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MS-14-O-2539 Polarity-Driven Polytypic Branching in Cu-Based Quaternary Chalcogenide Nanostructures

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Copper-based chalcogenide semiconductor nanocrystals are used in a variety of energy-related applications as a result of their suitable optical, electronic and thermoelectric properties.[1-4] In particular, ternary and quaternary copper-based chalcogenides offer a broad range of possibilities for morphological, chemical and structural control through chemical routes, thereby providing an opportunity for further functionality enhancement. For example, controlled combination of branching, polytypism, polarity and cation order can be used to nanoengineer the properties of the materials.

Here, a novel way of realizing property nanoengineering in $Cu_2Cd_xSnSe_y$ (CCTSe) polypods is presented. The pivotal role of polarity in determining the morphology, growth, and polytypic branching mechanism of the structure is demonstrated. Polarity is considered to be responsible for the formation of an initial seed, which takes the form of a tetrahedron with four cation-polar facets. Size and shape confinement of the intermediate pentatetrahedral seeds is also attributed to polarity, as their external facets are anion-polar. The final polypod extensions also branch out as a result of a cation-polarity-driven mechanism. Aberration-corrected HAADF-STEM is used to identify stannite cation ordering in this material; and linear STEM image simulations.[5]

Figure 1a shows a STEM micrograph of a CCTSe monopod. The first tetrahedral seed has a stannite structure with tetragonal symmetry (zinc-blende-like, ZB'). Secondary tetrahedra grow on the four facets of the initial one. The nanoparticles then branch out with wurtzite (WZ) structures and form the polypods (polytypic branching). Cation-polarity is maintained along the in the whole structure. However, the surface polarity switches in the secondary tetrahedra in order to retain the cation-polarity along the growth direction.

Aberration-corrected STEM was also used to establish that cation ordering exists in the ZB' stannite region, while the cations (Cu, Cd, and Sn) are distributed randomly in the WZ branches, as shown in Fig. 2.

References

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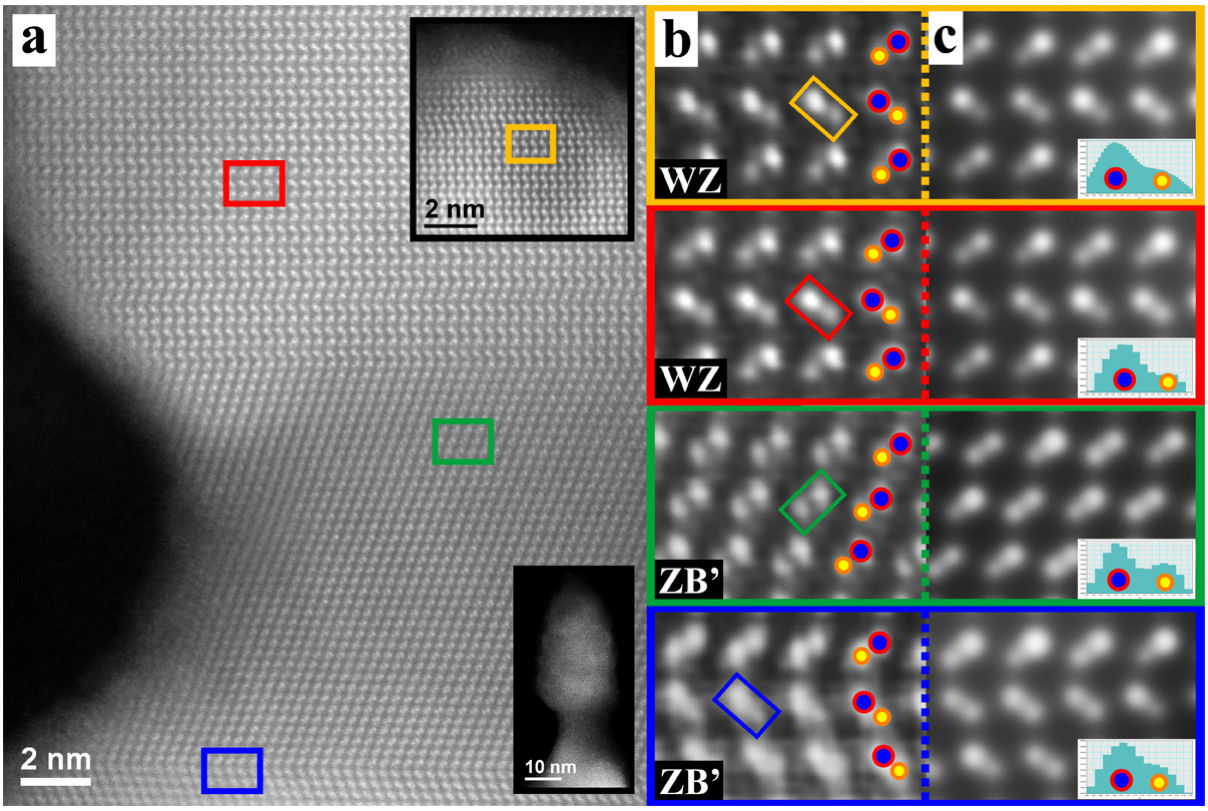

Fig. 1: Polarity measurement in a CCTSe monopod: (a) HAADF-STEM image along $[201]_{ZB'}=[11\text{-}20]_{WZ}$ zone axis; (b) magnified region indicated on image (a) by colored rectangles after deconvolution of the STEM probe shape; (c) linear simulations of the STEM images shown in (b); (d) intensity profiles measured from single dumbbell units (indicated on images (b)).

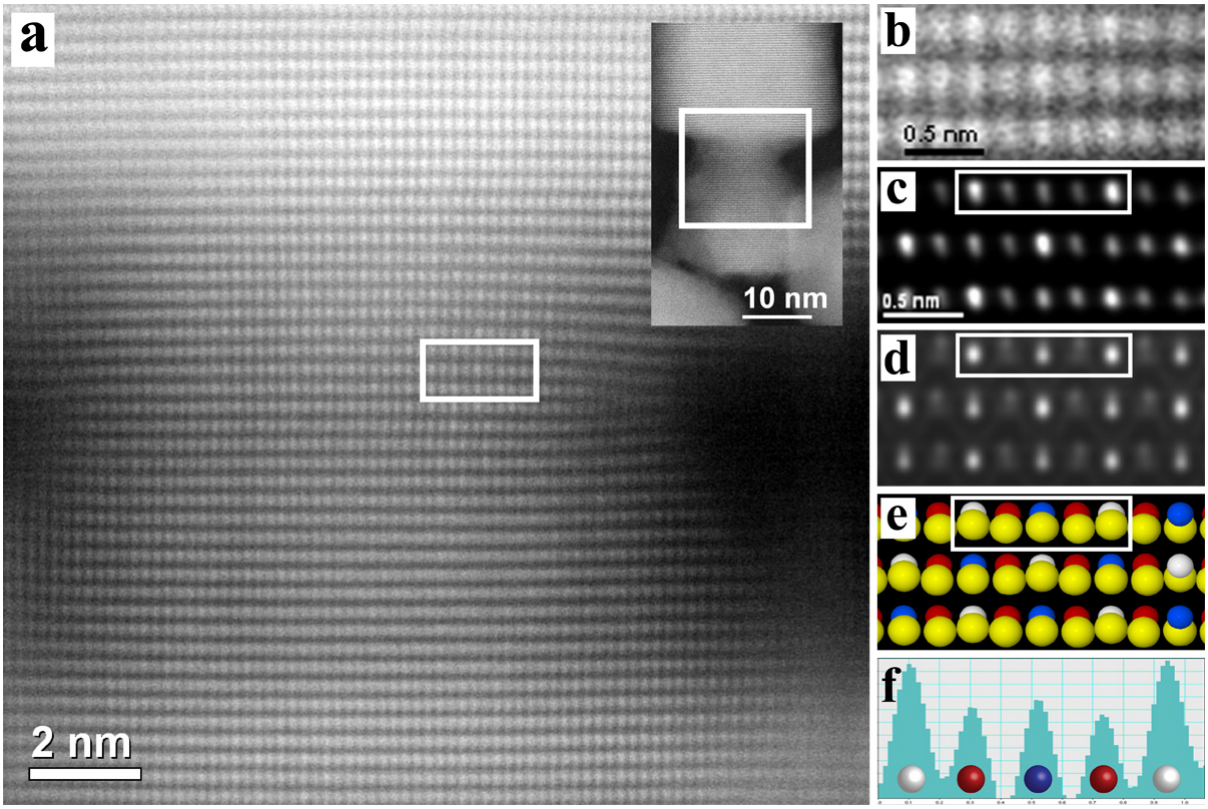

Fig. 2: (a) Atomic-resolution HAADF-STEM image acquired along the $[111]_{ZB'}$ zone axis of tetragonal (ZB') CCTSe (b) deconvolved, and (c) filtered part of the image (a); (d) corresponding linear simulation. (e) 3D atomic model illustrating the ordering effect; (f) intensity profile taken from image (c).