doi:10.1017/S1431927611007215
Microsc. Microanal. 17 (Suppl 2), 2011

Observation of Defects of $CuInSe_2$ by 300 kV Aberration Corrected Scanning Transmission Electron Microscope

T. Tanaka,[1,3] A. Takeshita,[2] T. Kubota,[4] Y. Oshima,[3,5] Y. Tanishiro,[1,3] K. Takayanagi[1,3]

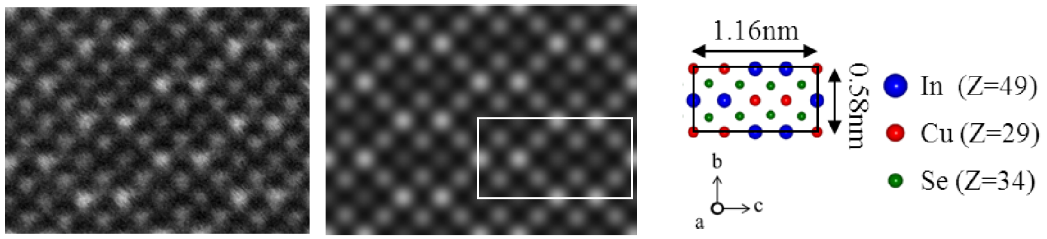
[1] Department of Physics, Tokyo Institute of Technology, 2-12-1-H-51, Oh-okayama, Meguro, Tokyo 152-8551, Japan
[2] Department of Materials Science and Engineering, Tokyo Institute of Technology, 2-12-1-H-51, Oh-okayama, Meguro-ku, Tokyo 152-8551, Japan
[3] Japan Science and Technology Agency, CREST, Chiyoda, Tokyo 102-0075, Japan
[4] Honda R&D Co., Ltd., Wako 351-0113, Japan
[5] Research Center for Ultra HVEM, Osaka University, 7-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

Chalcopyrite crystal, $CuInSe_2$ (CIS), is a key semiconductor for solar cell application. The polarity of CIS was proposed to be originated to fine defects such as an anti-site donor of In substitution of Cu site (In_{Cu}), and an acceptor of Cu vacancy (V_{Cu}) [1, 2]. Recently, not only lateral resolution but also depth of focus of electron microscope has been improved by using the aberration correction technique, which was applied to observation of arsenic (As) dopant in silicon crystal [3] and the cluster structure of antimony (Sb) dopants in the silicon crystal [4]. It is a challenging issue to detect defects in matrices of multiple elements by means of modern high-resolution HAADF-STEM method.

In the present study, the defects of CIS were directly observed by HAADF-STEM, using an R005 microscope equipped with cold field emission gun (Cold FEG) and spherical aberration corrector (Cs corrector) to achieve a sub-50 pm resolution [5]. The atomic columns of In (Z=49), Se (Z=34), and Cu (Z=29) were observed as bright dots as shown in FIG 1(a), and the intensities of defect-free columns were In : Se : Cu = 1.49 : 1.21 : 1.09, where the intensities were normalized by the average intensity of the HAADF image. FIG 2(a) is a HAADF-STEM image of CIS including defects with 33.6 nm in thickness. The atomic arrangement in the unit cell shown by dashed rectangle was different from that in defect-free unit cell shown by solid rectangle in Fig. 2(a). Cu columns including In_{Cu} shown by light blue and blue bars has higher intensities than defect-free Cu columns shown by light-red ones in FIG. 2(c). In columns including Cu_{In} shown by pink and red bars has lower intensities than defect-free In columns shown by purple ones in FIG. 2(d). These defect columns were shown by the corresponding colors in FIG. 2(b). Most of In_{Cu} and Cu_{In} defects were arranged in a place vertical to c-axis of CIS. On the other hands, intensity histogram of Se column, which has symmetric Gaussian distribution as shown in FIG. 2(e), shows that no defects were included in Se column. The intensities of defective In and Cu columns were compared to simulated intensities of defects and the site occupancies of In_{Cu}, V_{Cu}, Cu_{In} and V_{In} were estimated to be 9.0%, 0.1%, 4.9% and 0%.

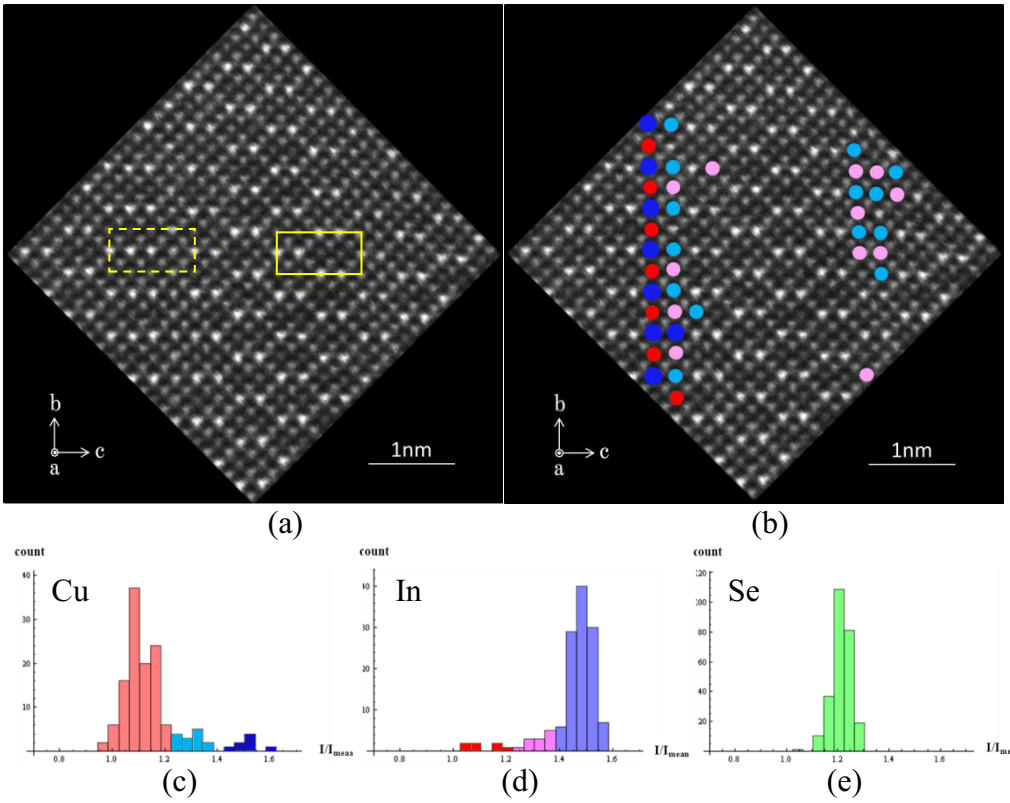
References

[1] A. Zunger, et al., 26 th PVSC, (1997) 313.
[2] S. Lany, et al., Phys. Rev. Lett. **100,** (2008) 016401.
[3] S. Kim, et al. Appl. Phys. Express, **3** (2010) 081301.
[4] Y. Oshima, et al. Phys. Rev. B **81** (2010) 035317.
[5] H. Sawada, et al. J. Elec. Microsc. **58** (2009), 357.



(a) (b) (c)

FIG. 1 (a) HAADF-STEM image of $CuInSe_2$ observed from [100] direction. No defects are observed in (a). (b) Simulated image corresponded to (a). (c) Schematic model in a unit cell of $CuInSe_2$. The unit cell corresponded to (c) are shown by a white rectangle in (b).



(a) (b)

(c) (d) (e)

FIG. 2 (a) The HAADF-STEM image of $CuInSe_2$ observed from [100] directions, 33.6 nm in thickness. Yellow solid and dashed rectangles represent a unit cell in defect-free and defective areas, which corresponds to that of Fig. 1 (c). (b) Color mapping of defect columns in the HAADF-STEM image. (c)-(e) Intensity histogram of intensity of Cu, In and Se columns, respectively. The histogram is count as a function of column intensity. The defect-free intensities of Cu, In, Se are 1.09, 1.49 and 1.21, which are normalized by averaged intensity of the image. No defect of Se column was found and the histogram of Se column is symmetric. The distribution of Cu column is ranged to the intensity of In, which corresponds to that of In_{Cu} described in the text. On the other hand, the intensity of the In column is ranged to that of Cu, which corresponds to that of Cu_{In}.

https://doi.org/10.1017/S1431927611007215 Published online by Cambridge University Press