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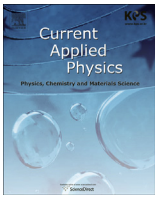

# $ZnSnP_2$ thin-film solar cell prepared by phosphidation method under optimized Zn/Sn atomic ratio of its absorbing layer

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## ABSTRACT

$ZnSnP_2$ film is a promising absorber for thin-film solar cell due to earth-abandant and nontoxic element. Phosphidation method is utilized for the fabrication of $ZnSnP_2$ films with different Zn/Sn atomic ratios. $ZnSnP_2$ film with the large $ZnSnP_2$ protrusions are demonstrated with Zn/Sn of ~1 (near stoichiometry), while the film with the relatively smooth surface is presented with Zn/Sn of above 1 (Zn rich). According to grazing incidence X-ray diffraction measurement, $Sn_4P_3$ secondary phase is appeared in $ZnSnP_2$ film with Zn/Sn of below 1 (Sn rich), whereas $Zn_3P_2$ secondary phase is presented in the film with Zn rich. On the other hand, $Sn_4P_3$ and $Zn_3P_2$ secondary phases are not observed in $ZnSnP_2$ thin film with near stoichiometry, thus leading to the longest carrier lifetime, implied by time-resolved photoluminescence measurement. Ultimately, the conversion efficiency of 0.021% with short-circuit current density of 5.03 mA/cm$^2$ is reported for $ZnSnP_2$ thin-film solar cell, where its absorbing layer possesses single $ZnSnP_2$ phase and Zn/Sn ratio near stoichiometry. The energy bandgap of $ZnSnP_2$ thin films by phosphidation method is estimated to be 1.38 eV by external quantum efficiency, implying that the $ZnSnP_2$ has sphalerite structure.

## 1. Introduction

Sustainable energy is intriguing since it can solve the energy problem by providing a clean and safe energy source [1]. One of the most promising technologies for the sustainable energy is photovoltaic (PV), a process of converting light energy into electricity. Presently, wafer-based silicon (Si) solar cells, generating electricity by PV effect, are playing a vital role in PV market. Nevertheless, Si wafers are prepared from the expensive process, thus leading to the high cost of the finished Si solar cells [1,2]. Thin-film solar cells are deemed less expensive alternative to wafer-based Si solar cells [1,2]. It was reported that Cu(In,Ga)$Se_2$ (CIGS)-based thin-film solar cells have attained the conversion efficiencies ($\eta$) of over 20% with a small area [3–5]. However, rare elements (In and Ga) in CIGS thin films are expected to drastically increase in the cost of CIGS production, thereby making it difficult for CIGS solar cell to meet the enhancing demand of PV market worldwide. $I_2$-II-IV-$VI_4$ quaternary semiconductors are therefore studied as the promising In- and Ga-free PV materials for absorbers of thin-film solar cells. 9.7%-efficient $Cu_2ZnSnSe_4$ (CZTSe) thin-film solar cell and 12.6%-efficient $Cu_2ZnSn(S,Se)_4$ (CZTSSe) thin-film solar cell have been attained [6,7]. The CZTSe thin film is fabricated by the selenization of the Cu-Zn-Sn precursors, which are prepared by sputtering method [6]. The CZTSSe thin-film solar cell is prepared using the hydrazine-based solution deposition technique [7]. Se in CZTSe and CZTSSe absorbers has detrimental impact on the environment and hydrazine is severely toxic and unstable, requiring extreme caution during handling.

The alternative absorbing layer for the thin-film solar cell is therefore investigated. It was reported that $ZnSnP_2$, an abundant and nontoxic material, demonstrates the p-type conductivity with carrier concentration of $10^{16}$-$10^{17}$ cm$^{-3}$, mobility of approximately 50 cm$^2$V$^{-1}$s$^{-1}$, and high absorption coefficient of about $10^5$ cm$^{-1}$ in visible light [8–12]. The energy bandgap ($E_g$) is 1.38 eV for $ZnSnP_2$ with sphalerite structure and 1.68 eV for $ZnSnP_2$ with chalcopyrite structure [13]. From the Shockley-Queisser limit under AM 1.5 spectrum, the theoretical $\eta$ of $ZnSnP_2$ single-junction solar cell is

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above 30% [12,14]. Recently, the solar cells using bulk crystals of $ZnSnP_2$ have been first reported with $\eta$ of 0.087% for the first time [15]. In this work, $ZnSnP_2$ thin film is interesting for low-cost solar cells. $ZnSnP_2$ thin film is consequently considered as a promising material as an alternative absorbing layer for the low-cost solar cell. The $ZnSnP_2$ has been fabricated by various methods such as chemical vapor deposition (CVD), molecular beam epitaxy (MBE), and liquid phase epitaxy (LPE) [16–18]. To prepare $ZnSnP_2$, toxic $PH_3$ gas is used in MBE and CVD systems and high temperature is needed in the LPE process, which is not appropriate for growing thin-films on soda-lime glass (SLG) substrates. $ZnSnP_2$ thin film is consequently prepared by the phosphidation method, which was reported in Ref. [10]. In the phosphidation method, Zn-Sn precursors react with phosphorus gas to form $ZnSnP_2$ thin film, which is considered suitable for an industrialized process [10].

In this work, $ZnSnP_2$ thin film with single phase was tried to be fabricated by the phosphidation method under the control of Zn/Sn atomic ratio. The influence of Zn/Sn atomic ratio on physical properties of $ZnSnP_2$ thin film was consequently scrutinized for the application of the $ZnSnP_2$ thin film as an absorbing layer of thin-film solar cell.

## 2. Experimental procedure

### 2.1. $ZnSnP_2$ thin-film formations and measurements

$ZnSnP_2$ thin film on Mo-coated SLG substrate was fabricated by the phosphidation method. In this method, after covering clean SLG with back electrode of 800-nm-thick Mo layer, the Zn/Sn stacked precursor layers were deposited by electron beam evaporation system, where 99.99% purity Zn and 99.999% purity Sn were used under back pressure of $5 \times 10^{-4}$ Pa. The resulting Zn-Sn precursor layers on Mo-covered SLG substrate were depicted in Fig. 1(a). In this work, the impact of Zn/Sn atomic ratio on the physical properties of resulting $ZnSnP_2$ thin film was investigated. The Zn/Sn atomic ratio was varied by the changes of Zn precursor and Sn precursor thicknesses, while total thickness of Zn-Sn precursor layers was constant at approximately 500 nm. The precursor thickness and composition were investigated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and energy dispersive X-ray spectroscopy (EDS), respectively.

After the preparation of Zn-Sn precursor layers on SLG substrate in Fig. 1(a), the phosphidation process was conducted to form $ZnSnP_2$ thin film. For the process, phosphorus source with two phases (Sn and $Sn_4P_3$) was chosen, where the molar ratio and total amount of Sn/$Sn_4P_3$ were approximately 3 and 2 g, respectively [10]. The co-existence of Sn and $Sn_4P_3$ is needed to control the phosphorus vapor during the phosphidation process, where it is based on the equation $Sn_4P_3(s) = 4Sn(l)+3/4P_4(g)$ [10]. The phosphorous gas was transported to Zn-Sn precursor layers using Ar carrier gas and the partial pressure of phosphorous was estimated to be around $10^{-2}$ atm. The phosphorous source and Zn-Sn precursor layers were heated at about 500 and 520 °C during phosphidation process, respectively. The phosphidation time is 30 min. The cooling time from phosphidation temperature (520 °C) to room temperature is approximately 2 h. $ZnSnP_2$ thin film on SLG substrate in Fig. 1(b) was finally formed after phosphidation of the Zn-Sn precursor layer. After the $ZnSnP_2$ fabrication, the cross-sectional and surface images of $ZnSnP_2$ films were examined by scanning electron microscopy (SEM). The material compositions of $ZnSnP_2$ films were characterized by ICP-AES and EDS methods. In addition, the $ZnSnP_2$ thin films were characterized by grazing incidence X-ray diffraction (GI-XRD) system to investigate crystallographic structure of the films. The GI-XRD patterns were obtained by PANalytical X′ Pert PRO with Cu $K_\alpha$ ($\lambda = 1.5405$ Å) radiation operated at 45 kV and 40 mA with an incident angle of 1.0° and step size scanning of 0.04°. Calculated penetration depth of Cu $K_\alpha$ radiation into $ZnSnP_2$ films with this incident angle is approximately 500 nm. The $ZnSnP_2$ films were furthermore measured by time-resolved photoluminescence (TRPL) with laser power, beam area and wavelength of 5.05 mW, 1.02 $mm^2$ and 532 nm, respectively (Hamamatsu C12132). TRPL lifetimes ($\tau_1$ and $\tau_1$) were calculated from the fitting of TRPL decay curve by using $I(t) = A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$, where t is the time after a laser pulse excitation, $I(t)$ is the luminescence intensity at time (t), $A_1$ and $A_2$ are coefficients, as well as $\tau_1$ and $\tau_2$ are the fast and slow components of the TRPL lifetimes, respectively [19–22].

### 2.2. Fabrication and measurement of $ZnSnP_2$ thin-film solar cell

After the fabrication of $ZnSnP_2$ thin films in Fig. 1(b), $ZnSnP_2$ thin-film solar cells with a structure in Fig. 1(c) were fabricated as follows. About 50-nm-thick CdS buffer layers were first deposited by chemical bath deposition on the resulting $ZnSnP_2$ films at the

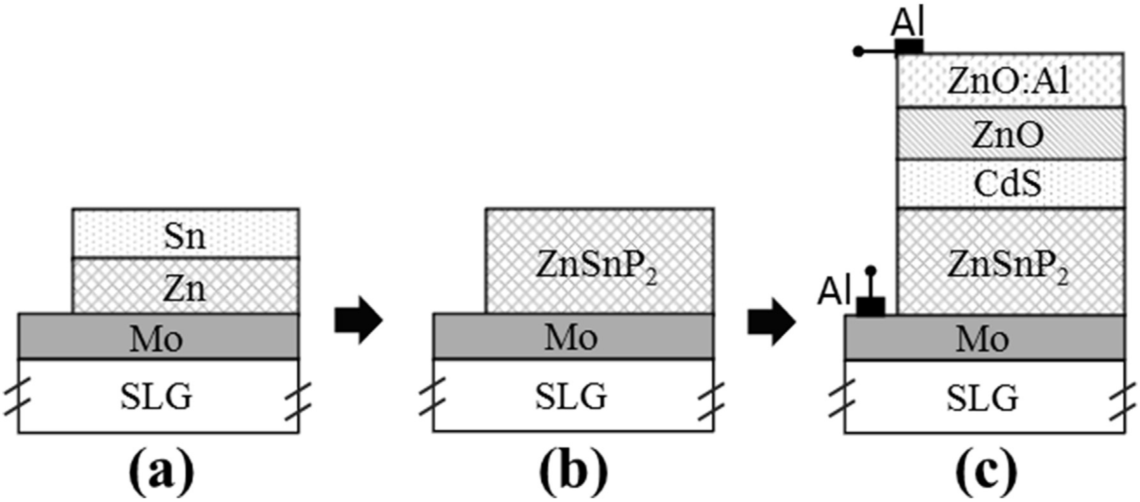

**Fig. 1.** (a) Zn-Sn precursor layers on Mo-coated SLG substrate, (b) $ZnSnP_2$ thin film on SLG substrate after phosphidation process, where Zn-Sn precursor layers react with phosphorus gas, and (c) $ZnSnP_2$ thin-film solar cell.