

## Local structure and electronic structure analyses of S, Se and Li in (Cu,Li)In(S,Se)<sub>2</sub>

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In terms of energy and resource problems, high efficiency thin film solar cells have been much attracted. Especially, Cu(In,Ga)(S,Se)<sub>2</sub> (CIGSSe) is the one of the most promising materials as high efficiency thin film solar cells due to their high light absorption coefficient and adjustable band gap energy ( $E_g$ ) by changing Ga/(In + Ga) and S/(S + Se) ratios. Recently, in order to fabricate CIGSSe solar cells with over 20% conversion efficiency, post deposition treatment of alkali metal compounds (PDT) for CIGSSe thin films is essential. It is reported that the carrier concentration in CIGSSe thin films increases and open circuit voltage for the solar cells is also improved by PDT, resulting in achievement of high-efficiency CIGSSe solar cells. We have investigated the substitution energies and migration energies of some alkali metal elements such as Li, Na and K in CuInSe<sub>2</sub> (CISe) by first principle calculation [1]. Substitution energy of Li for Cu in CISe is much lower than those of the other two alkali metal elements (Na and K). Furthermore, we have investigated the optical properties and crystal structure of Li doped CuIn(S,Se)<sub>2</sub> (CISSe), (Cu,Li)In(S,Se)<sub>2</sub> [2,3]. A certain amount of Li can be incorporated into Cu site in CISSe, and the amount for Li substitution in CISSe changes depending on S/(S + Se) ratio. The incorporation of Li into the structure of CISSe changes the band gap energy,  $E_g$  of CISSe. The  $E_g$  is affected by the level of valence band maximum (VBM) and conduction band minimum (CBM), which are drastically influenced by local structure of (Cu,Li)In(S,Se)<sub>2</sub>. Then, in this work, we investigated the local structure of Li, S, and Se in (Cu,Li)In(S,Se)<sub>2</sub> by using X-ray absorption fine structure (XAFS).

(Cu,Li)In(S,Se)<sub>2</sub> samples were prepared by a mechanochemical process and subsequent heating. Each elemental powder (Cu, In, S, Se, and Li<sub>2</sub>S) were weighed to objective composition, and subsequently mixed by using planetary ball milling under N<sub>2</sub> atmosphere (1000 rpm, 5 h). The mixed powders were heated under N<sub>2</sub> atmosphere at 550 °C for 30 min. XAFS measurement for obtained (Cu,Li)In(S,Se)<sub>2</sub> powders were carried out at BL-10 of the SR center (Ritsumeikan Univ.) for Se L<sub>3</sub>-edge and S K-edge and BL-2 of the SR center for Li K-edge. XAFS spectra for Se L<sub>3</sub>-edge and S K-edge were recorded in a total electron yield (TEY) method and partial fluorescence yield (PFY) method. XAFS spectra

for Li K-edge were recorded in a TEY method.

In S K-edge X-ray absorption near edge structure (XANES) spectra of CuIn(S,Se)<sub>2</sub> obtained by PFY mode, the intensity of the spectra at post edge increased with remaining of shape of the spectra by Se incorporation into S site. This result suggests that the 4 coordination state of local structure around S atoms in CuInS<sub>2</sub> are not changed by Se addition, however, the transition probability of an electron from S 1s orbital to S 3p orbital is improved by decreasing electron density due to the elongation of interatomic distance of Cu-S and In-S. Furthermore, large absorption band at 2482 eV were observed in Li doped samples. The absorption band was attributed to the SO<sub>4</sub> species. When the S K-edge XANES spectra were recorded in a TEY mode, which is more surface sensitive than PFY mode, the absorption band were more intense. Then, the result indicates that the sample surface is oxidized in air. Se L<sub>3</sub>-edge XANES spectra were not changed by the change of S/(S + Se) ratio and Li dope. Therefore, S species is only oxidized at the surface of (Cu,Li)In(S,Se)<sub>2</sub> not depending on S/(S + Se) ratio. Li K-edge XANES spectra were also not changed by the change of S/(S + Se) ratio and doping amount of Li. These spectra were attributed to that of Li<sub>2</sub>SO<sub>4</sub> [4]. There are Se M<sub>4</sub> and M<sub>5</sub>-edge around Li K-edge. Se M-edge XANES spectra were absolutely not observed in our obtained spectra in spite of (Cu,Li)In(S,Se)<sub>2</sub> contains much amount of Se, because the species at the several nm of sample surface which can be detected by TEY mode were entirely changed into Li<sub>2</sub>SO<sub>4</sub>. In summary, the evaluation for local structure of S and Se species in (Cu,Li)In(S,Se)<sub>2</sub> can be achieved by using soft X-ray XAFS. Li species in (Cu,Li)In(S,Se)<sub>2</sub> should be carefully evaluated not to be oxidized in air.

### References

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