Structure, Defect Formation, and Design of $CuInSe_2$ Grain Boundaries

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$CuInSe_2$ (CIS) shows a chalcopyrite structure and has a direct energy-gap. CIS has attracted great interest as a material for the photo-absorber layer in thin-film photovoltaic devices because the band gap is tunable by making a solid solution. On the other hand, the CIS is used as a polycrystalline form and thus a lot of GBs are present in the photo absorption layer. However, the effects of GB on the band gap and electronic band bending are still under debate. [1-2]

In this study, we performed a first-principles calculation and a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) to clarify the effect of GB on the band gap and potential barrier at the GB in CIS. Furthermore, we explore the way to design the GB properties of the chalcopyrite materials with an aid of information science.

In STEM observation, a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was used. The accelerating voltage was 200kV and the detection angles were 90-370 mrad. CIS thin film was deposited on MgO (001) substrate using pulsed laser deposition (PLD) method with the substrate temperature of 673K and laser energy was 60 mJ/m^2. The TEM specimen was fabricated using conventional method including gliding, dimpling, and ion-milling. In a first-principles calculation, projector augmented wave (PAW) method was used within a Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation using the Hubbard U correction (GGA+U) implemented in VASP code. The Heyd-Scuseria-Ernzerhof (HSE) hybrid functional scheme was applied in band gap calculations. Hartree-Fock exchange mixing parameters α and screening parameters ω were set to $\alpha = 0.30$ and $\omega = 0.13$.

To obtain the most stable GB structure, rigid body translation of one side of grain as respect to the other side of grain was performed. The step of translation was 1 Å. By the rigid body translation, we found that atomic structure converged to three types of atomic structures. Figure 1 shows HAADF-STEM image of a (112)[110] $\Sigma 3$ twin GB in CIS. Dumbbell structure is clearly observed. From the brightness of those atomic columns, the kinds of the atomic columns can be identified because the intensity of the HAADF image is known to be proportional to the square of the atomic number at

the column. Therefore it is found that the brighter spots which are upper atoms of the dumbbell in the HAADF-STEM image are cation columns and darker ones are Se columns. Moreover, GB was observed and the bondings across the GB are between cation and Se columns. The calculated structure was overplayed on the HAADF-STEM image. It is found that the calculated model is in good agreement with the observed image. We investigated the defect segregation behavior at the GB using the first principles calculation. Furthermore, the way to design the GB properties of chalcopyrite materials was explored based on information science.

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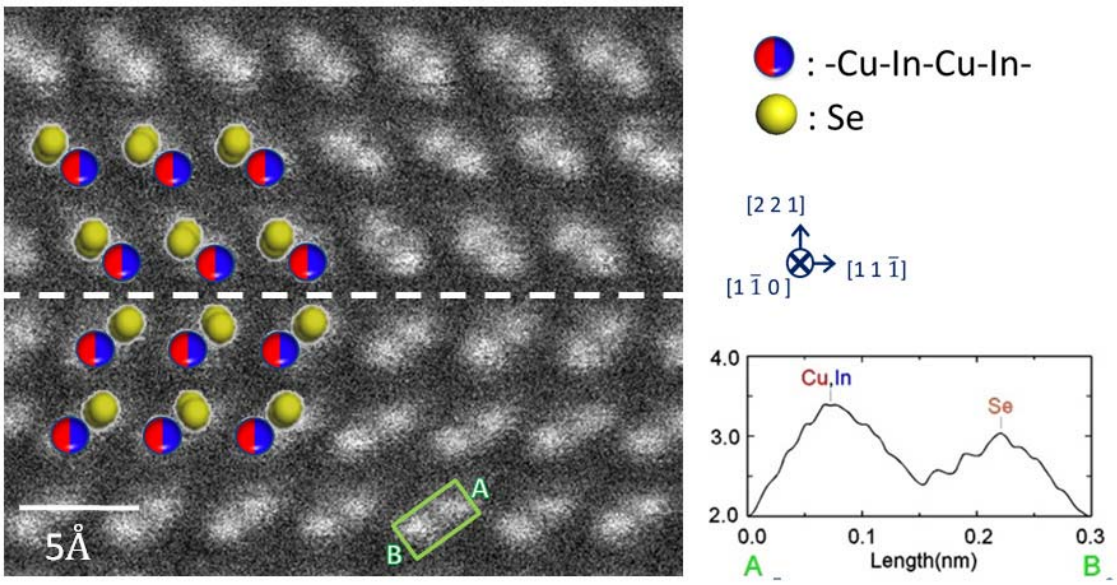

Figure 1 (Left) HAADF-STEM image of $CuInSe_2$ and calculated model. The dotted line represents the position of (112)[110] Σ3 twin GBs. (Right) The intensity profile along points A-B in the HAADF image.