Research Article

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Solution growth of chalcopyrite $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ single crystals for high open-circuit voltage photovoltaic device

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Abstract: I–III–VI₂ Chalcopyrite $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ (CIGS) has attracted attention as absorbing layer in photovoltaic (PV) device. In this study, we investigated the fundamental properties of CIGS single crystals, and fabricated single crystal-based PV device. CIGS single crystals without secondary phase were successfully grown by In-solvent traveling heater method (THM). The conversion of conduction type from n- to p-type can be observed above 0.3 of Ga ratio x because of high acceptor defect concentration. PV device based on high-quality CIGS bulk single crystal demonstrates high open-circuit voltage of 0.765 V with the efficiency of 12.6%.

Keywords: $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$, photovoltaic, open-circuit voltage, single crystal, solution growth

1 Introduction

The I–III–VI₂ chalcopyrite compounds have received much attention due to its various energy application over the past few decades. Especially, $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ (CIGS) have been well known for its potential in the development of high-efficiency and low-cost photovoltaic (PV) device. The bandgap energy can be changed from 0.9 eV for CuInSe_2 (CIS) to 1.68 eV for CuGaSe_2 (CGS) by the ratio of In and Ga, which is suitable for PV absorber material. Recently, Solar Frontier

(Idemitsu Kosan) demonstrated a polycrystalline thin-film PV device with the highest conversion efficiency of 23.35% [1]. The commercial modules have already offered stable conversion efficiencies in the range of 17–19% [2]. However, it is difficult to obtain higher efficiency on a module scale due to the difficulty in controlling the manufacturing process on large area substrate. Recently, wide bandgap I–III–VI₂ chalcopyrite compounds have been the focus of intense study for developing wide-gap top cells in tandem structure cells.

Grain boundary, which is typically carrier traps in PV device, plays a significant role in the device conversion efficiency in CIGS device. A local built-in potential exists on grain boundaries of CIGS, which is caused by positive charges trapped at grain boundary. The potential barrier can attract electrons and repulse holes and thus help in the collection of minority carriers [3]. It is known that when the Ga content is above 28%, the conversion efficiency decreases due to the lack of potential at grain boundary [4]. However, experimental evidence about whether the potential barrier at the grain boundary benefits the PV device performance is still not clear. Single-crystal CIGS device is needed as counterpart to investigate the reliable properties at grain boundary in polycrystalline device. In recent years, single-crystal CIGS PV device grown by molecular beam epitaxy has demonstrated a high conversion efficiency of 20% due to NaF doping, KF post-deposition treatment, and Ga compositional grading [5]. There have been few recent fundamental studies on the growth and characterization of CIGS single crystal because thin-film PV device has become the mainstream of current research. Indeed, the first of CIGS solar cell was based on a CIS single crystal and achieved 12% efficiency [6]. Considering the abovementioned results, the investigations of both the properties of single-crystal and polycrystalline CIGS are required for further improvement in efficiency. Especially, single-crystal CIGS device will be helpful to reveal the correlation between PV properties and grain boundary.

We will return to the starting point and investigate the bulk single crystals for insights that lead to even

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higher efficiency. It is generally difficult to grow high-quality single crystals of the I–III–VI₂ chalcopyrite compounds. This is because most compounds undergo peritectic and/or solid phase transitions during the cooling process. CIGS single crystals can be grown by the traveling heater method (THM) based on a solution growth technique [7,8]. Some of the advantages of the THM growth are that the growth temperature is lower than melt growth technology and larger crystals can be grown compared to traditional solution growth. We investigated the fundamental properties of CIGS single crystals, and fabricated single crystal-based PV device.

2 Materials and methods

Feed polycrystalline of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ ($x = 0\text{--}0.5$) was synthesized by using a melting reaction [9]. Cu (99.9999%), In (99.9999%), Ga (99.9999%), and Se (99.9999%) shots corresponding to each Ga ratio of x were used as starting materials. Prior to growth, Cu, In, and Ga were chemically etched with HCl solution for 60 s and then rinsed in ultra-pure 18 MΩ water. The ingots (15 g) with nominal compositions were synthesized by mixing the described amounts of elements in a carbon-coated 2 mm wall thickness quartz ampoule with 9 mm inner diameter under high vacuum of 10^{-6} Torr and then flame-sealed off. In a vertical furnace, the sealed ampoule was heated at $200^\circ\text{C}\cdot\text{h}^{-1}$ to 650°C and held at this temperature for 24 h to react the constituents and prevent explosion from the Se overpressure. Then, the sealed ampoule was heated at $100^\circ\text{C}\cdot\text{h}^{-1}$ to $1,100^\circ\text{C}$ and held at this temperature for 24 h to complete the reaction and ensure homogenization. The ampoule was then removed from the furnace and allowed to cool rapidly in air.

X is defined as the mol% of the CIGS solute in the In solution in this study:

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

The mixture of CIGS and In with $X = 80$ mol% from equation (1) was loaded into a carbon-coated quartz ampoule with 2 mm wall thickness and 10 mm inner diameter. The ampoule was flame-sealed off under high vacuum of 10^{-6} Torr and then inserted into the THM furnace. The THM furnace has three coil heaters (upper, main, and bottom) for controlling temperature gradient [10,11]. The upper heater temperature of 800°C was used to prevent a Se deficiency in the grown CIGS crystal. The Se species evaporated from liquid zone condensed on the cold wall of the ampoule without heating the upper part, thereby reducing the Se mole fraction in the crystal. For the THM growth, the main heater temperature (growth temperature) was 850°C which is 50°C higher than the liquids' temperature, and temperature gradient between the main and bottom heaters (the supersaturation region for single crystal growth) was about $40^\circ\text{C}\cdot\text{cm}^{-1}$. This temperature gradient can control the length of solution zone. The growth speed was 4–5 mm per day for 10 days. CIGS single crystals were cooled at the rate of $500^\circ\text{C}\cdot\text{h}^{-1}$ from 700°C after crystal growth. The sample wafers were cut from the middle of the CIGS ingots and polished with $0.5\text{ }\mu\text{m}$ Al_2O_3 paste, and finally rinsed with deionized water.

The structural properties were measured by X-ray diffraction (XRD; X'Pert PRO, Panalytical) and Raman spectroscopy (HORIBA T64000). The tube voltage, tube current, and step width for XRD were measured as 40 kV, 40 mA, and 0.01° , respectively, using a Cu K α radiation source. The 532 nm laser excitation source was used in the Raman measurements and focused on the sample by

Figure 1: Photographs of CIGS single crystals with Ga content $x =$ (a) 0.2 and (b) 0.5. (c) XRD of the cutting plane perpendicular to growth direction (= c -axis). Inset picture is CIGS wafer ($x = 0.5$).

Figure 2: Powder XRD patterns of CIGS single crystals (Ga content $x = 0.1$ – 0.5).

an objective lens with a numerical aperture of 0.55. The laser power on the sample was 100 mW. The spectra were calibrated based on 520 cm^{-1} of Si peak.

The average composition of the samples was analyzed using scanning electron microscopy (SEM; SU-3500 Hitachi) and energy-dispersive X-ray spectroscopy (EDS). The conventional ZAF (atomic number, absorption, and fluorescence) corrections were performed for EDS.

The electrical properties were obtained by Hall effect measurements (ResiTest8300; TOYO Corporation), operated in a 0.45 T magnetic field in van der Pauw geometry

at 300 K. An ohmic contact was made from In for n-type or Au for p-type conduction. Contacts, each with a diameter of 1 mm and thickness of approximately 200 nm, were evaporated onto the corners of the samples for electrical measurements.

For PV device fabrication, CIGS wafers with diameter of 10 mm and thickness of 0.5 mm were etched by 5% Br_2 /methanol solution for 5 min followed by RF sputtering deposition for all layers at room temperature in Ar. First, a blanket Mo (or Au) layer of 500 nm was deposited as the back-contact. The pn junction was formed by sputtering 50–100 nm of CdS buffer at 50 W followed by an intrinsic layer of 100 nm of ZnO (i-ZnO) and a transparent conducting oxide (TCO) layer of 200 nm of Al-doped ZnO (AZO: 2 wt% Al_2O_3 in ZnO). A grid of 1,500 nm Al was deposited at 150 W. An annealing treatment at 300°C in an ambient of flowing 96% Ar–4% H_2 for 10 min was applied after device fabrication. Device characterization included 1-sun current density–voltage (J – V) measurement in a home-built system and capacitance–voltage (CV) at 1 MHz with 30 mV AC voltage over the DC bias range of -2 to 0.5 V .

3 Results and discussion

In our previous study [10], CIGS single crystal ($x = 0.2$) was obtained by THM growth. It is successful to grow CIGS single crystals with various Ga fraction ($x = 0.1$ – 0.5) in this

Figure 3: Raman spectra of CIGS single crystals (Ga content $x = 0$ – 0.5).

Figure 4: Average compositions of each CIGS single crystal wafer (Ga content $x = 0$ – 0.5) by EDS measurement.

Figure 5: Electrical properties of (a) resistivity, (b) carrier concentration, and (c) mobility by Hall effect measurement. Circle and square symbols represent n-type and p-type, respectively.

study. Photographs of CIGS single crystal ($x = 0.2$ and 0.5) ingots are shown in Figure 1(a) and (b). The dimensions of single crystal ingot are 10 mm in diameter and 30 mm in length including zone solution region. CIGS single crystals were cut perpendicular to growth direction (= c -axis),

where the 008 reflect plane can be observed by XRD in Figure 1(c). The [001] crystallographic orientation can be observed in wafer samples without grain boundaries by visually inspecting. The powder XRD patterns of CIGS single crystal at 300 K are shown in Figure 2, and exhibit

Figure 6: Properties of PV device based on CIGS single crystal. (a) Device structure, (b) J - V curve, (c) EQE spectrum, and (d) the net acceptor concentration versus depletion width W from CV measurement. The value of depletion width W at 0 V bias is 210 nm. The p-type conversion of CIGS ($x = 0.2$) single crystal absorbing layer was carried out by Se-annealing.

major peaks corresponding to diffraction lines of the chalcopyrite structure of CIGS (ICDD data # 00-040-1487 CuInSe_2 and ICDD data #00-035-1102 $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$). 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. The peak shift to higher angle being proportional to the compositional x value, especially 112 peak position, can be observed following Vegard's law.

The combination of XRD and Raman spectroscopy is a useful tool for the investigation of secondary phases because the XRD peaks of CIGS especially overlap well with those of Cu_2Se . No secondary phases, such as Cu_2Se at 260 cm^{-1} [12,13], were observed in Raman measurement by 532 nm excitation source, as shown in Figure 3. A typical Raman peak of CIGS was observed with peak shift between 175 cm^{-1} for CIS and 185 cm^{-1} for CGS corresponding well to data for CIGS in the literature [12,13], indicating that single-phase CIGS was obtained for all samples. This peak is the A_1 symmetry mode resulting from the motion of Se atom with the Cu and In (Ga) atoms.

Figure 4 shows the average compositions of CIGS single crystal wafers from EDS mapping at the scale of several hundred micrometers, where the uncertainty is less than 1%. It can be clearly seen that the composition is homogeneous on the wafer.

The electrical properties such as (a) resistivity, (b) carrier concentration, and (c) mobility were determined by Hall effect measurements at 300 K as shown in Figure 5. The conversion of conduction type from n- to p-type can be observed above 0.3 of Ga ratio x in Figure 5(a). It has been shown that the lowest formation energy is Cu vacancy (V_{Cu} = acceptor) in CIS and CGS through first-principle calculations, which leads to p-type conduction [14,15]. The In (Ga) on Cu antisite defects (In_{Cu} and Ga_{Cu} = donor) are low in formation for n-type conduction, where the formation energy of Ga_{Cu} is larger than that of In_{Cu} [15]. It is assumed that In_{Cu} causes n-type conduction in CIGS ($x = 0\text{--}0.2$) single crystal under In-rich growth condition. CGS shows strong p-type conduction with hole concentration of 10^{18} to 10^{20} cm^{-3} by V_{Cu} and Cu on Ga antisite defects (Cu_{Ga}) under wider range of Ga-poor/rich condition and higher donor formation energy than CIS [15], which may lead to the conversion from n- to p-type above $x = 0.3$ in CIGS. The self-compensation results in lower carrier concentration and higher resistivity increasing Ga content. The mobility slightly decreased with increasing Ga content in CIGS single crystal because the impact of impurity scattering may be dominant by high defect concentration in CGS.

Single crystal-based PV device was fabricated by using CIGS ($x = 0.2$) sample as absorbing layer, and

device structure is shown in Figure 6(a). It is difficult for p-type CIGS above $x = 0.3$ as absorbing layer to work PV device due to low carrier concentration and high resistivity [5]. The p-type conversion of CIGS ($x = 0.2$) was carried out by Se-annealing under high vacuum at 750°C for 24 h, which indicates hole concentration of $10^{16}\text{--}10^{17}\text{ cm}^{-3}$, resistivity of $1\text{--}50\text{ }\Omega\text{-cm}$, and hole mobility of $35\text{--}80\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. A typical $J\text{--}V$ curve of the CIGS PV device under simulated AM1.5 irradiation (100 mW cm^{-2}) is shown in Figure 6(b). The efficiency of the obtained device was 12.6%. The short-circuit current density (J_{sc}) of 27.5 mA cm^{-2} , an open circuit voltage (V_{oc}) of 0.765 V, fill factor (FF) of 0.61, series resistance (R_{S}) of $8.7\text{ }\Omega\text{-cm}^2$, and shunt resistance (R_{SH}) of $167\text{ }\Omega\text{-cm}^2$ were obtained.

Considering the loss of J_{sc} , the external quantum efficiency (EQE) shows an overall low value in Figure 6(c) indicating that the recombination loss is large. Especially small EQE in the long wavelength region is deduced to be incomplete collection of carriers generated in CIGS. In addition, the EQE with a small short wavelength region is deduced to be light absorption by the CdS ($\sim 490\text{ nm}$) and/or ZnO ($\sim 370\text{ nm}$) layers [16]. The values of R_{S} and R_{SH} in this study are poorer than epitaxial CIGS device with $R_{\text{S}} = 1.3\text{ }\Omega\text{-cm}^2$ and $R_{\text{SH}} = 26,000\text{ }\Omega\text{-cm}^2$ [5], which may result in small FF value.

The bandgap value of CIGS ($x = 0.2$) is estimated to be 1.216 eV from EQE spectrum (derivative of EQE with respect to wavelength). Thus, the V_{oc} loss in this study is estimated to be 0.451 V. The V_{oc} value of CIGS single-crystal PV is higher than that of 0.740–0.750 V for CIGS (not alloying with S) thin-film device with 20% efficiency [17]. The net acceptor concentration in depletion region of single-crystal device was obtained from CV measurement as a function of depletion width W in Figure 6(d), which is based on Mott–Schottky plot (C^{-2} versus bias voltage) [18]. U-shape characteristic in CV profile can be observed due to different factors such as Ohmic properties at back contact and the presence of deep level defects [18]. The effect of the back-diode can show up under forward bias because of low Ohmic property at back contact which causes measured capacitance to be artificially reduced leading to an apparent increase in the acceptor concentration under a forward bias [19]. Under high reverse bias, the apparent increase in carrier concentration at the non-Ohmic back contact can be due to reasons such as the presence of deep acceptor levels, a Schottky contact, or actual increased p-type doping at the back contact. An apparent contribution to the acceptor concentration from a Schottky contact can occur when trap levels are populated under reverse bias because of increase in band bending but are otherwise above the Fermi level and thus unoccupied under normal conditions,

resulting in the right branch of the U-shape in Figure 6(d) [18]. The net acceptor concentration of 10^{16} cm^{-3} in CIGS single-crystal PV device is thus best estimated from bottom of the U-shaped CV profile in the small bias region. Even though further improvement of back contact is required for higher efficiency, we demonstrated high V_{oc} value as potential for CIGS single-crystal-based PV device.

4 Conclusion

We have experimentally studied the growth and basic properties of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ ($x = 0\text{--}0.5$) single crystal for higher efficiency PV device. Large size CIGS single crystals were successfully grown by the In-solution THM. No secondary phases were observed from XRD and Raman spectroscopy measurements. The conversion of conduction type from n- to p-type can be observed above 0.3 of Ga ratio x because CGS shows strong p-type conduction with higher hole concentration by V_{Cu} and Cu_{Ga} defects and higher donor formation energy than CIS. PV device based on high-quality CIGS bulk single crystal demonstrates high V_{oc} of 0.765 V with the efficiency of 12.6%. Improvements in the CIGS/CdS interface as n-type doping in the buffer layer and Ohmic property at back contact are our ongoing work.

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