Crystallographic and optical properties and band structures of CuInSe2, CuIn3Se5, and CuInS3 phases in Cu-poor Cu2Se–In2Se3 pseudo-binary system

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We prepared CuInSe2 and Cu-poor Cu–In–Se (CIS) phases such as CuIn3Se5 and CuIn5Se8 in the composition of (1 – x)CuInSe2–xIn2Se3 with 0.5 ≤ x ≤ 1.0. The crystal structure of the sample changed from chalcopyrite-type CuInSe2 to hexagonal CuIn5Se8 through stannite-type CuIn3Se5 with increasing x (decreasing Cu/In ratio). The band-gap energies of Cu-poor CIS samples, i.e., CuIn3Se5 (1.17 eV) and CuIn5Se8 (1.22–1.24 eV), are larger than that of chalcopyrite-type CuInSe2 (0.99 eV). The energy levels of the valence band maxima (VBMs) were estimated from the ionization energy by photoemission yield spectroscopy (PYS) measurements. The energy levels of the VBMs of the Cu-poor CIS samples decrease rapidly with decreasing Cu/In ratio. The ionization energy of stannite-type CuIn3Se5 is 0.4 eV larger than that of chalcopyrite-type CuInSe2. The ionization energy of Cu-poor CIS phases, such as CuIn3Se5 and CuIn5Se8, is deeper than that of Cu-poor CIS. To understand the electronic structure of Cu-poor CIS compounds, we performed first-principles band structure calculations on stannite-type CuIn3Se5 and a reference compound, tetragonal chalcopyrite-type CuInSe2, using the HSE06 nonlocal screened hybrid density functional. The calculated band-gap energy of tetragonal stannite-type CuIn5Se8 (1.19 eV) is larger than that of chalcopyrite-type CuInSe2 (0.94 eV).

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1. Introduction

CuInSe2 (CIS), Cu(In,Ga)Se2 (CIGS), and related compounds have attracted attention as the most promising materials for thin-film photovoltaic devices owing to the suitability of their tunable band-gap energy and their high absorption coefficient for solar radiation. Recently, several research groups have announced more than 20% conversion efficiency for CIS solar cells.1–3) The Swiss Federal Laboratories for Materials Science and Technology (EMPA)4) and Zentrum für Sonnenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW)5) groups fabricated high-efficiency CIS solar cells by the post-deposition of sodium fluoride (NaF) and potassium fluoride (KF) on CIS films and annealing in a Se atmosphere. After the post-deposition treatment and annealing, a Cu-deficient layer was formed at the surface of the CIS layer.6,7)

Figure 1 shows the reported phase diagram for the Cu2Se–In2Se3 pseudo-binary system.3) In this system, tetragonal chalcopyrite-type CuInSe2 (Cu/In = 1) and some Cu-poor compounds such as tetragonal stannite-type CuIn3Se5 (Cu/In = 0.33) and tetragonal and hexagonal CuIn5Se8 (Cu/In = 0.2) phases have been reported.8) Most of the CIS absorbers utilized for high-efficiency solar cells have been prepared by physical vapor deposition as typified by the “three-stage” process.7,8) In the first stage, an (In,Ga)2Se3 layer is deposited at a relatively low substrate temperature. In the second stage, the phase changes observed in CIS films during the deposition of Cu and Se on the In–Ga–Se precursor films were as follows: (In,Ga)2Se3→[Cu(In,Ga)2Se3]→Cu(In,Ga)Se2→CuIn(Ga)Se2→Cu-rich Cu(In,Ga)Se2. Finally, in the third stage, In, Ga, and Se are again deposited and the final composition of the CIS film is made Cu-deficient [Cu/(In + Ga) < 1]. The CIS absorber usually exhibits p-type conductivity because of the formation of a Cu-poor CIS thin film.9)

CuInSe2 (Cu/In = 1.0) crystallizes in a tetragonal chalcopyrite structure [space group: I42d (No. 122)]. The crystal structure of chalcopyrite-type CuInSe2 is shown in Fig. 2(a).

The chalcopyrite structure is based on the zincblende structure; the c-axis is almost twice as long as the a-axis of the basic zincblende structure, but the c/a ratio is not equal to 2.0 because CuInSe2 has two kinds of chemical bonds, i.e., Cu–Se and In–Se.10,11) Density functional calculations have shown that the formation energy for the Cu vacancy (VCu) is small in comparison with other types of vacancies.12,13) The p-type conductivity of the Cu-poor CIS phase is attributed to the formation of shallow acceptor levels of VCu.12)

A number of studies on Cu-poor Cu–In–Se (CIS) compounds such as CuIn3Se5 have been carried out since 1993.14–18) CuInSe3 and CuInS3 have attracted attention as the key compounds for high-efficiency CIS thin-film solar

Fig. 1. (Color online) Phase diagram for the Cu2Se–In2Se3 pseudo-binary system reported by Boehke and Kuhn.5) α: CuInSe2 with a tetragonal chalcopyrite structure, β: CuInSe2 with a tetragonal stannite structure, γ: CuInS3 with a hexagonal layered structure, δ: CuInSe2 with a cubic sphalerite structure.
cells. In the last stage of the three-stage process, small amounts of In, Ga, and Se are added to the CIS absorber layer and a slightly Cu-poor CIGS surface is formed. Therefore, a thin Cu-poor CIS compound layer including CuIn3Se5 and CuIn5Se8 exists on the surface of a Cu-poor CIS absorber. Schmid et al. first reported that the p-n junction between the p-type CIS and n-type CuIn3Se5 plays an important role in enabling high-efficiency CIS solar cells.

A number of structural studies on Cu-poor CIS compounds have been reported in the last few decades. One of the authors of this paper has also studied CuIn3Se5 and CuIn5Se8 for 20 years. For CuIn3Se5, three main types of crystal structures have been reported. First, Höhle et al. suggested the structure of the ordered vacancy chalcopyrite (OVC) or the ordered defect chalcopyrite (ODC) with the space group $I\overline{4}2d$. Second, Hanada et al. investigated the structure of CuIn3Se5 by a combination of convergent beam transmission electron microscopy (TEM) and Rietveld refinement of the X-ray diffraction. They concluded that CuIn3Se5 has a stannite-like structure with VCu and InCu defects. However, optical properties and band diagrams of Cu-poor CIS compounds are still under discussion.

To clarify the optical properties of Cu-poor CIS compounds, we synthesized the $(1 – x)$CuInSe2–(x)In2Se3 ($0.5 \leq x \leq 1.0$) samples. The phases in the obtained powders were identified by X-ray powder diffraction (XRD). The band-gap energies of the CIS samples were determined from the diffuse reflectance spectra of the ultraviolet-visible-near infrared (UV–vis–NIR) spectroscopy. The energy levels of the valence band maxima (VBM) of the Cu-poor CIS samples were estimated from the ionization energies measured by photoemission yield spectroscopy (PYS). We discuss the band diagrams of CuInSe2 and Cu-poor CIS compounds such as CuIn3Se5 and CuIn5Se8, which were estimated from the obtained ionization energy and band-gap energy. Additionally, in order to understand the electronic structure of Cu-poor CIS compounds, we performed first-principles band structure calculations on stannite-type CuIn3Se5 and reference compound, tetragonal chalcopyrite-type CuInSe2, using the HSE06 nonlocal screened hybrid density functional.

2. Experimental and theoretical procedures

2.1 Preparation of CuInSe2, CuIn3Se5, and CuIn5Se8 samples in Cu5Se–In2Se3 pseudo-binary system

CIS powder samples on the Cu-poor side of the Cu5Se–In2Se3 pseudo-binary system were synthesized by a mechanochemical process and post-heating. Starting materials of elemental powders such as Cu, In, and Se were weighed to give a molar ratio of $(1 – x)$CuInSe–(x)In2Se3 ($x = 0.50, 0.55, 0.60, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, 1.0$). The compositions of these samples are indicated by dots on the horizontal axis in Fig. 1. The chemical compositions of the samples with $x = 0.50, 0.75,$ and 0.83 correspond to CuIn3Se5 (Cu/In = 1), CuIn5Se5 (Cu/In = 0.33), and CuIn3Se8 (Cu/In = 0.2), respectively. The elemental powders were placed in 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 a N2 gas atmosphere. The mixed powders were heated to 550°C at a rate of 20°C/min and annealed at 550°C for 30 min in a N2 gas atmosphere in a single-zone silica tube furnace.

2.2 Crystallographic characterization

The phases in the obtained powders were identified by XRD using Cu-Kα radiation. XRD measurements for Rietveld analysis were performed using an X-ray diffractometer (Rigaku RINT-2400) equipped with a rotating-anode source and a curved graphite monochromator. The diffraction data were collected with a step width of 0.04° (2θ) and a counting time of 4 s for each step over a 2θ range from 5 to 120°. Rietveld refinement was carried out using Reflex Plus in Accelrys Materials Studio’s analytical and crystallization software. The crystal structures of CIS samples such as CuInSe2, CuIn3Se5, and CuIn5Se8 were refined on the basis of tetragonal chalcopyrite-type structure [space group: $I\overline{4}2d$ (No. 122)] and the tetragonal stannite-type structure (Paszkowicz’s model) [space group: $I\overline{4}2m$ (No. 121)].

2.3 Optical characterization and measurement of ionization energy

The optical properties of the CIS samples were characterized by UV–vis–NIR spectroscopy (JASCO V-670DS). Diffuse reflectance measurements were carried out using the CIS powders, which were pulverized for 2 h in an agate mortar. The band-gap energies of the CIS samples were determined from diffuse reflectance spectra. The band-gap energies were calculated from a Tauc plot of the diffuse reflectance data.

To discuss the band diagrams of the CIS samples, the energy levels of the VBM were estimated from the ionization energies. The ionization energy of the CIS samples was directly measured by PYS (Bunkoukeiki BIP-KV201).
2.4 First-principles calculations

We performed first-principles calculations on the basis of the density functional theory (DFT) as implemented in the program code CASTEP\(^{[20]}\) in Materials Studio version 7.0 SP2 (Accelrys). Calculations using a plane-wave pseudopotential method were performed using the nonlocal screened hybrid density functional method of Heyd–Scuseria–Ernzerhof (HSE06)\(^{[29,30]}\) as an electron exchange and correlation functional because a first-principles calculation based on the DFT using the local density approximation (LDA)\(^{[1,32]}\) and the generalized gradient approximation (GGA)\(^{[13,34]}\) usually underestimates the band-gap energy. The HSE06 functional provides a more accurate band-gap energy than the LDA and GGA functionals. Since performing a geometric optimization with the HSE06 functional is very time-consuming, the crystallographic parameters were optimized using the GGA–PBE functional. Ultrasoft pseudopotentials\(^{[35]}\) were applied with a plane-wave cutoff energy of 500 eV. The electronic structure calculations with the HSE06 functional were performed using norm-conserving pseudopotentials because CASTEP does not currently support the use of the HSE06 functional for ultrasoft pseudopotentials. Norm-conserving pseudopotentials with a plane-wave cutoff energy of 1,000 eV were employed for the HSE06 calculations. Self-consistent total energies were obtained using the density-mixing scheme\(^{[36]}\) in connection with the conjugate gradient technique.\(^{[37]}\) Atomic positions were optimized by the quasi-Newton method with the latest Broyden–Fletcher–Goldfarb–Shanno scheme.\(^{[38]}\)

The experimentally reported structure of CuInSe\(_2\) was adopted as the initial model, which was obtained from the Inorganic Crystal Structure Database (ICSD). For CuInSe\(_2\), the chalcopyrite-type unit cell (space group: \(I\bar{4}2d\)) with the lattice parameters \(a = 5.776(4)\) Å, \(c = 11.611(7)\) Å, and \(c/a = 2.01\) (ICSD \#86872) was employed. For Cu-poor CIS samples, a virtual model of the tetragonal CuIn\(_2\)Se\(_3\) with a stannite-type unit cell was constructed. The initial crystal structure model for the virtual tetragonal CuIn\(_2\)Se\(_3\) was made from the lattice parameters experimentally determined by Rietveld analysis. The crystal structures of tetragonal chalcopyrite-type CuInSe\(_2\) (a), tetragonal stannite-type CuIn\(_2\)Se\(_3\) (Paszkowicz’s model\(^{[25]}\) (b), and virtual tetragonal stannite-type CuIn\(_2\)Se\(_3\) used in the first-principles calculation (c) are shown in Fig. 2.

3. Results and discussion

3.1 Crystal structures of Cu-poor CIS samples

Figure 3(a) shows the XRD patterns of the \((1 - x)\)Cu\(_2\)Se–\((x)\)In\(_2\)Se\(_3\) with \(0.5 \leq x \leq 1.0\) synthesized by mixing the elemental powders with additional heating at 550 °C. The XRD pattern of the synthesized sample with \(x = 0.5\) (CuInSe\(_2\)) is in good agreement with the simulated pattern of chalcopyrite-type CuInSe\(_2\) (ICSD \#86872), and there is no peak of a secondary impurity phase. Therefore, we concluded that single-phase CuInSe\(_2\) can be obtained by a mechanochemical process with additional heating at 550 °C. Figure 3(b) shows a magnified view of the XRD patterns of the \((1 - x)\)Cu\(_2\)Se–\((x)\)In\(_2\)Se\(_3\) with \(0.5 \leq x \leq 1.0\). The characteristic peaks are magnified in the range \(2\theta = 10–50^\circ\). Figure 3(c) shows the simulated XRD patterns of chalcopyrite-type CuInSe\(_2\) [space group: \(I\bar{4}2d\) (No. 122)] (ICSD \#86872) and stannite-type CuIn\(_2\)Se\(_3\) [space group: \(I\bar{4}2m\) (No. 121)] (ICSD \#84346) are shown for reference. In the simulated XRD patterns shown in Fig. 3(c), the characteristic diffraction peaks of the chalcopyrite-type structure (A) of 101, 112, 103, 200, 211, 213, 204/220, and 301 are observed. On the other hand, the characteristic diffraction peaks of the stannite-type structure (B) of 002, 101, 112, 103, 200, 211, 114, 204/220, and 222 are observed. The diffraction peaks of 002, 110, 202, and 114 only appear for the stannite phase. In Fig. 3(b), the diffraction peaks of the
samples with $x = 0.5$ and $0.55$ can 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 can be indexed on the basis of a tetragonal stannite-type structure. For the samples with $0.80 \leq x \leq 0.95$, the diffraction peaks are identified to be from a mixed CuIn$_3$Se$_8$ phases with the tetragonal and hexagonal$^6$ structures. This result suggests that the crystal structure of the sample changed from chalcopyrite-type CuInSe$_2$ to hexagonal CuIn$_3$Se$_8$ through stannite-type CuIn$_2$Se$_5$ with increasing $x$ (decreasing Cu/In ratio). Although there is a region of the mixed phase of a chalcopyrite-type structure and a stannite-type structures in the phase diagram of the Cu$_2$Se–In$_2$Se$_3$ system (shown in Fig. 1), we did not clearly observe this mixed phase. The XRD pattern of a stannite-type structure is similar to that of a chalcopyrite structure. Most of the peaks of a chalcopyrite-type structure should also be included in the peaks of a stannite-type structure. Therefore, it is difficult to determine the region of existence of the mixed phase. However, both a chalcopyrite-type CuInSe$_2$ phase with $E_g$ of about 1.0 eV and a stannite-type CuIn$_2$Se$_5$ phase with $E_g$ of about 1.11 eV are observed in the diffuse reflectance spectra of the (1 – $x$)Cu$_2$Se–$x$In$_2$Se$_3$ powder samples with $x = 0.60$ and 0.65. These results are discussed in the next section.

The crystal structures of the CIS samples (0.50 $\leq x \leq 0.80$) were analyzed by Rietveld refinement using XRD data. The crystal structures of the CIS samples such as CuInSe$_2$, CuIn$_3$Se$_5$, and CuIn$_2$Se$_5$ were refined on the basis of the tetragonal chalcopyrite-type structure [space group: $I\bar{4}2d$ (No. 122)] and stannite-type structure (Paszkowicz’s model$^5$) [space group: $I\bar{4}2m$ (No. 121)]. Figure 4 shows the final profile fitting patterns of (a) chalcopyrite-type CuInSe$_2$ with $x = 0.5$ (Cu/In = 1.0) and (b) stannite-type CuIn$_3$Se$_5$ with $x = 0.75$ (Cu/In = 0.33) determined by Rietveld analysis. The determined crystallographic parameters of chalcopyrite-type CuInSe$_2$ and stannite-type CuIn$_3$Se$_5$ such as the lattice constants $a$ and $c$ and the atomic coordinates ($u$-parameter) of the Se atom are summarized in Fig. 4. The refined lattice parameters of chalcopyrite-type CuInSe$_2$ are $a = 5.778(4)$ Å, $c = 11.609(4)$ Å, $a/c = 2.01$, and $u_{\text{Se}}(\text{Se}) = 0.229$. These agree with the reported values of $a = 5.776(4)$ Å, $c = 11.611(7)$ Å, and $a/c = 2.01$, and $u_{\text{Se}}(\text{Se}) = 0.230$ (ICSD #86872). The final value of the R factor corresponding to the weighted residual error ($R_{wp}$) is 5.02%. The refined lattice parameters of stannite-type CuIn$_3$Se$_5$ are $a = 5.740(8)$ Å, $c = 11.49(2)$ Å, $a/c = 2.00$, $u_{\text{Se}}(\text{Se}) = 0.237$, and $u_{\text{Se}}(\text{Se}) = 0.116$. These agree with Paszkowicz’s reported values$^5$ of $a = 5.75812(2)$ Å, $c = 11.53593(7)$ Å, $a/c = 2.00$, $u_{\text{Se}}(\text{Se}) = 0.2308(3)$, and $u_{\text{Se}}(\text{Se}) = 0.1155(2)$. The final value of the R factor is $R_{wp} = 6.68\%$.

Figure 5 shows the $R_{wp}$ values obtained by Rietveld refinement of the Cu-poor CIS samples (0.50 $\leq x \leq 0.85$). For the samples with $0.50 \leq x \leq 0.55$, the $R_{wp}$ values of the chalcopyrite structure ($I\bar{4}2d$) are lower than 5%. For the samples with $0.60 \leq x \leq 0.80$, the $R_{wp}$ values of the stannite structure ($I\bar{4}2m$) are lower than 8% and lower than those of the chalcopyrite structure. The $R_{wp}$ values of the samples with $x = 0.85$ are considerably higher than those of the other samples (0.50 $\leq x \leq 0.80$) because the sample with $x = 0.85$ comprises mixed CuIn$_3$Se$_8$ phase with the tetragonal and hexagonal structures. The key feature of the Cu$_2$Se–In$_2$Se$_3$ pseudo-binary system in Fig. 1 is that CuInSe$_2$ has a solid-solution region with a chalcopyrite structure on the Cu-poor (Cu/In < 1) side of the Cu$_2$Se–In$_2$Se$_3$ system. In the further Cu-poor side of the system, there are tetragonal stannite-type CuIn$_3$Se$_5$ (Cu/In = 0.33) and hexagonal CuIn$_2$Se$_5$ phases.
Therefore, in the second stage of the “three-stage” process, the crystal structure of the Cu–In–Ga–Se film changes as follows: (In, Ga)_2Se_3 → [Cu(In, Ga)_2Se_3] (hexagonal) → Cu(In, Ga)_2Se_3 (tetragonal stannite-type) → Cu(In, Ga)_2Se_2 (tetragonal chalcopyrite-type).

In a previous study, we synthesized the Cu-based chalcogenide compounds CuSb(S, Se)_2 by a mechanochemical process and post-heating. We confirmed that the actual composition ratio of the synthesized powder measured by energy dispersive X-ray analysis (EDX) was almost consistent with the feed composition in the preparation. 39) In the present study, the regions of existence of the chalcopyrite- and stannite-type phases are consistent with those in the CuSb-Se–InSb pseudo-binary phase diagram (Fig. 1). Therefore, we believe that there is no significant difference between the feed composition in the preparation and the actual composition of the synthesized powder.

The refined lattice parameters a and c are respectively shown in Figs. 6(a) and 6(b), both of which decrease with increasing x (decreasing Cu/In ratio). The c/a ratios of the samples with 0.60 ≤ x ≤ 0.80 (stannite phase) are smaller than those of the samples with x = 0.50 and 0.55 (chalcopyrite phase).

3.2 Band-gap energy of Cu-poor CIS samples

Figure 7(a) shows the diffuse reflectance spectra of the (1–x)Cu_xSe–(x)In_xSe_3 powders with 0.5 ≤ x ≤ 1.0 measured by UV–vis–NIR spectroscopy. The reflectance edges of the Cu-poor CIS samples shifted to shorter wavelengths with increasing x (decreasing Cu/In ratio). Figure 7(b) shows a magnified view (900–1300 nm) of the diffuse reflectance spectra of the (1–x)Cu_xSe–(x)In_xSe_3 powders. The shape of the diffuse reflectance spectra of the samples with x = 0.6 and 0.65 is two-step. In the phase diagram of the CuSb-Se–InSb pseudo-binary phase diagram, CuIn_2Se_3 → [CuIn_2Se_3] (hexagonal) → CuIn_2Se_3 (tetragonal stannite-type) → CuIn_5Se_8 (tetragonal chalcopyrite-type). The chalcopyrite-type structure with space group of I42d and stannite-type structure with space group of I42m (No. 122) in the (1–x)Cu_xSe–(x)In_xSe_3 system. Note that the lattice parameters for the samples with x = 0.60 and 0.65 are refined on the basis of a tetragonal stannite-type structure, although these samples are a mixed phase of chalcopyrite- and stannite-type structures.

3.1 Composition ratio of the synthesized powder measured by EDX was almost consistent with the feed composition in the preparation. 39) In the present study, the regions of existence of the chalcopyrite- and stannite-type phases are consistent with those in the CuSb-Se–InSb pseudo-binary phase diagram (Fig. 1). Therefore, we believe that there is no significant difference between the feed composition in the preparation and the actual composition of the synthesized powder.
system, the samples with $x = 0.60$ and 0.65 are the mixed phase of chalcopyrite- and stannite-type structures. Therefore, we considered that the samples with $x = 0.60$ and 0.65 have two different band-gap energies (i.e., chalcopyrite- and stannite-type).

CuInSe$_2$ is known as a semiconductor and has a direct band gap ($\Gamma$--$\Gamma$) of 1.04 eV. Additionally, our first-principles calculations in this study showed that both tetragonal chalcopyrite-type CuInSe$_2$ and tetragonal stannite-type CuIn$_2$Se$_3$ have a direct band gap ($\Gamma$--$\Gamma$). Therefore, the band gaps of the CIS samples were estimated by assuming they were direct transition-type semiconductors. Figure 8(a) shows an $F(R)\nu^2$ vs $\nu$ plot of the diffuse reflectance spectra of the $(1-x)$Cu$_2$Se--(x)In$_2$Se$_3$ powders with $0.5 \leq x \leq 1.0$ on a normal scale (a) and a magnified view (b). $F(R)$ denotes the Kubelka–Munk function of the reflectance spectra. An $F(R)\nu^2$ vs $\nu$ plot for the sample with $x = 0.65$ (the mixed phase of chalcopyrite- and stannite-type structures) is shown in (c).

Figure 9 shows the band-gap energies of $(1-x)$Cu$_2$Se--(x)In$_2$Se$_3$ samples with $0.5 \leq x \leq 1.0$ estimated from the $F(R)\nu^2$ vs $\nu$ plot of the reflectance spectra. Note that the samples with $x = 0.60$ and 0.65 are a mixed phase of chalcopyrite- and stannite-type structures. Therefore, two different band-gap energies (i.e., chalcopyrite- and stannite-type) were determined for the samples with $x = 0.60$ and 0.65.

reported value (1.04 eV). In our previous report on Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe), the band-gap energy determined from the diffuse reflectance spectra of the powder was also about 0.05 eV smaller than that determined from the transmittance spectra of the film. The band-gap energies of
the CIS samples with \( x = 0.50 \text{--} 0.55 \) are about 1.0 eV and almost the same value.

For the samples with \( x = 0.6 \) and 0.65, the two different band-gap energies (i.e., chalcopyrite- and stannite-type) are estimated from the \( [F(R_{hv})] \) vs \( hv \) plot, as shown in Fig. 8(c), since these samples are a mixed phase of chalcopyrite- and stannite-type structures in the phase diagram of the \( \text{Cu}_2\text{Se} \text{--In}_2\text{Se}_3 \) system. The band-gap energies of the sample with \( x = 0.60 \) were determined to be 0.99 eV for a chalcopyrite phase and 1.09 eV for the stannite phase. The band-gap energies of the samples with \( x = 0.65 \) are determined to be 0.99 eV for the chalcopyrite phase and 1.11 eV for the stannite phase.

On the other hand, the band-gap energies of the samples with \( x = 0.70 \) and 0.75 in the tetragonal stannite phase are 1.13 and 1.17 eV, respectively. The band-gap energies of the Cu-poor CIS samples increase in a stepwise manner with increasing \( x \) (decreasing Cu/In ratio). The band-gap energy of 1.17 eV for \( \text{CuIn}_3\text{Se}_5 \) (\( x = 0.75, \text{Cu}/\text{In} = 0.33 \)) with the tetragonal stannite phase is larger than that of chalcopyrite-type \( \text{CuIn}_2\text{Se}_2 \) (0.99 eV), and it is in good agreement with the reported values (1.18 \text{--} 1.24 eV).\(^{41}\) Moreover, the band-gap energy of \( \text{CuIn}_2\text{Se}_2 \) (\( x = 0.83, \text{Cu}/\text{In} = 0.2 \)) with the mixed tetragonal and hexagonal phase is around 1.22 \text{--} 1.24 eV, which is larger than that of chalcopyrite-type \( \text{CuIn}_2\text{Se}_2 \) and stannite-type \( \text{CuIn}_2\text{Se}_2 \). This value is also in good agreement with the reported values (1.34 \text{--} 1.35 eV).\(^{42}\)

3.3 Ionization energy of Cu-poor CIS samples and their band diagram

To apply CIS films to a p-type absorber layer for a thin-film compound solar cell, it is important to know the parameters of the band diagram, such as the depth of the top of the valence band from the vacuum level, which corresponds to the energy levels of the VBM from the vacuum level. A material with a higher energy position of the VBM of around \( -5 \) eV can easily become p-type because electrons can be easily removed from the valence bands to form holes.

To discuss the band diagrams of the Cu-poor CIS samples such as \( \text{CuIn}_2\text{Se}_2 \), \( \text{CuIn}_3\text{Se}_5 \), and \( \text{CuIn}_5\text{Se}_8 \), energy levels of the VBM from the vacuum level were estimated from the ionization energies. The ionization energies of the Cu-poor CIS samples were directly measured by PYS. The photoelectron yield has the following relationship for semiconductors: \( Y \propto I_s \propto A(h\nu - E_W) \), where \( Y \) is the photoelectron yield, \( I_s \) is the photocurrent, \( A \) is a constant, \( h\nu \) is the photon energy, and \( E_W \) is the difference in energy between the vacuum level and the Fermi level, determined by linear fitting of the \( I_s^{1/3} \) vs \( h\nu \) plot. Before measuring the CIS samples, we calibrated the work function of the Au film (as a standard substance), which corresponds to the Fermi energy level from the vacuum level. The work function of the Au film measured by PYS (4.75 eV) is 0.35 eV smaller than that of the reported value (5.1 eV).\(^{43}\) Therefore, we corrected the ionization energies of the CIS samples measured by PYS by adding 0.35 eV.

Figure 10 shows the photoemission yield spectroscopy spectrum of \( \text{CuIn}_2\text{Se}_2 \) and \( (1 - x)\text{Cu}_2\text{Se}-(x)\text{In}_2\text{Se}_3 \) powders with 0.5 \( \leq x \leq 1.0 \). The detection limit of their photoelectron yield shifts to the higher-energy side with increasing \( x \) (decreasing Cu/In ratio). Figure 11 shows the energy levels of the VBM and CBM of the \( (1 - x)\text{Cu}_2\text{Se}-(x)\text{In}_2\text{Se}_3 \) samples from the vacuum level. The ionization energies of \( \text{CuIn}_2\text{Se}_2 \) and \( \text{CuIn}_5\text{Se}_8 \) are 5.65 and 5.75 \text{--} 5.95 eV, respectively. The energy level of the VBM of \( \text{CuIn}_2\text{Se}_2 \) is -5.25 and -4.26 eV (electron affinity), respectively.

For samples of the \( (1 - x)\text{Cu}_2\text{Se}-(x)\text{In}_2\text{Se}_3 \) powders with 0.5 \( \leq x \leq 1.0 \), the detection limit of their photoelectron yield shifts to the higher-energy side with increasing \( x \) (decreasing Cu/In ratio). Figure 11 shows the energy levels of the VBM and CBM of the \( (1 - x)\text{Cu}_2\text{Se}-(x)\text{In}_2\text{Se}_3 \) samples from the vacuum level. The ionization energies of \( \text{CuIn}_2\text{Se}_2 \) and \( \text{CuIn}_5\text{Se}_8 \) are 5.65 and 5.75 \text{--} 5.95 eV, respectively. The energy level of the VBM of \( \text{CuIn}_2\text{Se}_2 \) is -5.25 and -4.26 eV (electron affinity), respectively.

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in the PYS measurement. We could not separate the two VBMs of the two different crystalline phases.

By adding the value of the optical band gap (in Fig. 9) to the VBM, the estimated energy levels of the CBM for CuInSe2, CuIn5Se8, and CuIn3Se5 are $-4.26$, $-4.48$, and $-4.53$ to $4.71$ eV, respectively. The energy level of the CBM also decreases with increasing $x$ (decreasing Cu/In ratio), but the difference in the energy level of the CBM between CuInSe2 and CuIn5Se8 (0.22 eV) is smaller than that of the VBM (0.4 eV). The energy levels of the VBMs of the Cu-poor CIS samples decrease significantly with decreasing Cu/In ratio.

The results obtained in this paper suggest that the energy level of the VBM of a Cu-poor CIS film can be controlled by the Cu/In ratio. In particular, CuIn3Se5 is expected to be useful for controlling the valence band offset ($\Delta E_v$) of a CIS solar cell. CuIn5Se8 has a tetragonal stannite-type crystal structure, which is similar to the chalcopyrite structure of CuInSe2 (not similar to hexagonal CuIn5Se8). It has a wider band gap than with CuInSe2, and the energy levels of the VBMs are deeper below the vacuum level than that of CuInSe2. Most recently, Nishimura et al. reported the control of the valence offset at a CdS/Cu(In,Ga)Se2 interface to reduce the interfacial recombination in CIGS solar cells.\textsuperscript{46} Cu(In,Ga)3Se5 layers (5–30 nm) were inserted into the CdS/Cu(In,Ga)Se2 interface of CIGS solar cells with a flat band profile for the Cu(In,Ga)3Se2 layers with band-gap energies of 1.2 and 1.4 eV. They found that the open-circuit voltage ($V_{OC}$) for a CIGS film with a flat band profile was clearly improved from 0.66 to 0.75 V for the band gap of 1.4 eV, although $V_{OC}$ was only increased from 0.63 to 0.64 V for the band gap of 1.2 eV. Then, a Cu(In,Ga)3Se2 layer was applied at the CdS/CIGS interface for a CIGS film with a single-graded band profile having an average band gap of 1.4 eV. They achieved a conversion efficiency of 14.4% and $V_{OC}$ of 0.72 V when 30-nm-thick Cu(In,Ga)3Se5 was inserted, although the conversion efficiency and $V_{OC}$ were 10.5% and 0.57 V without the Cu(In,Ga)3Se2 layer, respectively. They suggested that the valence band offset $\Delta E_v$ is important to suppress the interfacial recombination by repelling holes at the CdS/CIGS interface.

3.4 Band structure of Cu-poor CIS samples

We performed first-principles band structure calculations on tetragonal CuInSe2 and CuIn3Se5 to understand the electronic structure of Cu-poor CIS compounds. The structural optimization calculation for a perfect crystal of CuInSe2 was performed using the chalcopyrite-type unit cell (I$\bar{4}$2$d$) with 16 atoms. The lattice parameters $a$ and $c$ and the internal atomic position ($u$-parameter) of the Se atom, $u$(Se), in the chalcopyrite structure were optimized by minimizing the total energy at 0 K. The relaxation procedures were truncated when all the residual forces for the relaxed atoms were less than 0.01 eV/Å. For CuInSe2, the chalcopyrite-type unit cell (space group: I$\bar{4}$2$d$) with the lattice parameters $a = 5.776(4)$ Å, $c = 11.6117(7)$ Å, and $c/a = 2.01$ (ICSD #86872) was employed as the initial model.

For Cu-poor CIS samples, a virtual model of tetragonal CuIn3Se5 with the stannite-type unit cell was constructed. The virtual tetragonal CuIn3Se5 includes two Cu vacancies and one InCu antisite (2VCu + InCu) in the tetragonal unit cell. The defect formation energy and electronic structure of CIS have been theoretically studied in detail by the basic sciences research group of the National Renewable Energy Laboratory (NREL).\textsuperscript{53} In 1998, they calculated the formation energies of atomic vacancies (V$_{Cu}$ and V$_{In}$), antisite atoms (Cu$_{In}$ and In$_{Cu}$), the interstitial atom (Cu$_i$), and defect pairs such as (2VCu + In$_{Cu}^+$) and (V$_{Cu}$ + V$_{In}$) and defect pairs of CIS such as (2VCu$^-$ + In$_{Cu}^+$) and those of CuGaSe$_2$ (CGS) and CuAlSe$_2$ (CAS), which were calculated using the different atomic chemical potentials of the constituent elements.\textsuperscript{13} In CIS, the formation energies of the Cu vacancy (V$_{Cu}$) and defect pairs (2VCu$^-$ + In$_{Cu}^+$) are smaller than those of other types of defects, especially under Cu-poor conditions. In the previous work, the band-gap energy of CIS was considerably underestimated because DFT using the LDA and GGA usually underestimates the band-gap energy. For this reason, the band-gap energy of CIS was corrected to match the experimental value. In this study, the band structures of chalcopyrite CuInSe2 and virtual tetragonal stannite-type CuIn3Se5 were calculated with the HSE06 functional in order to improve the theoretical band-gap energy.

The initial crystal structure model for the virtual tetragonal stannite-type CuIn$_3$Se$_5$ (I$\bar{4}$2$m$) with 16 atoms was made using the lattice parameters $a = 5.735(2)$ Å, $c = 11.49(3)$ Å, and $c/a = 2.00$, which were experimentally determined by Rietveld analysis of the XRD data. After the geometric optimization, the band structures of chalcopyrite CuInSe2 and virtual tetragonal stannite-type CuIn3Se5 [shown in Fig. 2(c)] were calculated with the HSE06 functional.

Figures 12(a) and 12(b) show the calculated band structure of chalcopyrite CuInSe2 (a) and virtual tetragonal stannite-type CuIn3Se5 (b). In the calculated band structures, the VBMs of CuInSe2 and CuIn3Se5 are set to 0 eV. The band structure of the chalcopyrite-type CuInSe2 shows that both the VBM and the CBM are located at the $\Gamma$-point. Therefore, CuInSe2 has a direct band gap ($\Gamma$–$\Gamma$). Both the VBM and CBM of tetragonal stannite-type CuIn3Se5 are also located at the $\Gamma$-point, and CuIn3Se5 has a direct band gap ($\Gamma$–$\Gamma$). The band-gap energy of CuIn3Se5 calculated with the HSE06 functional is 0.94 eV. This value is slightly underestimated in comparison with the reported experimental value of 1.0 eV.
1.04 eV. However, the band-gap energy of CuInSe₂ calculated with the HSE06 functional is considerably improved in comparison with that calculated with the GGA functional of 0.94 eV.

The theoretically calculated band-gap energy of virtual tetragonal stannite-type CuIn₅Se₈ (1.19 eV) is larger than that of chalcopyrite-type CuIn₅Se₈ (0.94 eV). Both the theoretical and experimental direct band gaps of stannite-type CuIn₅Se₈ are wider than those of chalcopyrite-type CuIn₅Se₈. The difference in the theoretical band-gap energy between the chalcopyrite-type CuInSe₂ and stannite-type CuIn₅Se₈ is 0.25 eV. This theoretical prediction agrees with our experimental band-gap energy. We conclude that the band gaps of CuIn₅Se₈ are wider than those of chalcopyrite-type CuInSe₂. The VBMs of CuInSe₂ and CuIn₅Se₈ are set to 0 eV. Calculations of the chalcopyrite-type CuInSe₂. For the virtual stannite-type CuIn₅Se₈, two VCu and one InCu are included in the unit cell. With decreasing Cu/In ratio, the concentration of Cu atom in the unit cell decreases and Cu atoms in the chalcopyrite CuInSe₂ are gradually replaced by Cu vacancies and In antisites. On average, the Se atoms of stannite-type CuIn₅Se₈ are coordinated by 1/2 Cu atom, two In atoms and 1/2 InCu atom, and one V₁Cu. The calculated bond length of Cu–Se in the virtual stannite-type CuIn₅Se₈ (2.45 Å) is longer than that in the chalcopyrite-type CuInSe₂ (2.429 Å). Therefore, the dispersion of the antibonding orbital of Cu 3d + Se 4p at the top of the valence band becomes flat and the energy level of the VBM becomes lower. NREL’s group¹² provided an explanation that the increase in the band gap of CuIn₅Se₈ is caused by reduced Se 4p–Cu 3d interband repulsion due to the diminished Cu d character caused by Cu vacancies.

The bond length of In₃Cu–Se (2.625 Å) in the virtual stannite-type CuIn₅Se₈ is shorter than that of In–Se in the chalcopyrite-type CuInSe₂ (2.645 Å). However, the bond lengths between the second-nearest-neighbor In atom (In₂nd) of the InCu antisite and the surrounding Se atoms are affected by formation of In₄Cu and V₁Cu. There are two different bond lengths for In₂nd–Se (2.627 and 2.705 Å). The bond length of 2.705 Å is much longer than that in the chalcopyrite-type CuInSe₂ (2.645 Å). The orbital of the CBM for the chalcopyrite-type CuInSe₂ is dispersed from VBM + 0.94 eV to VBM + 3.00 eV, while those for the stannite-type CuIn₅Se₈ disperse from VBM + 1.19 eV to VBM + 3.00 eV. The dispersion of the antibonding orbital of In 5s + Se 4p at the CBM is also flat. Thus, the energy level of the CBM also decreases with decreasing Cu/In ratio.

4. Conclusions

To clarify the detailed crystallographic and optical properties of Cu-poor CIS compounds, we synthesized Cu-poor CIS samples such as CuInSe₂, CuIn₃Se₅, and CuIn₅Se₈ in the composition of (1 − x)Cu[subscript]x-Se–(x)In[subscript]₁Cu[subscript]₁Se with 0.5 ≤ x ≤ 1.0 by a mechanochemical process and post-heating. XRD data showed that the crystal structure of the sample changed from a tetragonal chalcopyrite-type (x = 0.5 and 0.55) to tetragonal stannite-type (0.60 ≤ x ≤ 0.75) with increasing x (decreasing Cu/In ratio). For the samples with 0.80 ≤ x ≤ 0.95, the diffraction peaks were identified to be those of a mixed phase of the tetragonal and hexagonal structures. The band-gap energies of the Cu-poor CIS samples increase in a stepwise manner with increasing x (decreasing Cu/In ratio). The band-gap energies of the Cu-poor CIS samples, i.e., CuIn₃Se₅ (1.17 eV) and CuIn₅Se₈ (1.22–1.24 eV), were larger than that of chalcopyrite-type CuInSe₂ (0.99 eV). The difference between the experimental and theoretical band-gap energy for the chalcopyrite-type CuInSe₂ and stannite-type CuIn₅Se₈ was about 0.25 eV. We considered that the samples with x = 0.60 and 0.65 are a mixed phase of chalcopyrite- and stannite-type structures because of the two-step shape of their diffuse reflectance spectra. The energy levels of the VBM from the vacuum level were estimated from the ionization energies by PYS measurements. The energy level of the VBM of stannite-type CuIn₅Se₈ (−5.65 eV) is deeper than that of chalcopyrite-type CuInSe₂ (−5.25 eV). The energy levels of the VBM of the Cu-poor CIS samples decrease significantly with decreasing Cu/In ratio. From the results of first-principles calculation, the band-gap energy of tetragonal stannite-type CuIn₅Se₈ (1.19 eV) calculated with the HSE06 functional is larger than that of chalcopyrite-type CuInSe₂.
(0.94 eV). The band gaps of CuIn\textsubscript{3}Se\textsubscript{5} and CuIn\textsubscript{5}Se\textsubscript{8} with a tetragonal stannite-type structure are widened by lowering the orbital of the valence band.

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1. A. Chirilă, P. Reinhard, F. Pianezzi, P. Bloesch, A. R. Uhl, C. Fella, L. Kranz, D. Keller, C. Gretenre, H. Hagendorfer, D. Jaeger, R. Erni, S. Nishiwaki, S. Buecheler, and A. N. Tiwari, *Nat. Mater.*, 12, 1107 (2013).
2. M. Nakamura, N. Yoneyama, K. Horiguchi, Y. Iwata, K. Yamaguchi, H. Sugimoto, and T. Kato, *Conf. Rec. 40th IEEE Photovoltaic Specialists Conf.*, 2014, p. 107.
3. P. Jackson, D. Harisikos, R. Wuerz, O. Kiovski, A. Bauer, T.-M. Friedlmeier, and M. Powalla, *Phys. Status Solidi C*, 11, 04ES15 (2016).
4. T. Wada and T. Maeda, *Jpn. J. Appl. Phys.*, 55, 04ES15 (2016).
5. S. Yamazoe, H. Kou, and T. Wada, *J. Mater. Res.*, 26, 1504 (2011).
6. T. Wada and H. Kinoshita, *J. Phys. Chem. Solids*, 66, 1987 (2005).
7. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, and M. C. Payne, *Z. Kristallogr.*, 220, 567 (2005).
8. J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.*, 118, 8207 (2003).
9. J. E. Peralta, J. Heyd, G. E. Scuseria, and R. L. Martin, *Phys. Rev. B*, 74, 073101 (2006).
10. D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.*, 45, 566 (1980).
11. J. Perdew and A. Zunger, *Phys. Rev. B*, 23, 5048 (1981).
12. J. P. Perdew, J. A. Chevary, K. A. Jackson, M. R. Pederson, D. J. Singh, S. H. Vosko, and C. Fiolhais, *Phys. Rev. B*, 46, 6671 (1992).
13. A. D. Becke, *J. Chem. Phys.*, 96, 2155 (1992).
14. D. Vanderbilt, *Phys. Rev. B*, 41, 7892 (1990).
15. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 54, 11169 (1996).
16. M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.*, 64, 1045 (1992).
17. W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, Cambridge, U.K., 1992) 2nd ed., p. 418.
18. K. Takei, T. Maeda, and T. Wada, *Thin Solid Films*, 582, 263 (2015).
19. F. Gao, S. Yamazoe, T. Maeda, K. Nakamishi, and T. Wada, *Jpn. J. Appl. Phys*, 51, 10NC29 (2012).
20. M. León, R. Serena, S. Levecenko, A. Nicorici, J. M. Merino, E. J. Friedrich, and E. Arushanov, *J. Appl. Phys.*, 103, 103503 (2008).
21. F. Jiang and J. Feng, *Appl. Phys. Lett.*, 89, 221920 (2006).
22. H. B. Michaelson, *J. Appl. Phys.*, 48, 4729 (1977).
23. W. Jaegermann, T. Löher, and C. Pettenkofer, *Cryst. Res. Technol.*, 31, 273 (1996).
24. H. Sakakima, M. Nishitani, K. Yamamoto, and T. Wada, *Jpn. J. Appl. Phys.*, 54, 08KC07 (2015).
25. T. Negami, Y. Hirai, Y. Kurokawa, and A. Yamada, *Jpn. J. Appl. Phys.*, 54, 08KC08 (2015).