

Crystallographic and optical properties, and band-diagrams of CuInSe_2 , CuIn_3Se_5 , and CuIn_5Se_8 phases in Cu-poor $\text{Cu}_2\text{Se-In}_2\text{Se}_3$ pseudo-binary system

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Abstract

We prepared Cu-poor CIS phases such as CuInSe_2 , CuIn_3Se_5 , and CuIn_5Se_8 in the composition of $(1-x)\text{Cu}_2\text{Se-(x)In}_2\text{Se}_3$ with $0.5 \leq x \leq 1.0$. The crystal structure of the sample was changed from chalcopyrite-type CuInSe_2 to hexagonal CuIn_5Se_8 through a stannite-type CuIn_3Se_5 with increasing x . The band gap energies of these samples increased stepwise with decreasing Cu/In ratio. The energy levels of the VBMs were estimated from the ionization energies by photoemission yield spectroscopy (PSY) measurements. The energy levels of the VBMs of the Cu-poor CIS samples decrease dramatically by decreasing Cu/In ratio.

1. Introduction

Recently, EMPA [1] and ZSW [2] groups recently reported the high-efficiency CIGS solar cells more than 20%. Their groups fabricated the CIGS solar cells by post-deposition of sodium fluoride (NaF) and potassium fluoride (KF) on CIGS films and annealing in Se atmosphere. After the post-deposition treatment and annealing, Cu-deficient layer was formed at the surface of the CIGS layer. In the $\text{Cu}_2\text{Se-In}_2\text{Se}_3$ pseudo-binary system [3], some Cu-poor compounds such as tetragonal chalcopyrite-type CuInSe_2 , tetragonal stannite-type CuIn_3Se_5 , and tetragonal and hexagonal CuIn_5Se_8 phases have been reported. A number of studies on Cu-poor CIS compounds have been carried out from 1993 [4]. Our group also has studied CuIn_3Se_5 and CuIn_5Se_8 for 20 years [5-7]. Recently, we reported detail crystal structure of Cu-poor CIS compounds by x-ray absorption fine structure (XAFS) [8].

In order to clarify the detail optical property and band diagram of Cu-poor CIS compounds, we synthesized $(1-x)\text{Cu}_2\text{Se-(x)In}_2\text{Se}_3$ ($0.5 \leq x \leq 1.0$). We investigated crystallographic and optical properties of the Cu-poor CIS samples. Then we determined their band gap energies and ionization energies.

2. Experimental Procedures

Starting materials of elemental powders such as Cu, In, and Se were weighed to give a molar ratio of $(1-x)\text{Cu}_2\text{Se-(x)In}_2\text{Se}_3$ ($x=0.5, 0.55, 0.60, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, 1.0$). The chemical composition of the samples with $x=0.5, 0.75, 0.83$ are corresponding to CuInSe_2 (Cu/In=1), CuIn_3Se_5 (Cu/In=0.33), and CuIn_5Se_8 (Cu/In=0.2), respectively. Elemental powders were put into a grinding jar made of zirconia along with zirconia balls.

The milling was conducted in a planetary ball mill (Fritsch premium line P-7) under a rotational speed of 800 rpm with a milling period of 20 min in an N_2 gas atmosphere. The mixed powders were heated at 550°C for 30 min in an N_2 gas atmosphere.

The phases in the obtained powders were identified by X-ray powder diffraction using Cu-K α radiation. The crystal structures of the Cu-poor CIS samples were analyzed by Rietvelt refinement using X-ray diffraction data on the basis of tetragonal chalcopyrite-type structure [space group: I4-2d (No. 122)] and stannite-type structure (Paszkwicz's model [5]) [space group: I4-2m (No. 121)], and hexagonal structure [6]. Optical properties of the Cu-poor CIS samples were characterized by UV-vis-NIR spectroscopy (JASCO V-670DS). The band-gap energies of the Cu-poor CIS samples were determined by diffuse reflectance spectra. The ionization energy of the Cu-poor CIS samples was directly measured by photoemission yield spectroscopy (PYS) (Bunkoukeiki: BIP-KV201).

3. Results and discussion

3.1 Preparation of Cu-poor CIS

Figure 1 shows the X-ray diffraction (XRD) patterns of the $(1-x)\text{Cu}_2\text{Se-(x)In}_2\text{Se}_3$ with $0.5 \leq x \leq 1.0$ synthesized by mixing the elemental powders and additional heating at 550°C . The diffraction peaks of the samples with $x=0.5$ and $x=0.55$ could be indexed on the basis of a tetragonal chalcopyrite-type structure. For the Cu-poor CIS samples with $0.60 \leq x \leq 0.75$, the diffraction peaks could be indexed on the basis of a tetragonal stannite-type structure [5]. For the samples with $0.80 \leq x \leq 0.95$, the diffraction peaks are identified to be the mixed CuIn_5Se_8 phases of the tetragonal and hexagonal structures.

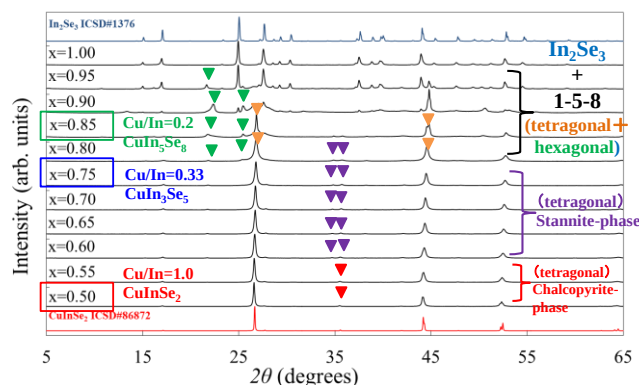


Figure 1 X-ray diffraction patterns of Cu-poor CIS samples in the $(1-x)\text{Cu}_2\text{Se-(x)In}_2\text{Se}_3$ pseudo-binary system.

3.2 Band gap energy and band diagram of Cu-poor CIS

Figure 2(a) shows the diffuse reflectance spectra of the $(1-x)\text{Cu}_2\text{Se}-(x)\text{In}_2\text{Se}_3$ with $0.5 \leq x \leq 1.0$ powders measured by UV-vis-NIR spectroscopy. The reflectance edges of the Cu-poor CIS samples shifted to shorter wavelengths by increasing x . Figure 2(b) shows $(F(R)h\nu)^2$ vs. $h\nu$ plot of the diffuse reflectance spectra of the $(1-x)\text{Cu}_2\text{Se}-(x)\text{In}_2\text{Se}_3$ with $0.5 \leq x \leq 1.0$ powders. The band-gap energies were calculated by Tauc plot of the diffuse reference data.

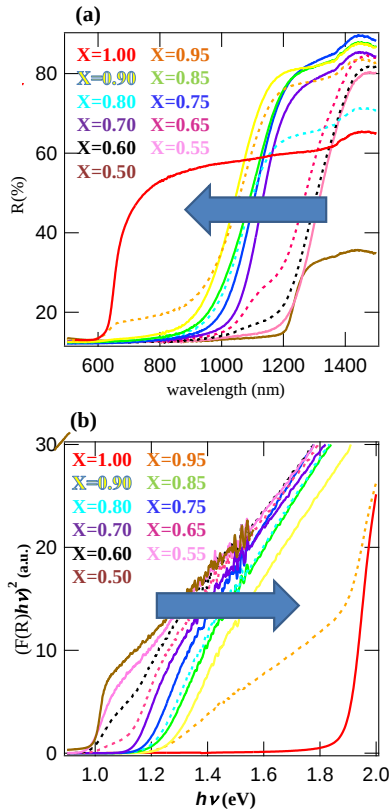


Figure 2 Diffuse reflectance spectra (a) and $(F(R)h\nu)^2$ vs. $h\nu$ plot (b) of Cu-poor CIS samples in the $(1-x)\text{Cu}_2\text{Se}-(x)\text{In}_2\text{Se}_3$ pseudo-binary system measured by UV-vis-NIR spectroscopy.

Figure 3 shows the band-gap energies of $(1-x)\text{Cu}_2\text{Se}-(x)\text{In}_2\text{Se}_3$ with $0.5 \leq x \leq 1.0$ estimated from the $(F(R)h\nu)^2$ vs. $h\nu$ plot of the reflectance spectra. The determined band-gap energies of $(1-x)\text{Cu}_2\text{Se}-(x)\text{In}_2\text{Se}_3$ with $x=0.5, 0.55, 0.60$ of tetragonal chalcopyrite phase are 0.99, 0.98, and 0.99 eV, respectively. The band-gap energy of the samples with $x=0.65, 0.70, 0.75$ of tetragonal stannite phase are 1.11, 1.13, and 1.17 eV, respectively. The band-gap energies of the Cu-poor CIS samples increase stepwise with decreasing Cu/In ratio.

Figure 4 shows photoemission yield spectroscopy spectrum of CuInSe_2 ($x=0.5$). The determined ionization energy of the CuInSe_2 was 4.90 eV, which is higher than the Jaegermann's value (-5.4 eV) [7]. Recently, we confirmed that the ionization energy determined by PYS was in good agreement with the value determined by X-ray photoelectron spectroscopy with UV photoelectron yield spectroscopy

py for BaCuSeF [12]. The valence band maximum (VBM) and conduction band minimum (CBM) of CuInSe_2 are estimated to be -4.90 eV and -3.91 eV, respectively. The energy level of the VBM was estimated from the ionization energies by PSY measurements. The energy level of the CBM was calculated from the estimated VBM and estimated band gap energy shown in Fig. 3. The energy levels of the VBMs of the Cu-poor CIS samples change stepwise and decrease dramatically by decreasing Cu/In ratio. The energy level of the CBM also decreases with decreasing Cu/In ratio.

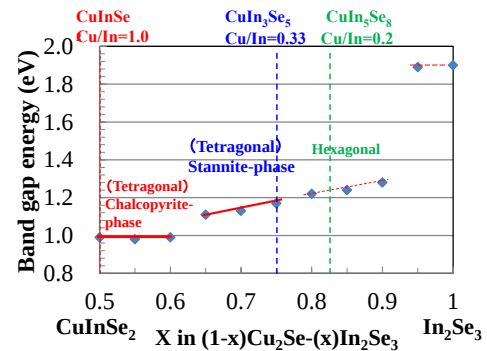


Figure 3 Band-gap energies of Cu-poor CIS samples in the $(1-x)\text{Cu}_2\text{Se}-(x)\text{In}_2\text{Se}_3$ pseudo-binary system estimated from the $(F(R)h\nu)^2$ vs. $h\nu$ plot.

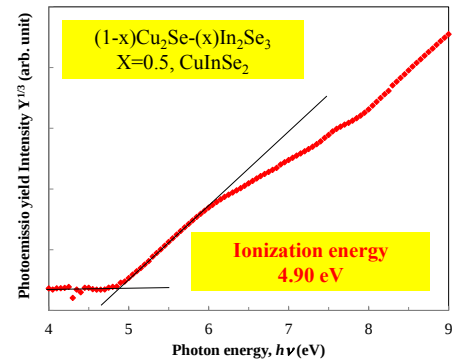


Figure 4 Photoemission yield spectroscopy spectrum of CuInSe_2 ($x=0.5$).

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