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Solution growth of chalcopyrite compounds single crystal

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ABSTRACT

I–III–VI_2 chalcopyrite compound Cu(In_x, Ga_{1-x})Se_2 (CIGS) single crystal were successfully grown by traveling heater method (THM). The powder X-ray diffraction (XRD) pattern of the CIGS showed preferred orientations of (112), (220) and (312) planes, confirming the chalcopyrite structure. In Raman spectra, the A_1 mode peaks expected for CIGS were observed, and no secondary phases were observed. The full-width at half-maximum (FWHM) of the X-ray rocking curve (XRC) for the (112) oriented CIGS single crystal is 103 arcsec. The composition of the CIGS single crystal was homogeneous and the stoichiometric ratio of CIGS was found to be slightly Cu-poor, In-rich, Ga-rich and Se-poor. The good-quality single-phase CIGS single crystals can be obtained from these results.

1. Introduction

The chalcopyrite Cu(In,Ga)Se_2 (CIGS) alloy system has received strong interest in recent years because of its potential for the development of high efficiency and low cost solar cells and modules. The bandgap energy can be varied between 0.9 and 1.68 eV by ratio of In and Ga and the absorption coefficient is very high of order 10^5 cm^{-1}. Cu deficiency also plays a role in determining the bandgap as well as in doping. CIGS thin film solar cells have recently demonstrated a record efficiency of 20.8%, the absolute record for all thin film photovoltaics [1]. Chalcopyrite based technologies have already entered the stage of industrial mass production, with commercial modules that provide stable efficiencies in the range of 12%–13% [2]. However, attaining higher efficiency at module scales is challenging due to the difficulty of controlling the production processes on large area substrates. There have been few recent fundamental studies on the growth and characterization of CIGS single crystals. The first of CIGS solar cell was based on a $CuInSe_2$ (CIS) single crystal and achieved 12% [3]. In this study we return to the starting line and investigate single crystals in order to gain insights that will lead to even higher efficiency.

It is generally difficult to grow high-quality single crystals of the I–III–VI_2 chalcopyrite compounds, because most of the compounds go through a peritectic reaction or solid state transition during the cooling process. CIGS single crystals can be grown by traveling heater method (THM), a solution growth technique, as we have demonstrated our previous studies [4,5]. Some advantages of THM growth are that the growth temperature is low compared with that of melt growth techniques and that larger crystals can be grown compared with conventional solution growth.

In this paper, large size CIGS single crystals were obtained by THM and characterized by using X-ray diffraction (XRD), Raman spectroscopy, X-ray rocking curve (XRC), electron probe microanalysis (EPMA) and Hall effect measurement.

2. Experimental procedure

A feed polycrystalline CIGS (In/Ga = 8/2) was synthesized by melting growth. Prescribed amounts of elemental copper, indium, gallium, and selenium, corresponding to the composition of stoichiometric CIGS, were charged into a quartz ampoule. The grades of copper and selenium were 5 N and that of indium and gallium were 6 N. The ampoule, charged with the elements, was sealed off after evacuation to a pressure of 10^{-6} Torr. Then the ampoule was inserted into a vertical furnace, heated to 1100 °C at a rate of 100 °C/h, and kept at this temperature for 24 h.

For the THM growth, an excess of In is added to the stoichiometric polycrystalline CIGS, which has mole fraction.

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$$X[\text{mol\%}] = \frac{\text{CIGS[mol]}}{\text{CIGS[mol]} + \text{In[mol]}} \times 100 \quad (1)$$

The polycrystalline CIGS solute ingots weighed approximately 50 g, and the desired weight of the In solvent was calculated from Eq. (1). The CIGS single crystal was grown from a single phase In solution with $X = 60–90$ mol% [5]. A polycrystalline CIGS feed ingot and the In solvent were charged into a carbon-coated quartz ampoule with a diameter of 16 mm. The ampoule was sealed under high vacuum (10^{-6} Torr), and then inserted into the THM furnace. Growth of the CIGS single crystal from the single phase liquid In solution was performed by pulling the ampoule through the THM furnace at a speed of 4–5 mm/day for 10 days at a temperature of 850 °C.

The CIGS sample's single crystal structure was examined by powder XRD using Cu-Ka radiation (tube voltage 40 kV, tube current 40 mA, and step size 0.01°). An Ar ion laser (514 nm) was used in the Raman spectroscopy, and focused on the sample using an objective lens with a numerical aperture (NA) of 0.55. The power of the incident laser was 100 mW on the sample. The orientation and crystallinity of CIGS single crystal were investigated by X-ray rocking curves (XRCs). The tube voltage, tube current and step width were 45 kV, 40 mA and 0.002°. The composition of the CIGS single crystals along the growth direction was determined by electron probe microanalysis (EPMA). The electrical properties were determined by Hall effect measurements, which were carried out using the Van der Pauw method at room temperature. The sample wafers were cut from the middle of the CIGS ingots and polished with 0.05 μm Al_2O_3 powder, and finally rinsed with de-ionized water. An Ohmic contact was made from In, because the thermoprobe analysis showed n-type conduction.

3. Results and discussion

It is successful to grow CIGS single crystal from $X = 80$ mol% In solution. A photograph of two $CuIn_{0.8}Ga_{0.2}Se_2$ single crystal wafers is shown in Fig. 1. The ingot was 16 mm in diameter and 40 mm in length, which is larger than other reports [4]. Fig. 2 shows the XRC for a (112) oriented CIGS single crystal wafer. The obtained CIGS crystallinity is very good, because the value of full-width at half-maximum (FWHM) is 103 arcsec.

The powder XRD patterns of CIGS single crystal at room temperature are shown in Fig. 3, and exhibit major peaks

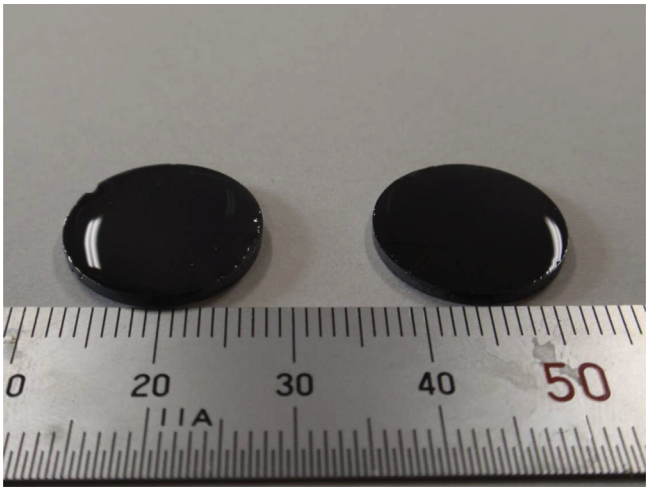

Fig. 1. The photograph of CIGS single crystal wafer.

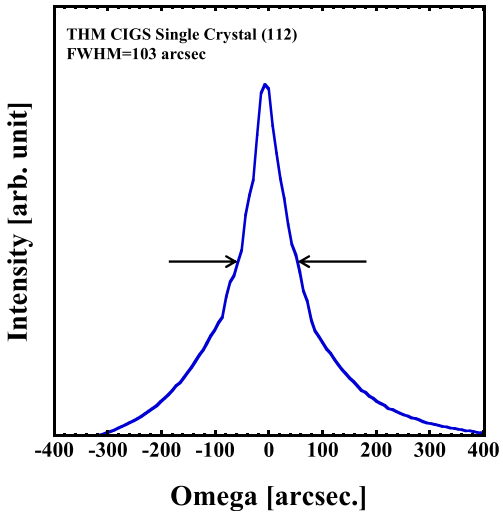

Fig. 2. The XRC of (112) oriented CIGS single crystal.

corresponding to diffraction lines of the chalcopyrite structure of CIGS (ICDD data #00-035-1102 $CuIn_{0.7}Ga_{0.3}Se_2$). No distinct peaks of secondary phases are observed in the XRD pattern. The diffraction peaks from (112), (220) and (312) planes were observed clearly in all samples indicating the formation of CIGS phase.

However, it is difficult to investigate single phase from XRD measurement because the peaks of CIGS almost correspond to that of Cu_2Se, especially. Therefore, Raman spectroscopy is useful to investigate the structure and phase purity of CIGS besides XRD. Raman spectroscopy was carried out at three different positions (centre and near both edges) on a wafer, and those spectra are shown in Fig. 4. The typical Raman peak of CIGS was observed at 175 cm^{-1}, which corresponds well to data for CIGS in the literature [6,7]. This peak is the A_1 symmetry mode which results from the motion of Se atom with the Cu and In (Ga) atoms. No Raman peaks of the secondary phases such as Cu_2Se 263 cm^{-1} were observed in the spectra [7]. Therefore, single phase CIGS was obtained, because

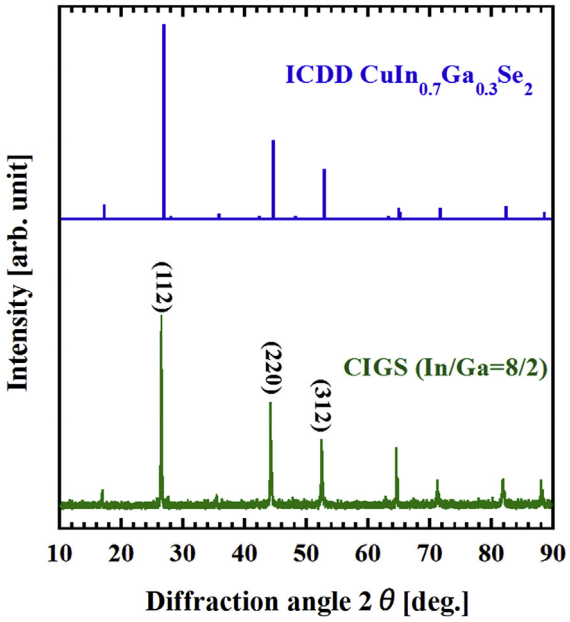

Fig. 3. The powder XRD of the CIGS single crystal grown with $X = 80$ mol%.