Supporting Information

Real-time Atomic Scale Observation of Void Formation and Anisotropic Growth in II-VI Semiconducting Ribbons

Xing Huang,[†,*] Travis Jones,[†] Hua Fan,[†] and Marc-Georg Willinger[‡,*]

[†]Department of Inorganic Chemistry, Fritz-Haber Institute of Max-Planck Society, Faradayweg 4-6, 14195, Berlin, Germany.

[‡]Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Research Campus Golm, 14424, Potsdam, Germany.

Keywords: In-situ TEM, void anisotropic growth, thermodynamics, surface energy, morphological transformation, ZnS ribbon

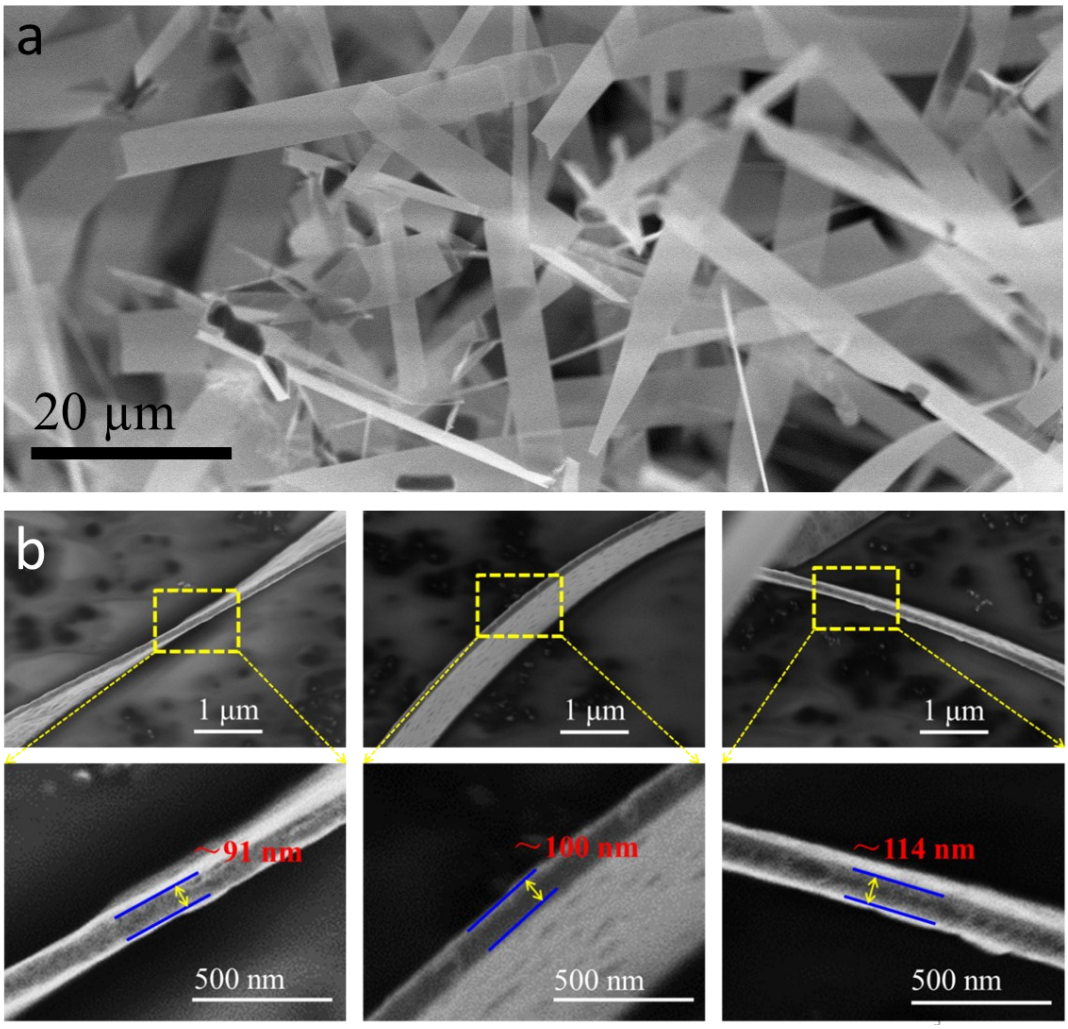


Figure S1. (a) SEM image of as-prepared ZnS ribbons at low magnification; (b) Cross-section SEM images of ZnS ribbons recorded at relatively high magnification.

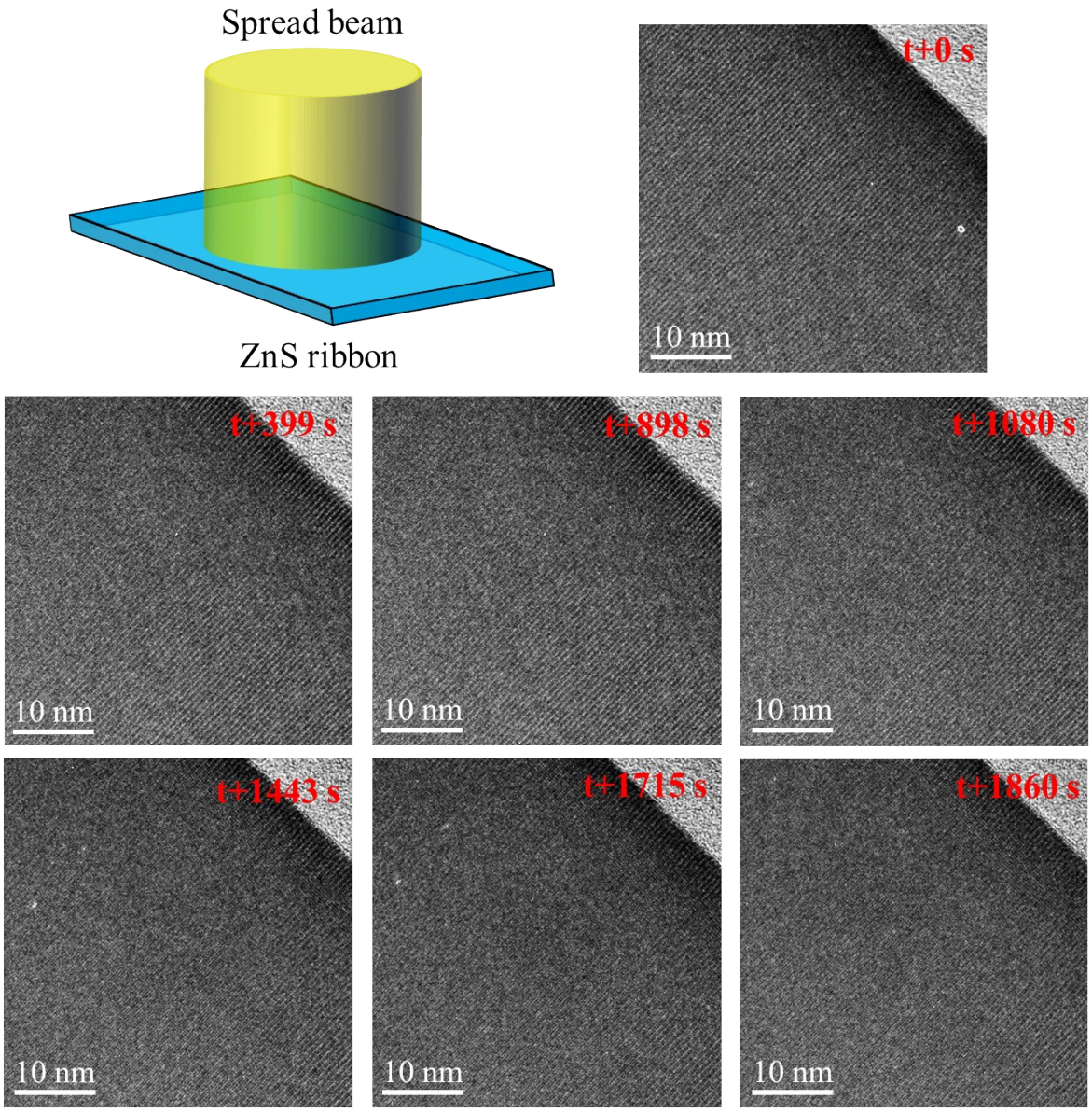


Figure S2. Schematic drawing of electron beam illumination and sequences of HRTEM images recorded during real-time observation of ZnS ribbon upon annealing at 600 °C under a dose rate of 1.3×10^5 e/nm^{2}s. The ribbon is relatively stable upon heating and irradiation of spread electron beam.

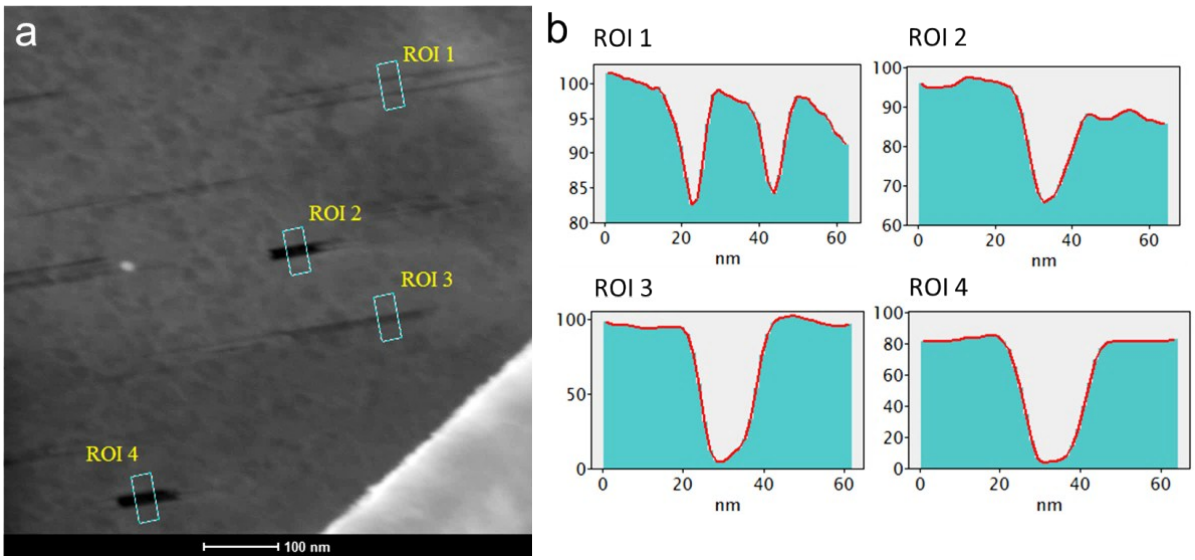


Figure S3. (a) High angle annular dark field scanning TEM (HAADF-STEM) image of a ZnS ribbon with voids pre-formed under irradiation of electron beam in TEM mode at 600-700°C under an electron dose rate of 11000e/nm^{2}s; (b) Intensity profiles of the dotted rectangular regions marked in image (a). The intensity profiles extracted from the marked regions exhibit clear variations of intensity across the voids. Due to the thinner thickness, the regions where voids locate show much lower counts compared to their adjacent regions.

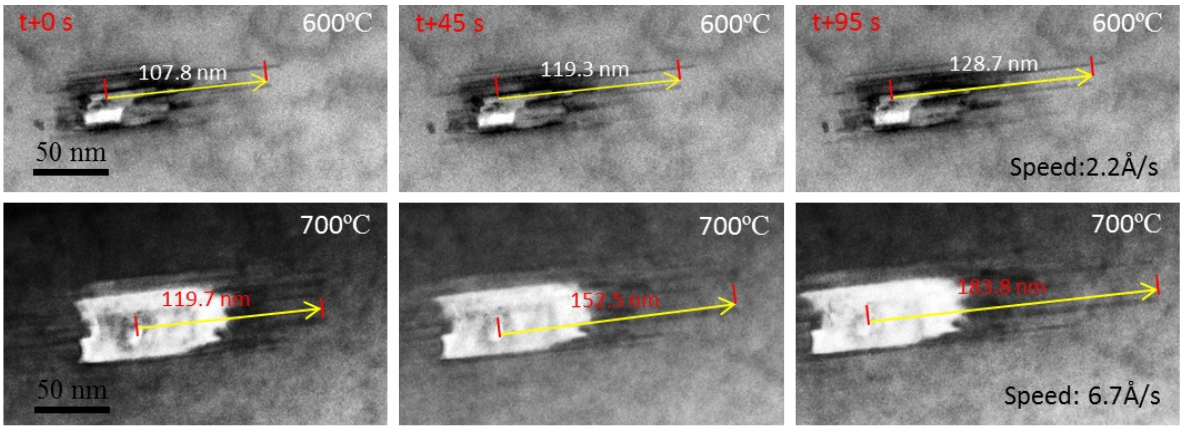


Figure S4. Comparison of the void growth behaviors at 600 and 700°C under an electron dose rate of 11000e/nm^{2}s.

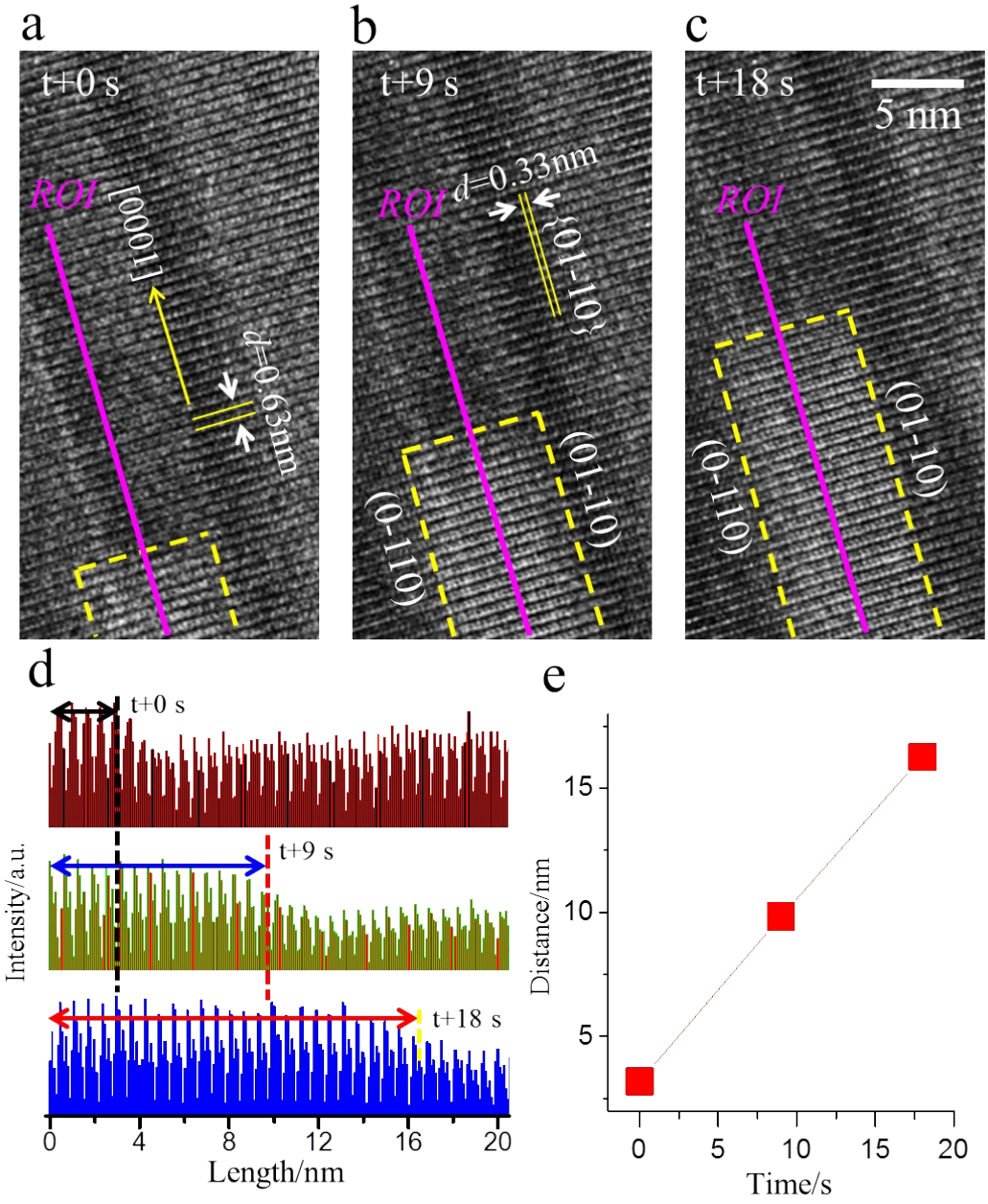
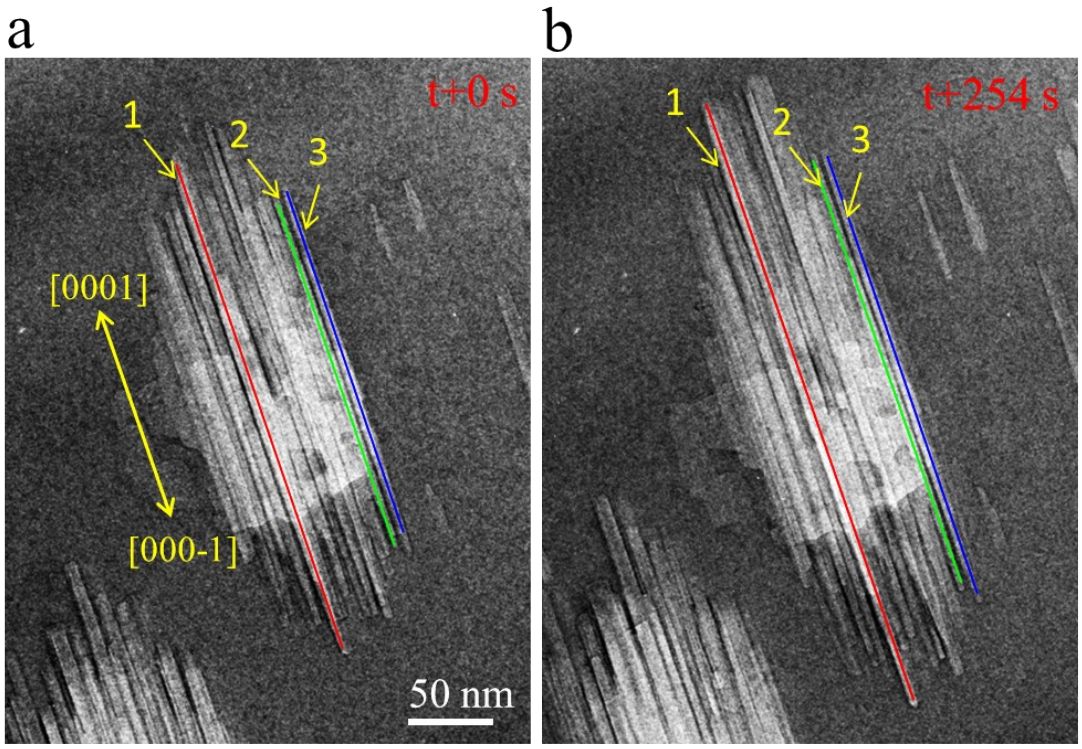


Figure S5. (a-c) Time-resolved HRTEM images recorded during void growth at 600 ºC under an electron dose rate of 1.3×10^5 e/nm^{2}s; (d) Intensity profile of images along the pink line; variation of intensity due to the growth of void is indicated; (e) Grown length of the void as a function of time.



c

Void	Direction	Distance/nm
Void 1	[000-1]	31.77
Void 1	[0001]	35.79
Void 2	[000-1]	29.26
Void 2	[0001]	23.67
Void 3	[000-1]	25.4
Void 3	[0001]	25.66

Figure S6. (a,b) Time-sequence TEM images recorded at 600 ºC under an electron dose rate of 6810e/nm^{2}s, showing the growth of void from both side of voids, *i.e.*, [0001] and [000-1] directions. The voids 1, 2 and 3 are indicated with red, green, and blue lines, respectively; (c) A table, showing the total growth length of void 1, 2 and 3 towards [0001] and [000-1] directions in 254s.

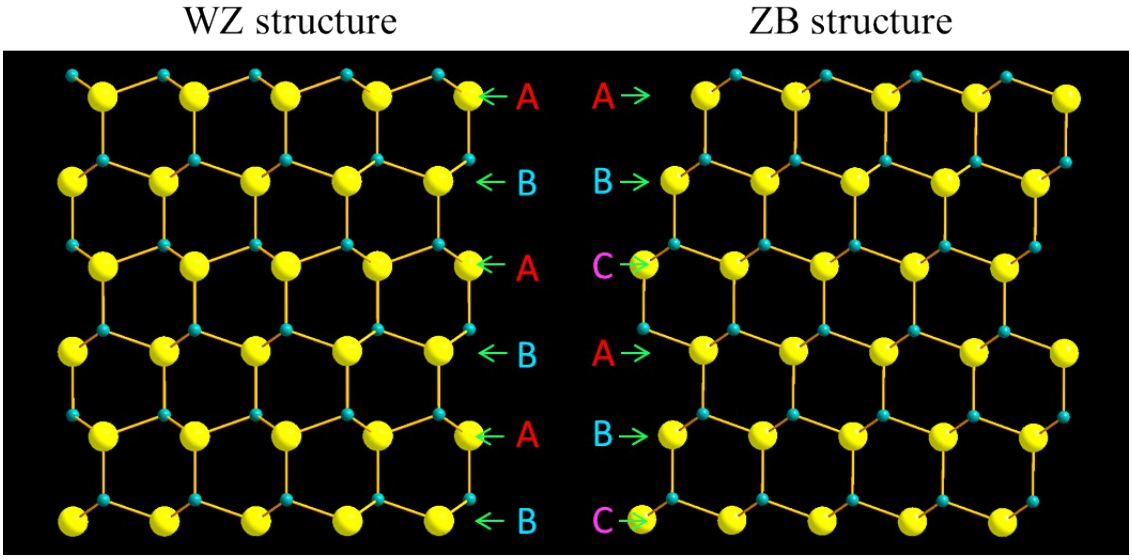


Figure S7. Structural models for WZ and ZB structured ZnS, respectively. WZ ZnS shows a AB stacking along [0001] direction, while ZB ZnS shows a ABC stacking sequence along [111] direction.

Movie M1, Movie M2, and Movie M3

In-situ TEM observation of void anisotropic growth kinetics on WZ ZnS ribbon at 600ºC.

Movie M4

In-situ TEM observation of void oscillatory kinetics involving periodic void growth and shrinkage on WZ ZnS ribbon at 600ºC.

Movie M5

In-situ TEM observation of kinetics of void morphological transformation on WZ-ZB-WZ structured ZnS ribbon at 600ºC.