Analysis of crystal twining in thin-film kesterite semiconductors by atomic resolution transmission electron microscopy

Xie, L.[1], Park, J.[2], Giraldo, S.[3], Saucedo, E.[3], Walsh, A.[2] and Leifer, K.[1]

[1] Uppsala University, Sweden, [2] Thomas Young Centre and Department of Materials, Imperial College London, United Kingdom, [3] Catalonia Institute for Energy Research (IREC), University of Barcelona, Spain

Interest in $Cu_2ZnSn(S,Se)_4$ (CZTSSe) based solar cells has begun to increase rapidly. Compared with the $Cu(In,Ga)(S,Se)_2$ (CIGS) absorbers, CZTSSe is highly competitive due to the use of earth abundant, cheap and low-toxicity elements. However, the CZTSSe system is currently less mature than CIGS. Chemical and structural inhomogeneities in CZTSSe lead to a reduction in the open-circuit voltage of the system.[1] This gives motivation for the further development and optimization of CZTSSe based technologies to improve the energy conversion efficiency. A full understanding of structural and chemical properties requires a characterization technique capable of spatially resolving the chemical compositions and structures in nanometer resolution. Aberration-corrected transmission electron microscopy (TEM) has the capability of accomplishing these analysis tasks.

Antisite domain boundaries (ADBs) are formed abundantly in the CZTS nanocrystals.[2] The formation of such ADBs was explained by the sintering process with small CZTS grains and the changes in stoichiometry at the surface of the CZTS nanocrystals. Whether these types of defects can further propagate in the thin CZTS absorber layer remains unclear.
Here, we studied the stacking faults (SFs) formed in CZTS thin films. In the STEM-HAADF imaging mode, we oriented one CZTS grain (~ 450 nm) into [110] zone axis and there are dots like contrasts in the STEM-HAADF image at atomic resolution (Figure 1). The dots that are showing brighter contrast indicate those atomic columns that contain Sn atoms since Sn has the largest atomic number in CZTS. The lines constructed by the brighter dots are (004) lattice planes. The weaker contrast dots indicate the atomic columns that are without Sn atoms. The dumbbell like structure is the projection of characteristic tetragonal structure in a zinc-blende unit cell along the [110] zone axis.

A sharp twin boundary was observed, changing the stacking order of (112) lattice planes from "ABCABCABC" to "ABCABACBA" as shown in Figure 1. The simulated atomic model (Figure 1B) of such twining grain boundary fits very well with STEM-HAADF image (Figure 1A). On the mirror plane B, the bright dots indicate atomic columns that contain Sn atoms on the (112) lattice plane. The dumbbell is rotated by 106□#176; when the layer B deposited onto the layer A and such a "ABA" SFs forms wurtzite CZTS at the twining interface. First-principle calculations have shown that the formation of such SFs in CZTS can induce a higher conduction band edge, and thus act as electron barriers making electron extraction difficult.[3] Compared to other orientations, the growth of a cubic-hexagonal-cubic twining interface by (112) surfaces is thermodynamically favorable and has a significant lower epitaxial temperature in GaAs or CIGS systems.[4] This could also apply on the CZTS system due to the structural similarities. Consequently, this class of defects could be ubiquitous in the CZTS system. The device performance should be closely connected with the (112) surfaces of the absorber layer. A better understanding of the properties of (112) surfaces and their interaction with the CdS buffer layer present in CZTS solar cells are required.

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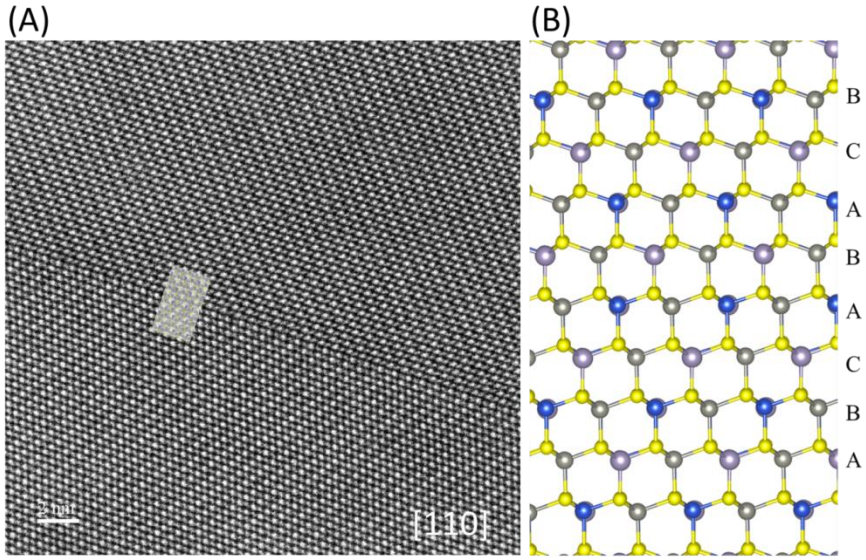

Figure 1. Twin boundary and stacking faults formed in the thin film CZTS absorber layer. (A) STEM-HAADF image of the twining boundary when the CZTS crystal was oriented into [110] zone axis. The inset image is the model of Σ3 (112) grain boundary. (B) A model to show the twin boundary by changing the stacking order of (112) lattice planes. The presented boundary has a stacking order of "ABA" in the middle of the supercell.

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