

Crystallographic and optical properties and band diagrams of CuGaS_2 , CuGa_3S_5 , and CuGa_5S_8 phases in Cu-poor Cu_2S - Ga_2S_3 pseudo-binary system

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Abstract

We synthesized Cu-poor Cu-Ga-S samples such as CuGaS_2 , CuGa_3S_5 , and CuGa_5S_8 in the composition of $(1-x)\text{Cu}_2\text{S}-(x)\text{Ga}_2\text{S}_3$ with $0.5 \leq x \leq 1.0$. The crystal structure of the sample changed from a tetragonal chalcopyrite-type ($0.50 \leq x \leq 0.60$) to tetragonal stannite-type ($0.75 \leq x \leq 0.85$) with increasing x (decreasing Cu/Ga ratio). For the samples with $0.65 \leq x \leq 0.70$, the diffraction peaks were identified to be those of a mixed phase of the chalcopyrite-type and stannite-type structures. The band-gap energies of the Cu-poor Cu-Ga-S samples increase in a stepwise manner with increasing x . The band-gap energy of 2.61 eV for CuGa_3S_5 and around 2.66-2.72 eV for CuGa_5S_8 is larger than that of chalcopyrite-type CuGaS_2 (2.45 eV). The energy levels of the valence band maximum (VBM) and conduction band minimum (CBM) of the Cu-poor Cu-Ga-S samples decrease significantly with decreasing Cu/Ga ratio.

1. Introduction

CuInSe_2 (CIS), Cu(In,Ga)Se_2 (CIGS), and related compounds have attracted attention as the most promising materials for thin-film photovoltaic devices. In the Cu_2Se - In_2Se_3 pseudo-binary system [1], tetragonal chalcopyrite-type CuInSe_2 (Cu/In=1) and some Cu-poor compounds such as tetragonal stannite-type CuIn_3Se_5 (Cu/In=0.33) and tetragonal and hexagonal CuIn_5Se_8 (Cu/In=0.2) phases have been reported [2]. CuIn_3Se_5 is expected to be useful for controlling the valence band offset (ΔE_v) at CdS/CIS interface in a CIS solar cell. Recently, Nishimura *et al.* reported the control of the valence band offset at a CdS/ Cu(In,Ga)Se_2 interface by the insertion of thin $\text{Cu(In,Ga)}_3\text{Se}_5$ layer to reduce the interfacial recombination in CIGS solar cells [3]. They suggested that the valence band offset ΔE_v is important to suppress the interfacial recombination by repelling holes in CIGS layer near the CdS/CIGS interface.

Recently, we reported crystallographic and optical properties of CuInSe_2 , CuIn_3Se_5 , and CuIn_5Se_8 phases in a Cu-poor $(1-x)\text{Cu}_2\text{Se}-(x)\text{In}_2\text{Se}_3$ pseudo-binary system [4]. The crystal structure of the sample changed from chalcopyrite-type CuInSe_2 to hexagonal CuIn_5Se_8 through a stannite-type CuIn_3Se_5 with increasing x (decreasing Cu/In ratio). The band-gap energies of the Cu-poor Cu-In-Se samples increase in a stepwise manner with decreasing Cu/In ratio. The band-gap energies of the Cu-poor Cu-In-Se samples, i.e. CuIn_3Se_5 (1.17 eV) and CuIn_5Se_8 (1.22-1.24 eV), were larger than that

of chalcopyrite-type CuInSe_2 (0.99 eV). The energy levels of the valence band maxima (VBMs) of the Cu-poor Cu-In-Se samples decrease with decreasing Cu/In ratio.

Most recently, conversion efficiency of 15.5% was achieved on a pure-sulfide Cu(In,Ga)S_2 (CIGS) solar cell [5]. We studied $\text{CuIn}_3(\text{S,Se})_5$ and $\text{CuGa}_3(\text{S,Se})_5$ systems [6]. Single-phase solid solutions with a tetragonal stannite-type structure could not be obtained for $\text{CuIn}_3(\text{S}_x\text{Se}_{1-x})_5$ with $0.1 \leq x < 0.1$. On the other hand, we successfully obtained single-phase solid solutions for $\text{CuGa}_3(\text{S}_x\text{Se}_{1-x})_5$ with $0.0 \leq x \leq 1.0$. In the reported phase diagram of the Cu_2S - Ga_2S_3 [7] system, CuGa_3S_5 does not exist, but CuGa_5S_8 with unknown crystal structure exists in the Cu-poor side of CuGaS_2 .

To clarify the crystallographic and optical properties of Cu-poor Cu-Ga-S compounds, we synthesized the $(1-x)\text{Cu}_2\text{S}-(x)\text{Ga}_2\text{S}_3$ ($0.5 \leq x \leq 1.0$) samples. We investigated crystallographic and optical properties of the Cu-poor Cu-Ga-S samples. Then we determined their band gap energies and ionization energies.

2. Experimental procedures

In order to prepare the Cu-Ga-S powder samples on the Cu-poor side of the Cu_2S - Ga_2S_3 pseudo-binary system, starting materials of elemental powders such as Cu, Ga, and S were weighed to give a molar ratio of $(1-x)\text{Cu}_2\text{S}-(x)\text{Ga}_2\text{S}_3$ ($x=0.50, 0.55, 0.60, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, 1.0$). The chemical compositions of the samples with $x=0.50, 0.75$, and 0.83 correspond to CuGaS_2 (Cu/Ga=1), CuGa_3S_5 (Cu/Ga=0.33), and CuGa_5S_8 (Cu/Ga=0.2), respectively. The milling was conducted in a planetary ball mill (Fritsch premium line P-7) under a rotational speed of 800 rpm for 20 min in a N_2 gas atmosphere. The mixed powders were annealed at 550 °C for 30 min in a N_2 gas atmosphere.

The phases in the obtained powders were identified by X-ray powder diffraction (XRD) using Cu-K α radiation. The band-gap energies of the samples were determined from the diffuse reflectance spectra of the ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy (JASCO V-670DS). The ionization energy of the samples was directly measured by photoemission yield spectroscopy (PYS) (Bunkoukeiki: BIP-KV201). The energy levels of the VBM were estimated from the ionization energies to discuss their band diagrams.

3. Results and discussion

Figure 1 shows the XRD patterns of the $(1-x)\text{Cu}_2\text{S}$ -

(x)Ga₂S₃ with $0.5 \leq x \leq 1.0$. The crystal structure of the sample changed from a tetragonal chalcopyrite-type ($0.50 \leq x \leq 0.60$) to tetragonal stannite-type ($0.75 \leq x \leq 0.85$) with increasing x (decreasing Cu/Ga ratio). For the samples with $0.65 \leq x \leq 0.70$, the diffraction peaks were identified to be those of a mixed phase of the tetragonal chalcopyrite-type and tetragonal stannite-type structures. For the samples with $0.90 \leq x \leq 0.95$, the diffraction peaks are identified to be the mixed phases of the tetragonal stannite-type structure and Ga₂S₃ structures. It is understood from the present study that tetragonal stannite-type CuGa₃S₅ and CuGa₅S₈ exist in the Cu-poor side of CuGaS₂. These are the difference from the Cu₂S-In₂S₃ pseudo-binary system. In the Cu₂S-In₂S₃ system, CuIn₅S₈ does not have stannite-type but spinel-type structure.

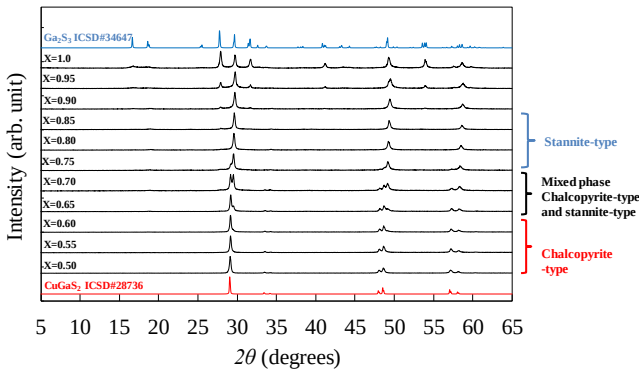


Fig. 1 X-ray diffraction patterns of the (1-x)Cu₂S-(x)Ga₂S₃ samples with $0.5 \leq x \leq 1.0$.

Figure 2 shows the band-gap energies of (1-x)Cu₂S-(x)Ga₂S₃ estimated from the reflectance spectra. The determined band-gap energies of (1-x)Cu₂S-(x)Ga₂S₃ with $x = 0.5$ and 0.55 in the tetragonal chalcopyrite phase are 2.45 and 2.46 eV, respectively. These values are in good agreement with the reported value of CuGaS₂ (2.43 eV) [8]. The band-gap energies of the Cu-poor Cu-Ga-S samples increase in a stepwise manner with increasing x. The band-gap energy of 2.61 eV for CuGa₃S₅ ($x = 0.75$, Cu/Ga = 0.33) with the tetragonal stannite phase is larger than that of chalcopyrite-type CuGaS₂ (2.45 eV). Moreover, the band-gap energy of CuGa₅S₈ ($x = 0.83$, Cu/Ga = 0.2) with the tetragonal stannite-type phase is around 2.66-2.72 eV, which is larger than that of chalcopyrite-type CuGaS₂ and stannite-type CuGa₃S₅.

Figure 3 shows the energy levels of the VBM and the conduction band minimum (CBM) of the (1-x)Cu₂S-(x)Ga₂S₃ samples from the vacuum level. The VBM level of CuGaS₂ determined from the ionization energy measured by PYS (-5.85 eV) is deeper than those of CuInS₂ (-5.54 eV) and CuInSe₂ (-5.25 eV) [4]. The ionization energy of the Cu-poor Cu-Ga-S sample measured by PYS corresponds to the VBM level from the vacuum level. The ionization energies of CuGa₃S₅ and CuGa₅S₈ are 6.39 and 6.42-6.61 eV, respectively. The energy levels of the VBMs of the Cu-poor Cu-Ga-S samples decrease significantly with decreasing Cu/Ga ratio. The energy level of the CBM can also be determined by adding the value of the optical band gap (in Fig. 2) to the

VBM. The energy level of the CBM also decreases with increasing x (decreasing Cu/Ga ratio).

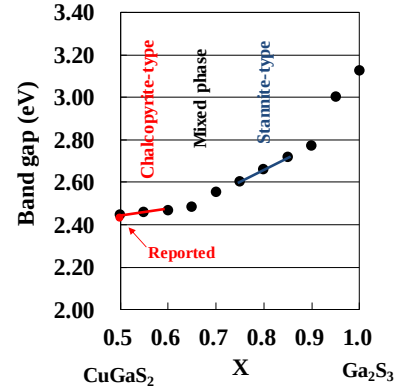


Fig. 2 Band-gap energies of the (1-x)Cu₂S-(x)Ga₂S₃ samples with $0.5 \leq x \leq 1.0$ estimated from their reflectance spectra.

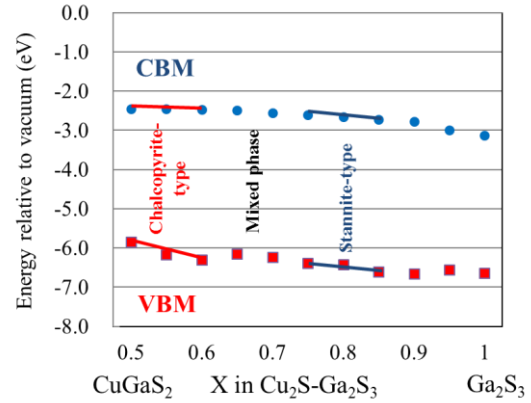


Fig. 3 Energy levels of the VBM and the CBM of the (1-x)Cu₂S-(x)Ga₂S₃ samples from the vacuum level

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