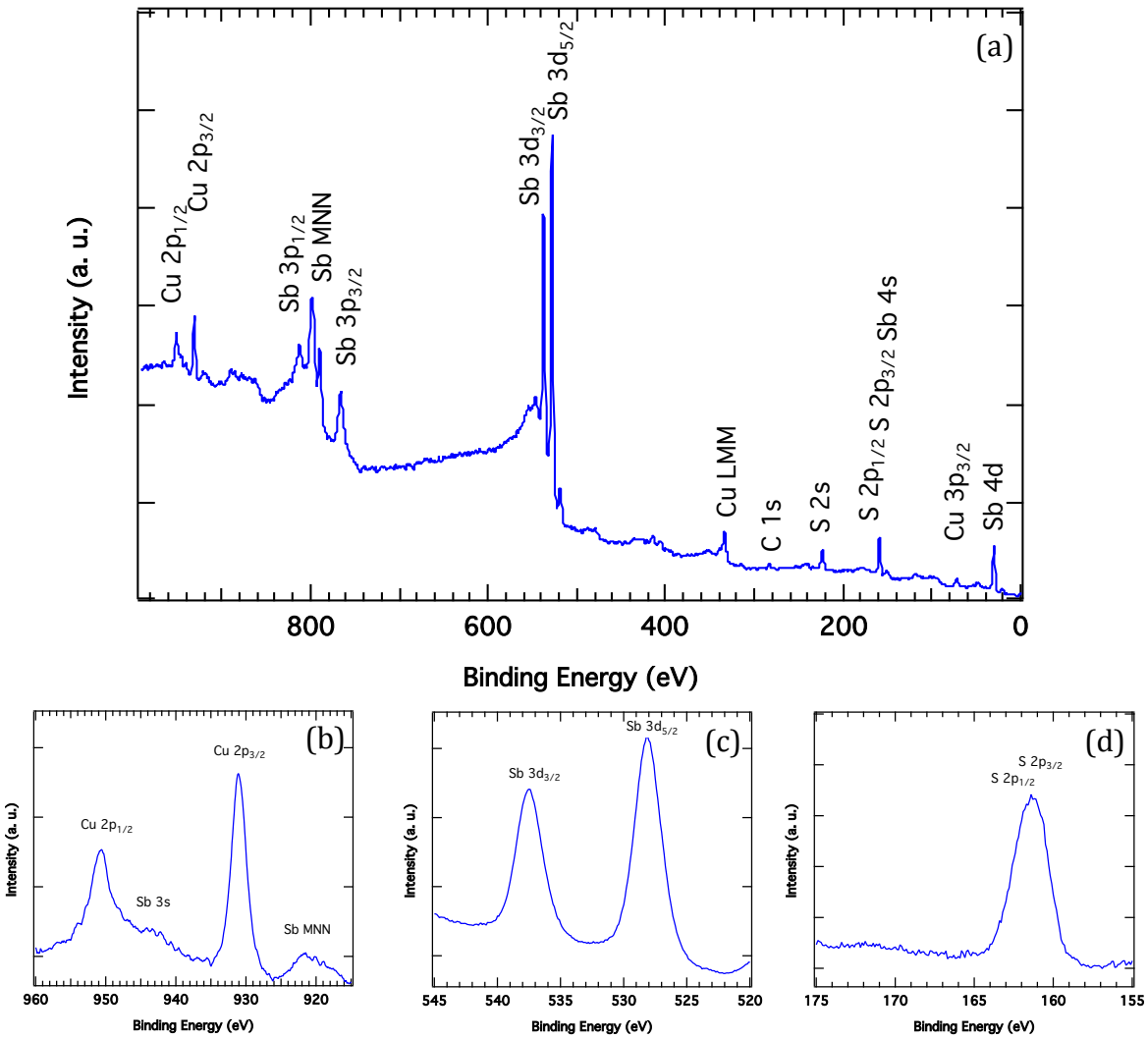

Figure S3. (a) XPS survey scan for an ALD-grown $CuSbS_2$ thin film. High resolution scans of the (b) Cu 2p, (c) Sb 3d, and (d) S 2p regions were used to determine the valence state of the elements in the $CuSbS_2$ films.

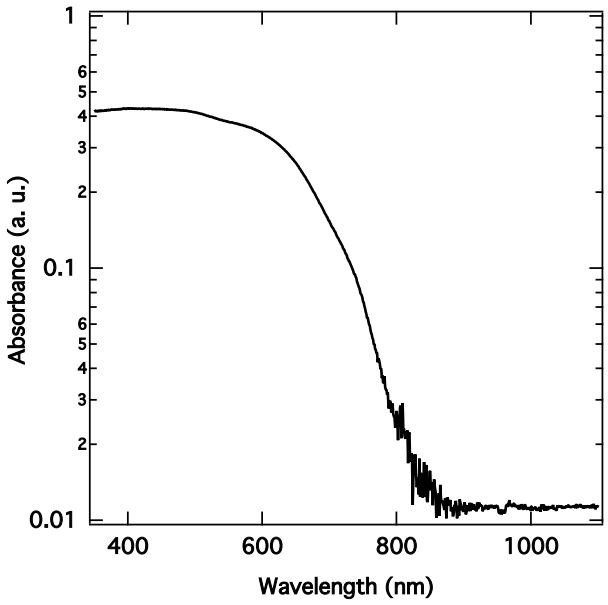

Figure S4. UV-vis-NIR spectrum (log scale) for an 80 nm $CuSbS_2$ thin film deposited at 100 °C and post-annealed at 225 °C for 15 minutes. The absence of sub-band gap absorption suggests conductive impurities—$Cu_{2-x}S$ or $Cu_{12}Sb_4S_{13}$—are not present in the thin film.

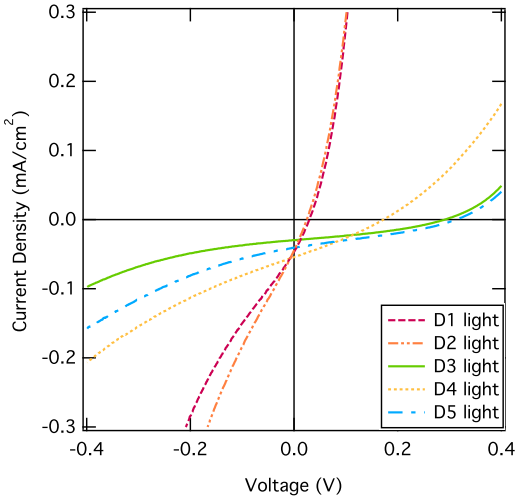

Figure S5. J-V curves for $CuSbS_2$ thin film devices under illumination. For clarity the dark J-V scans have been omitted.

1. Yang, B.; Wang, L.; Han, J.; Zhou, Y.; Song, H.; Chen, S.; Zhong, J.; Lv, L.; Niu, D.; Tang, J., $CuSbS_2$ as a Promising Earth-Abundant Photovoltaic Absorber Material: A Combined Theoretical and Experimental Study. *Chem. Mater.* **2014**, *26*, 3135-3143.

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5. Garza, C.; Shaji, S.; Arato, A.; Tijerina, E. P.; Castillo, G. A.; Das Roy, T. K.; Krishnan, B., P-Type $CuSbS_2$ Thin Films by Thermal Diffusion of Copper into Sb_2S_3. *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 2001-2005.