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$ZnSnP_2$ solar cell with (Cd,Zn)S buffer layer: Analysis of recombination rates

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ABSTRACT

A $ZnSnP_2$ bulk crystal was prepared by flux method and cut into a $ZnSnP_2$ wafer with thickness of 200 μm, which was utilized as the absorber of a $ZnSnP_2$ solar cell with a Al/ZnO:Al/ZnO/(Cd,Zn)S buffer/$ZnSnP_2$ wafer/Cu structure. A 3.44%-efficient $ZnSnP_2$ solar cell was obtained. Moreover, we assessed performance of the $ZnSnP_2$ solar cell concentrating on main loss mechanisms limiting device efficiency. Based on investigations of the majority carrier barrier at $ZnSnP_2$ and the Cu back electrode, the barrier height is estimated to be 59 meV, which could limit the fill factor of the solar cell and should be decreased. In addition, voltage-independent recombination rates at the buffer/absorber interface (R_0^i), in the space-charge region (R_0^d), and in the quasi-neutral region (R_0^b) of the $ZnSnP_2$ solar cell were determined from illumination dependence of the open-circuit voltage. It was found that R_0^d is 2.65×10^{13} cm^{-2}s^{-1}, much high than $R_0^i + R_0^b$ of 1.2×10^9 cm^{-2}s^{-1}. The high R_0^d was attributed to the mechanical surface polish of the $ZnSnP_2$ wafer. It is thought that R_0^b should be lower than R_0^i because of the large $ZnSnP_2$ grain and non-optimized buffer/absorber interface. These findings suggested that R_0^i and R_0^d should be further decreased to enhance photovoltaic performance.

1. Introduction

Among the most promising technologies for sustainable energy are the photovoltaics (PVs) used in solar cells to convert light energy into electricity [1,2]. There have been great advances recently in solar cells with compound semiconductors as absorbers. One of the most efficient solar cells incorporating a compound semiconductor is the $Cu(In,Ga)Se_2$ (CIGSe)-based solar cell: Conversion efficiencies (η) of over 20% have been reported [3–5]. However, the CIGSe absorber contains the rare element (In), which increases the CIGSe production cost. Thus, I_2-II-IV-VI_4 quaternary compound semiconductors are investigated as rare-metal-free PV materials. The highest η values reported to date for $Cu_2ZnSnSe_4$ (CZTSe) and $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells are 9.7% and 12.6%, respectively [6,7]. Nevertheless, CZTSe and CZTSSe absorbers contain toxic Se, which has a detrimental impact on the environment.

Thus, researchers have been seeking rare-metal-free compounds free of toxic elements for the solar cells to lower production cost and minimize environmental harm. $ZnSnP_2$, which is considered to be an abundant and nontoxic material, possesses p-type conductivity with a carrier concentration of 10^{16}–10^{17} cm^{-3}, a mobility of approximately 50 cm^{2}V^{-1}s^{-1}, and a high absorption coefficient of about 10^5 cm^{-1} under visible light [8–12]. The energy bandgaps (E_g) for $ZnSnP_2$ with sphalerite and chalcopyrite structures are approximately 1.38 and 1.68 eV, respectively [13]. According to the Shockley-Queisser limit under an AM 1.5 G spectrum, the theoretical η of a $ZnSnP_2$ single-junction solar cell is above 30% [12,14]. It has been recently reported that solar cells incorporating bulk crystals of $ZnSnP_2$ and $ZnSnP_2$ thin film were successfully fabricated for the first time with η values of 0.087% and 0.021%, respectively [15,16], where the well-known Al/ZnO:Al (AZO)/ZnO/CdS/$ZnSnP_2$/Mo structure was adopted, which is similar to that of the CIGSe solar cell [3–5]. However, the η of the $ZnSnP_2$ solar cells is much lower than 1%. This is because the poor conduction band offset (ΔE_C) at the CdS buffer/$ZnSnP_2$ absorber interface, where ΔE_C was estimated to be −1.2 eV, forming a cliff at the interface [17], thus increasing the carrier recombination and deteriorating cell performance especially the open-circuit voltage (V_{OC}) [18]. Moreover, the CdS layer absorbs light with wavelengths below 520 nm, owing to its E_g of 2.4 eV. Therefore, an alternative buffer layer should be sought to replace the CdS buffer layer to enhance the η of the $ZnSnP_2$ solar cells. It is known that the introduction of Zn into CdS to form (Cd,Zn)S leads to an increase in E_g, thus increasing the η of CIGSe and $Cu(In,Ga)(S,Se)_2$ solar cells [19,20].

In this work, therefore, a $ZnSnP_2$ solar cell with a (Cd,Zn)S buffer layer was fabricated to enhance η. In addition, to gain a deeper understanding of the factors governing cell performance, the majority

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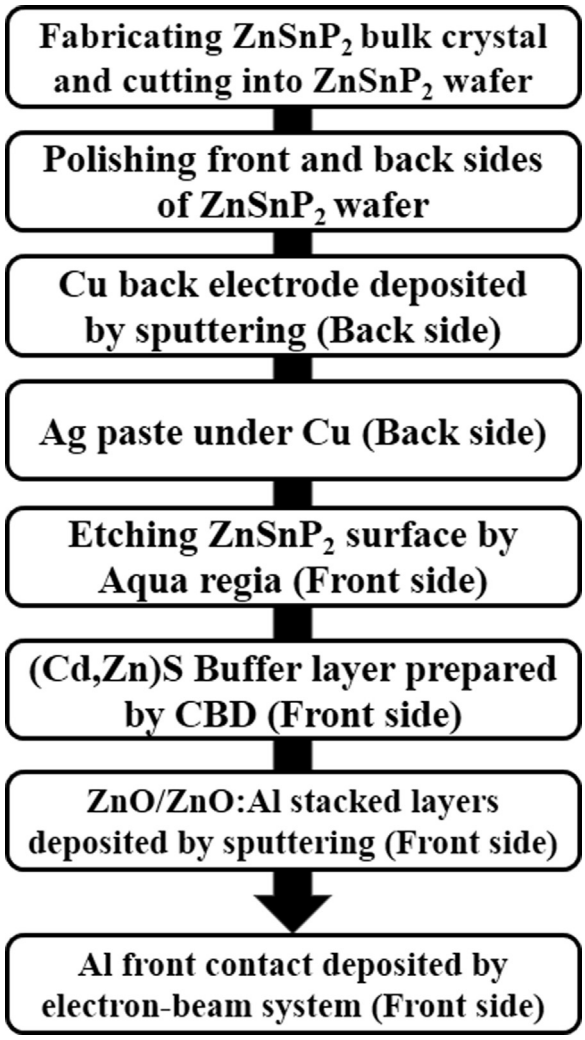

Fig. 1. Fabrication process of $ZnSnP_2$ solar cell with (Cd,Zn)S buffer layer.

carrier (hole) barrier at $ZnSnP_2$ and the back electrode as well as the recombination pathways were investigated in the $ZnSnP_2$ solar cell. The recombination pathways were studied on the basis of quantitative extractions of the recombination rates at the (Cd,Zn)S/$ZnSnP_2$ absorber interface, in the space charge region (SCR), and in the quasi-neutral region (QNR).

2. Experimental

A $ZnSnP_2$ solar cell with a (Cd,Zn)S buffer layer was fabricated by the process in Fig. 1. According to Fig. 1, $ZnSnP_2$ bulk crystals were grown by the flux method reported in Ref. [21], as follows. Zn shots (99.99%, Kojundo Chemical Laboratory), Sn shots (99.99%, Kojundo Chemical Laboratory) and red phosphorus flakes (99.9999%, Kojundo Chemical Laboratory) were sealed in an evacuated quartz ampoule under a pressure below 10^{-2} Pa. The quartz ampoule was then set in the vertical furnace and heated to 700 °C for homogenization. The $ZnSnP_2$ crystal growth was performed from the bottom up, by raising the furnace. The furnace speed was adjusted so that the cooling rate of the quartz ampoule would be approximately 0.7 °C/h. The temperature of the bottom of the ampoule was monitored by a thermocouple during $ZnSnP_2$ crystal growth. The grown $ZnSnP_2$ bulk crystals were cut into wafers with a diameter of 5 mm and a thickness of 0.5 mm. Next, the front and back sides of each $ZnSnP_2$ wafer were mechanically polished with emery papers and finally 1 μm diamond slurry on a buff sheet. The final thickness of each $ZnSnP_2$ wafer was approximately 200 μm.

Next, a solar cell with a (Cd,Zn)S buffer layer was fabricated by the process illustrated in Fig. 1. The structure of the solar cell is Al/AZO/ZnO/(Cd,Zn)S/$ZnSnP_2$/Cu/Ag paste, which is almost similar to that of the CIGSe solar cell [3–5]. In the solar cell fabrication process, for the back side of the $ZnSnP_2$ wafer, Cu back electrode was deposited by direct current sputtering on the polished surface of $ZnSnP_2$ wafers. Ag paste was then placed on Cu back electrode.

As for the front side of the $ZnSnP_2$ wafer, an etch using a mixture (aqua regia) of HCl and HNO_3 with a molar ratio of 3:1 was conducted for 15 min on the opposite surface of the Cu back electrode. Next, a (Cd,Zn)S buffer layer was prepared by chemical bath deposition (CBD) at a bath temperature of 80 °C and a deposition time of 4 min for the buffer thickness of 50 nm. The solution for (Cd,Zn)S growth containd $CdSO_4$ (1.5 mmol/L), $ZnSO_4$ (7 mmol/L), ammonia (0.37 mol/L), and thiourea (50 mmol/L). It is notable that the [Zn]/([Zn] + [Cd]) composition ratio in the resulting (Cd,Zn)S on soda-lime glass (SLG) with an E_g of 2.6 eV was 0.25, which was measured by an energy dispersive spectroscopy (EDS) operated at 4 kV. The EDS system was attached to a scanning electron microscope.

After the preparation of the (Cd,Zn)S buffer layer on the $ZnSnP_2$ absorber, 50-nm-thick ZnO and 300-nm-thick AZO stacked layers were deposited by radio frequency magnetron sputtering. During ZnO/AZO sputtering, the sample was water-cooled to maintain the substrate temperature at room temperature; ZnO (99.99% purity) and ZnO-Al_2O_3 (2 wt%; 99.99% purity) were utilized as target materials, respectively. Finally, front Al (1 μm) grids on the resulting solar cell were deposited by electron beam evaporation. The cell performance parameters, short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (*FF*), and η, of the $ZnSnP_2$ solar cell were determined from the photo current density-voltage (*J-V*) characteristics under Air Mass 1.5 G illumination (100 mW/cm^2). The external quantum efficiencies (EQEs) were measured at bias voltages of 0, −0.5, and −1.0 V using a measurement system (CEP-25RR, Bunkoukeiki). The E_g values of the AZO, (Cd,Zn)S, and $ZnSnP_2$ layers in the solar cell were estimated from the first derivative of the EQE spectrum at a bias voltage of 0 V.

The temperature dependent *J-V* characteristics of the $ZnSnP_2$ solar cell with a (Cd,Zn)S buffer layer were also investigated under Air Mass 1.5 G illumination using a cryostat cooled with liquid-N_2 and heated by a temperature controller (Model 9700, Scientific Instruments). The temperature (*T*) was in the 200–300 K range. J_{SC} as a function of V_{OC} is given [22,23],

$$J_{SC} = J_0 \exp(\frac{qV_{OC}}{\mathrm{nk}T}) = J_{00} \exp(\frac{qV_{OC}}{nkT})\exp(\frac{-E_A}{nkT}) \quad (1)$$

where n and J_0 are, respectively, the ideality factor and reverse saturation current density of the diode, kT/q is the thermal voltage, J_{00} is a weakly temperature-dependent term, and E_A is the activation energy of the dominant recombination. According to Eq. (1), V_{OC} can be expressed as,

$$V_{OC} = \frac{E_A}{q} - \frac{nkT}{q} \ln(\frac{J_{00}}{J_{SC}}). \quad (2)$$

Eq. (2) suggests that if n, J_{SC}, and J_{00} are independent of temperature, the graph of V_{OC} as a function of T should be a straight line, and the extrapolation of this line to $T = 0$ K yields qV_{OC} at $T = 0$, defined as E_A. To measure the carrier density (N_A) of the $ZnSnP_2$ absorber and the built-in potential, capacitance–voltage (*C–V*) measurements were performed on the $ZnSnP_2$ solar cell using an LCR meter (Hewlett Packard 4284 A) at a repetition rate and amplitude of 4 kHz and 10 mV at room temperature. Finally, the illumination dependence of V_{OC} was characterized through Suns-V_{OC} measurements by a WCT-120 system (Sinton Instruments).