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Growth of single-phase $CuInGaSe_2$ photo-absorbing alloy films by the selenization method using diethylselenide as a less-hazardous Se source

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Abstract

Selenization growth of purely single-phase, polycrystalline $CuIn_{1-x}Ga_xSe_2$ ($0 \leq x \leq 1$) alloy films was demonstrated using a less-hazardous metalorganic selenide, diethylselenide [$(C_2H_5)_2Se$: DESe], without additional thermal annealing. Approximately 2.0-μm-thick films of the alloys exhibited X-ray diffraction peaks originating exclusively from the chalcopyrite structure. Low temperature photoluminescence spectra of the alloy films were dominated by a couple of characteristic donor-acceptor pair emissions that are particular to the state-of-the-art $CuInGaSe_2$ photo-absorbing layers.
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1. Introduction

Chalcopyrite-structure $Cu(In,Ga)(S,Se)_2$ alloys [1] are attracting attention as a promising candidate for the light-absorbing medium of high conversion efficiency (η), low cost, lightweight, and radiation-resistant solar cells. In fact, polycrystalline $CuIn_{1-x}Ga_xSe_2$ (CIGS)-based solar modules with η approximately 13% have been put into practical use [2]. For large-area application purposes, selenization methods, which are reactive solid-phase growth methods, using H_2Se gas [3–6] or elemental Se vapor [7–9] are the most promising preparation techniques for yielding high quality CIGS thin films. Distinct from multisource physical vapor deposition or metalorganic chemical vapor deposition, this process is fairly simple and does not require expensive apparatus. However, the growth of large-size, homogeneous CIGS alloys is difficult in the case of selenization with elemental Se vapor due to the limitation on the location of the Se reservoir. Also, because H_2Se is highly toxic and is usually stored in high-pressure cylinders, the handling and environmental effects of concerns are involved. As an alternative to these Se sources, the authors have proposed the use of diethylselenide [$(C_2H_5)_2Se$: DESe], which is one of the organoselenium liquids, as a selenization source for the growth of $CuInSe_2$ (CIS) compound [10,11] and CIGS alloys with a small $CuGaSe_2$ (CGS) molar fraction x ($0 \leq x \leq 0.29$) [12]. As a result, densely packed, single-phase, adhesive polycrystalline films have been obtained. Since DESe is liquid at room temperature and is stored in stainless-steel cylinders under atmospheric pressure, the danger of widespread leakage is less likely than in the case of H_2Se.

The $CuIn_{0.4}Ga_{0.6}Se_2$ alloy has the ideal bandgap (Eg ≈ 1.4 eV) for solar cell applications. However, the growth of $CuIn_{0.4}Ga_{0.6}Se_2$ as well as $CuIn_{1-x}Ga_xSe_2$ solid solutions with high CGS molar fraction, x, is known to be difficult because of the phase separation or phase gradation between CIS and CGS along the growth direction [4,5]. This may be due to the difference in the reaction rates of the two end-point compounds. DESe decomposes into atomic Se more easily than H_2Se gas or Se vapor due to weaker bond strength of Se–C than Se–H or Se–Se [13,14]. Therefore, comparable reaction rates to form CIS and CGS can be expected, which may result in the preparation of segregation-free CIGS alloy films of high x. In this article, the advantage of using DESe is shown for the selenization growth of single-phase GIGS solid solutions of all compositions.

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2. Experiments

Sequentially stacked CuGa/CuIn/Cu layers with a total thickness of approximately 670 nm were used as the starting material. The layer structure is generally called as a 'precursor'. They were evaporated using three K-cells on unintentionally heated Mo-coated soda-lime glass (SLG) substrates. The Ga compound was placed near the surface of the *precursor*, because Se reacts more easily with In than with Ga. The gross thickness and molar fraction of Ga [Ga/(In+Ga)] of the *precursor* were controlled by *in-situ* monitoring of each layer thickness using a quartz crystal oscillator. Here we define the thickness fraction of CuGa by X=Ga/(In+Ga). The deposition pressure was 1×10^{-3} Pa. The *precursors* were selenized using DESe at 515 °C for 90 min under atmospheric pressure. The flow rates of DESe and the N_2 carrier gas were 35 μmol/min and 2 L/min, respectively. The details of the selenization equipment have been described in our previous reports [11,12].

The surface morphology was observed with a scanning electron microscope (SEM). Lattice constants and the crystal phase were evaluated by X-ray diffraction (XRD) measurements. The value of x in the CIGS films was determined from the lattice parameter assuming Vegard's law. Electron-probe microanalysis (EPMA) was also carried out to quantify the solid concentrations of the constituent atoms. Photoluminescence (PL) was excited by the 532.0 nm line of a frequency-doubled quasi-cw Nd:YAG laser (60 mW) and dispersed by a 50-cm-focal-length grating monochromator. The phase-sensitive detection was carried out using a GaAs:Cs photomultiplier and a liquid-N_2-cooled Ge photodetector.

3. Results and discussion

By the selenization technique using DESe, single-phase polycrystalline CIGS films with a thickness of approximately 2.0 μm were formed. The CIGS films (x=0.1, 0.4, 0.5, and 0.8) are composed of densely packed 1−3-μm-diameter columnar grains, as shown in the surface SEM images in Fig. 1. The films adhered well to the Mo/SLG substrate, which was confirmed by the peeling test.

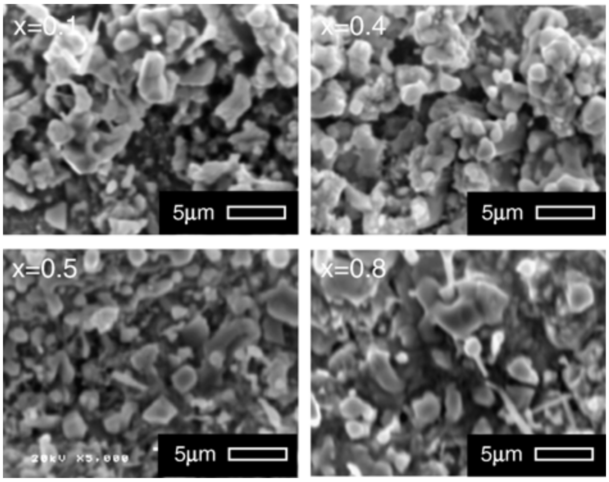

Fig. 1. SEM images of $CuIn_{1-x}Ga_xSe_2$ films (x=0.1, 0.4, 0.5, and 0.8).

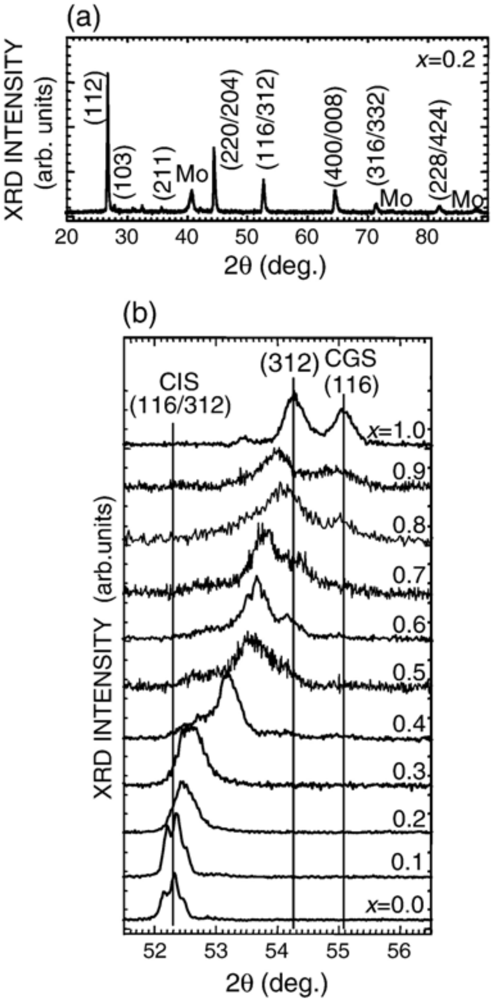

Fig. 2. XRD patterns of (a) a $CuIn_{0.8}Ga_{0.2}Se_2$ film, (b) CIGS films as a function of x. The expected angles of (312) (116) diffraction peaks for CIS and CGS are indicated by vertical lines.

Representative XRD pattern of a $CuIn_{0.8}Ga_{0.2}Se_2$ film is shown in Fig. 2(a). The result shows that single-phase CIGS solid solution without any secondary phases such as $(In,Ga)_2Se_3$ or Cu_2Se was successfully obtained. Phase separation was also examined by XRD measurements. The XRD patterns of the $CuIn_{1-x}Ga_xSe_2$ films near the (312) and (116) diffraction peak angles are shown in Fig. 2(b). The expected diffraction angles of the peaks due to CIS and CGS are represented by solid vertical lines. As shown, single-phase CIGS alloys of entire molar fractions were successfully formed; *i.e.* distinct peaks corresponding to CIS, CGS, or any combination of the two phases were not observed. In general, when conventional H_2Se gas or elemental Se vapor is used as a selenization source, In tends to diffuse toward the surface and Ga toward the substrate, leading to phase separation or gradation into CIS and CGS [4,5,9]. The achievement of single-phase CIGS solid solution without the external annealing indicates the superiority of using DESe as a selenization source. The diffraction peaks shifted to the higher angle with an increase in x. This result indicates a decrease in