CRYSTALLOGRAPHIC, AND OPTICAL PROPERTIES OF CHALCOPYRITE-TYPE (Cu_{1-x}Ag_x)InSe_2 AND STANNITE-TYPE (Cu_{1-x}Ag_x)In_3Se_5 AND (Cu_{1-x}Ag_x)In_5Se_8 SYSTEMS

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Recently, we reported the crystallographic and optical properties of CuInSe_2, CuIn_3Se_5, and CuIn_5Se_8 phases in the Cu_2Se-In_2Se_3 system [1]. The crystal structure changed from chalcopyrite-type CuInSe_2 to stannite-type CuIn_3Se_5 with increasing In_2Se_3 content. CuIn_3Se_5 and CuIn_5Se_8 have a deeper valence band maximum (VBM) from the vacuum level, and they are expected to be useful for controlling the valence band offset ($\Delta E_V$) and conduction band offset ($\Delta E_C$) at the CdS/Cu(In,Ga)_3Se_5/Cu(In,Ga)Se_2 interface in CIGS solar cells. A Tokyo Institute of Technology group fabricated Ag(In,Ga)Se_2 solar cell with a conversion efficiency of 10.7% for a chalcopyrite-material-based tandem solar cell [2]. AgInSe_2 has a chalcopyrite structure, and a wider band gap (1.24 eV) than that of CuInSe_2 (1.04 eV). In the Ag:Se-In:Se system [3], a small region of the AgInSe_8 phase exists in the Ag-poor side of AgInSe_2.

In this study, we prepared the (Cu_{1-x}Ag_x)InSe_2, (Cu_{1-x}Ag_x)In_3Se_5 and (Cu_{1-x}Ag_x)In_5Se_8 (0.0 ≤ x ≤ 1.0) powders by a mechano-chemical process of the elemental Cu, Ag, In and Se powders and sequential heating in N_2 gas atmosphere. From X-ray diffraction (XRD) analyses, (Cu_{1-x}Ag_x)InSe_2 solid solution samples were successfully obtained for 0.0 ≤ x ≤ 1.0. Figure 1 shows the XRD patterns of the (Cu_{1-x}Ag_x)InSe_2 powders. All the XRD peaks are in good agreement with those for the chalcopyrite-type structure and shift to the lower angle side with increasing Ag content, x. For XRD patterns of the (Cu_{1-x}Ag_x)In_3Se_5 system, most of the diffraction peaks were in good agreement with those for the stannite-type structure and shifted to the lower angle side with increasing x. However, in their XRD patterns, small diffraction peaks of the chalcopyrite phase were observed for the samples with x ≥ 0.1. Therefore, we considered that single-phase (Cu_{1-x}Ag_x)In_3Se_5 solid solutions were obtained for the sample with x = 0.0 and 0.1. The samples with x > 0.1 were almost the single phase of the stannite-phase with a small amount of the chalcopyrite phase. The band-gap energies were determined by the diffuse reflectance spectra. The band-gap energy of the (Cu_{1-x}Ag_x)InSe_2 samples increased from 1.00 eV for CuInSe_2 to 1.22 eV for AgInSe_2. The energy level of the valence band maximum (VBM) from the vacuum level was estimated from the ionization energy measured by photoelectron emission spectroscopy (PYS). The energy levels of the conduction band minimum (CBM) could also be determined by adding the value of the band gap energy to the VBM level. Figure 2 shows the energy levels of the VBMs and CBMs of the (Cu_{1-x}Ag_x)InSe_2 samples. The VBMs of the (Cu_{1-x}Ag_x)InSe_2 samples clearly decrease from -5.29 eV for CuInSe_2 to -5.80 eV for AgInSe_2. On the other hand, the CBMs slightly decrease with increasing Ag content. For the (Cu_{1-x}Ag_x)In_3Se_5 system, their band gap energy increased from 1.16 eV for CuIn_3Se_5 to 1.44 eV for AgIn_3Se_5. The energy levels of the VBMs of the (Cu_{1-x}Ag_x)In_3Se_5 solid solution samples also decreased with increasing Ag content, while the CBMs slightly decreased, as is the case for (Cu_{1-x}Ag_x)InSe_2.

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