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Fabrication of CdSnP₂ Thin Films by Phosphidation for Photovoltaic Application

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Abstract

We report on the fabrication of CdSnP₂ thin films for photovoltaic application. The phosphidation method, where co-sputtered Cd-Sn precursor thin film reacts with phosphorus gas, was utilized for the preparation of CdSnP₂ thin films. In order to establish the fabrication process, the temperature dependence on product phases was investigated and CdSnP₂ thin films were obtained by the phosphidation at 350 °C for 30 min under the phosphorus vapor pressure of 10⁻² atm. CdSnP₂ thin films showed a *n*-type conduction. The resistivity, the carrier concentration and the mobility were evaluated to be 3.5–3.7×10² Ω cm, 1–3×10¹⁵ cm⁻³ and 4.7–17 cm² V⁻¹ s⁻¹, respectively. CdSnP₂ thin films with relatively flat and smooth surface were obtained, although it was reported that ZnSnP₂ with the same crystal structure grew as the protrusion shape by the VLS growth mode. In order to investigate these difference in growth mechanism between CdSnP₂ and ZnSnP₂, the reaction process in Cd-Sn-P system was investigated and discussed based on the chemical potential diagrams. As the result, it was understood that Cd, Sn and P₄ directly reacted to form CdSnP₂, while ZnSnP₂ was formed via the reaction among Zn₃P₂, Sn and P₄ after Zn reacts with P₄ to produce Zn₃P₂. Therefore, it is speculated that simple reaction route results in the high growth speed and smooth flat morphology was obtained in the fabrication of CdSnP₂ thin films.

1. Introduction

CuIn_{1-x}Ga_xSe₂ (CIGS) and CdTe are promising materials for thin film photovoltaic devices. The solar cells based on these chalcogenide compounds recorded the high conversion efficiencies of 22.6 %¹ for CIGS and 22.1 %² for CdTe, respectively. However, the usage of rare or toxic elements prevents the widespread use of these compound semiconductors. From these backgrounds, materials composed of non-toxic and earth-abundant elements have been researched and Cu₂ZnSnS_{4-x}Se_x achieved the high conversion efficiency of 12.6 %.³ In addition, Cu₂SnS₃,⁴ Cu₂O,⁵ SnS,⁶ FeS₂,⁷ and Zn₃P₂⁸ have been also investigated for the same concept.

ZnSnP₂ is also a promising material for solar absorber consisting of safe and earth-abundant elements. In the previous works, it was reported that ZnSnP₂ showed a *p*-type conduction with the carrier concentration of 10¹⁶–10¹⁸ cm⁻³ and a direct bandgap of ~ 1.6 eV.^{9–16} Based on Shockley-Queisser limit,¹⁷ the theoretical conversion efficiency of about 30% is calculated in the single-junction solar cell using ZnSnP₂ under the condition of AM 1.5 G solar spectrum.¹⁸ The absorption coefficient of ZnSnP₂ was reported to be approximately 10⁵ cm⁻¹ in visible light range,^{18,19} which is comparable to that of CIGS.^{18,20} Our research group reported that solar cells using ZnSnP₂ thin films²¹ and bulk crystals^{15,22,23}. The solar cells using ZnSnP₂ bulk crystals recorded the best conversion

efficiency of 3.44 % ($J_{SC} = 12.3 \text{ mA/cm}^2$, $V_{OC} = 0.472 \text{ V}$, $FF = 0.594$).²³ The solar cell structure was Al/ZnO;Al/ZnO/(Cd,Zn)S/ZnSnP₂/Cu. In this device, the value of V_{OC} was largely low considering the bandgap of ZnSnP₂. XPS measurements revealed that CdS/ZnSnP₂ showed a large conduction band offset, $\Delta E_C = -1.2 \text{ eV}$,²⁴ which suggested that band alignment was— necessary to achieve a high conversion efficiency.

In this study, we focused on CdSnP₂ as a *n*-type material in the ZnSnP₂ solar cells. CdSnP₂ has a chalcopyrite structure as well as ZnSnP₂ and its bandgap is 1.17 eV.²⁵ Kumagai *et al.* carried out the first-principles calculation in ZnSnP₂ with chalcopyrite structure to obtain its band structure.²⁶ They reported that the valence band maximum (VBM) at the Γ point is mainly composed of P orbitals with slight hybridization with Zn and Sn orbitals and the conduction band minimum (CBM) is primarily composed of Zn and Sn cations orbitals. Consequently, the level of VBM in CdSnP₂ might be similar to that in ZnSnP₂ because of the same crystal structure and anions. This results in the ΔE_C value of -0.5 eV between ZnSnP₂ and CdSnP₂ considering the difference of bandgap in both compounds and the improvement of band alignment is expected compared to CdS. In addition, it was reported that ZnSnP₂ and CdSnP₂ form a solid solution in all composition range,²⁷ which suggests the intermixing of Zn and Cd atoms at CdSnP₂/ZnSnP₂ interface and *pn*-junction with few band offset and interfacial defect can

1 be formed. However, few reports on the formation of CdSnP_2 thin films are available.

2 In this report, we thus tried to establish the fabrication process to obtain CdSnP_2 thin
3 films, where Cd-Sn precursor thin films react with phosphorus gas, so-called
4 phosphidation. Particularly, the impact of reaction temperature on product phases was
5 investigated and morphology change was discussed based on the chemical potential
6 diagrams.

7 **2. Experimental method**

8 Cd-Sn thin films with the thickness of $0.5\ \mu\text{m}$ were fabricated as a precursor on soda
9 lime glass substrates by magnetron direct current sputtering with a base pressure of
10 $5 \times 10^{-4}\text{Pa}$. The 1 inch target materials of Cd (99.9 %, Kojundo Chemical Laboratory) and
11 Sn (99.99%, Furuuchi Chemical) were co-sputtered for 45 min under an Ar atmosphere
12 with the pressure of $0.8\ \text{Pa}$ and the gas flow rate of $20\ \text{sccm}$. The power densities for Cd
13 and Sn targets were set at 0.6 and $3.2\ \text{W}/\text{cm}^2$, respectively. During the sputtering, the
14 substrates were rotated at $12\ \text{rpm}$ without heating. For the safety sputtering of Cd, the
15 target materials were sufficiently cooled down for more than 30 min. Dust collecting
16 should be utilized when sample are extracted from a sputtering chamber. The thickness
17 and composition were measured by inductively coupled plasma-atomic emission
18 spectroscopy (ICP-AES, SII Nano Technology SPS3520UV). The samples were

dissolved in inverse aqua regia ($\text{HNO}_3\text{:HCl} = 3\text{:}1$) and the solution 1/10~~-~~ diluted with deionized water was used for the ICP-AES measurements. Considering the higher vapor pressure of Cd, the molar ratio $[\text{Cd}]/[\text{Sn}]$ was controlled to be about 1.2 in the precursor thin films.

Then, Cd-Sn thin films reacted with phosphorus gas to obtain CdSnP_2 thin films by phosphidation. The details of the experimental conditions were described in our previous work.²⁸ We used two phase sample with Sn and Sn_4P_3 as a phosphorus source and phosphorus gas was transported to the precursor thin films using Ar carrier gas, which was deoxidized by passing through a Ti sponge heated at 900 °C. The partial pressure of phosphorus was set at approximately 10^{-2} atm by controlling the temperature of two phase sample. In this study, the phosphidation temperatures were 300, 350 and 400 °C. After the phosphidation, the thin films were cooled down in the furnace by turning off the heater, or quenched outside the furnace. The surficial and cross-sectional morphology of thin films before and after phosphidation were analysed by scanning electron microscopy (SEM, HITACHI S-3500H and HITACHI SU-1500) The product phases were identified by X-ray diffraction (XRD, Panalytical X'Pert Pro Alpha-1), where $\text{CuK}\alpha_1$ ($\lambda=1.5406$ Å) was used as an incident X-ray (45 kV, 40 mA) in Bragg–Brentano (θ – 2θ) configuration.

In order to evaluate the electrical properties, Hall effect and resistivity measurements

were carried out at room temperature based on van der Pauw method using Hall-resistivity

measurement system (Toyo Technica, ResiTest8300).

For the consideration of growth mechanism in the phosphidation method, we used the

chemical potential diagrams. The review on the chemical potential diagrams is well

summarized by Yokokawa.²⁹ A chemical potential diagram shows a stable potential

region in various substances and each axis represents a chemical potentials of constituent

elements. The chemical potential diagram of the Cd-Sn-P system was drawn using the

software, Chesta 3.2.6.9, developed by Hatada. In order to obtain the potential diagrams,

the thermodynamic data for Cd (g) and Sn (g) were derived from the database edited by

Barin³⁰. The Gibbs energies of formation for CdP₂ (s), Cd₃P₂ (s) and CdSnP₂ (s) reported

by Sirota *et al.*³¹ and Smolyarenko *et al.*³² were also utilized.

3. Results and discussion

3.1. Effect of phosphidation temperature

In order to obtain CdSnP₂ thin films with the single-phase, the phosphidation of Cd-Sn

precursor thin films was carried out at various reaction temperatures such as 300, 350 and

400 °C. In each experiment, Cd-Sn precursor thin films reacted with phosphorus gas for

30 min and then was cooled down in the furnace. Figure 1 shows the XRD profiles of Cd-

Sn precursor thin films before and after phosphidation. In the precursor thin film, Cd and

Sn were identified and alloy was not observed, because Cd-Sn system is a typical eutectic system. The formation of CdSnP_2 as a main phase was observed in the phosphidation at 300 and 350 °C. In particular, all reflections observed in the sample prepared at 350 °C were corresponded to the reflections of CdSnP_2 . In addition, those samples show (112) plane orientation of CdSnP_2 , which is a close-packed plane in chalcopyrite structure. ICP-AES analysis showed that the composition of the thin film fabricated at 350 °C was 27.2 at. % Cd, 23.6 at. % Sn and 53.2 at.% P, which is Cd-rich composition compared with the stoichiometric ratio of CdSnP_2 . In some samples prepared by the same condition, Cd_3P_2 was identified from XRD profiles. Therefore, the existence of Cd_3P_2 as a secondary phase is considered even in the case that Cd_3P_2 is not identified in XRD profiles as shown in Fig. 1. While, Cd_6P_7 and Sn were identified in addition to CdSnP_2 in the sample for 400 °C.

Figure 2 shows SEM images of Cd-Sn precursor thin films before and after phosphidation. The Cd-Sn precursor thin film was composed of sub-micron particles. On the other hand, the sub-micron particles were not observed in the thin film after phosphidation at 300 °C, which was the morphology indicating that metal precursor melted. The phosphidation at 350 °C resulted in the CdSnP_2 thin film consisting of particles with the diameter of about 1 μm. The particles with the diameter of a few μm

were formed on the surface of the thin film in the sample after phosphidation at 400 °C. Such particles might be secondary phases containing Sn. The cross-sectional SEM observation was carried out in Cd-Sn precursor thin film and CdSnP₂ thin film fabricated by the phosphidation at 350 °C as shown in Fig. 3. In the Cd-Sn precursor thin film, it is observed that sub-micron particles were deposited on the glass substrate, while CdSnP₂ film shows the dense microstructure consisting of granular particles compared with the Cd-Sn precursor thin film. This implies that phosphidation reaction proceeded as metal precursor partly-melted. In addition, it is confirmed that the thickness of the film was reduced, which might be attributed to the evaporation of precursor metal. ICP-AES analysis also clarified that a half amount of precursor metal, Cd and Sn, evaporated during the phosphidation experiments at 350 °C, which has to be improved in future work. The Hall measurement indicates that CdSnP₂ thin films prepared by the phosphidation has the *n*-type conduction as well as the CdSnP₂ bulk crystals grown by the solution method.²⁵ CdSnP₂ thin films showed a *n*-type conduction. The resistivity, the carrier concentration and the mobility were evaluated to be 3.5–3.7×10² Ω cm, 1–3×10¹⁵ cm⁻³ and 4.7–17 cm² V⁻¹ s⁻¹, respectively.

As mentioned above, CdSnP₂ thin films were obtained by the phosphidation of Cd-Sn precursor thin films at 350 °C for 30 min. In addition, CdSnP₂ thin films has relatively

smooth morphology compared with ZnSnP_2 thin films. In our previous work, a different surface morphology was observed in ZnSnP_2 thin films fabricated even by a similar phosphidation process.²⁸ Some ZnSnP_2 protrusions with the length of a few μm were formed on the ZnSnP_2 thin film by so-called VLS (Vapor-Liquid-Solid) growth mode.^{28,33} It is interesting that CdSnP_2 and ZnSnP_2 showed different morphologies in spite of the similarity in constituent elements and crystal structures.

3.2. Growth mechanism of CdSnP_2 thin film

The time dependence of phosphidation in CdSnP_2 was investigated in order to clarify the growth mechanism. Here, we prepared a sample discontinued at 250 °C on the way heating up to 300 °C and another one after the phosphidation of Cd-Sn thin film at 300 °C for 2 min. Each sample was quenched outside the furnace in order to freeze the state during the phosphidation, while samples as shown in the previous section were conventionally cooled in the furnace after phosphidation. Figure 4 shows the XRD profile for each sample. The discontinued sample indicates that phosphidation reaction had not started at the heating stage because precursor metals such as Cd and Sn were identified. On the other hand, CdSnP_2 is observed as a main phase even in the phosphidation for 2 min, which suggests that the reaction rate to form CdSnP_2 is higher compared with ZnSnP_2 fabricated by the same phosphidation method. In the case of ZnSnP_2 , 5 min

phosphidation did not finish the formation of ZnSnP_2 even in the higher reaction temperature of 450 °C. It is also understood that partly-melted precursor metal is an important factor for fast phosphidation reaction from the SEM images of the film surface shown in Figure 5, as previously predicted.

Here, the difference of the surface morphologies between CdSnP_2 and ZnSnP_2 films is discussed. In this study, we consider the difference in growth mechanism between both based on the chemical potential diagrams, because the morphology might depend on the growth mechanism of each thin film. Figure 6 shows the chemical potential diagrams of the Cd-Sn-P system at 300 °C together with the diagram of the Zn-Sn-P system at 450 °C, which was previously reported by our group.²⁸ The logarithms of the partial pressures of Cd (g), Zn (g), Sn (g) and P_4 (g) were used as the axes, which represent their chemical potentials. The dotted line indicates the partial pressure of P_4 (g) controlled in the experiments: 10^{-2} atm.

We discuss the phosphidation process of Cd-Sn precursor thin films as well as the case of Zn-Sn films. The point A in Figure 6a represents the state for Cd-Sn precursor thin films before phosphidation. Then, the chemical potential of phosphorus in the film increases with keeping the equilibrium of Cd (l) and Sn (l) as the phosphidation reaction proceeds, and at the point B, CdSnP_2 (s) forms. On the other hand, in the Zn-Sn-P system

1 shown in Figure 6b, the phosphorus potential for the formation of ZnSnP_2 (s) shown by
2 point D is much higher than that for Zn_3P_2 (s) shown by point C. It is thus understood that
3 the formation of Zn_3P_2 (s) preferentially occurs before ZnSnP_2 (s) in the Zn-Sn-P system.
4 Such a behaviour was experimentally observed in our previous work.²⁸ The previous
5 work also showed that the surface morphology of ZnSnP_2 thin films was rough and some
6 protrusions were grown. To discuss the roughness of ZnSnP_2 thin films, two issues during
7 phosphidation should be considered. One is the microstructure of the Zn-Sn precursor
8 thin films before phosphidation, where it was observed that the separation of Zn and Sn
9 grains and the cohesion of Sn with the grain size of a few micron. The separation is
10 expected from the phase diagram of the Zn-Sn system. The other one is a phosphidation
11 process, which was investigated experimentally and thermodynamically. The formation
12 of ZnSnP_2 protrusions by VLS growth mode is due to the above two issues. On the other
13 hand, the grain size in Cd-Sn precursor thin films is sub-micron as shown in Figure 2a
14 although the separation of Cd and Sn is observed. In addition, the equilibrium chemical
15 potential of phosphorus with CdSnP_2 is lower than that with Cd_3P_2 as shown in Figure 6a,
16 which suggests that CdSnP_2 forms without the formation of other phases as described
17 above. These are different with the case of ZnSnP_2 , and key conditions to obtain a smooth
18 surface of CdSnP_2 films.

4. Conclusions

In this study, we investigated the temperature dependence in phosphidation of Cd-Sn thin films on product phases and CdSnP₂ thin films were prepared at 350 °C for 30 min under the phosphorus vapor pressure of 10⁻² atm. CdSnP₂ thin films showed a *n*-type conduction. CdSnP₂ thin films showed a *n*-type conduction. The resistivity, the carrier concentration and the mobility were evaluated to be 3.5–3.7×10² Ω cm, 1–3×10¹⁵ cm⁻³ and 4.7–17 cm² V⁻¹ s⁻¹, respectively. The SEM observation suggested that CdSnP₂ thin films with relatively flat and smooth surface were obtained, although the formation of ZnSnP₂ protrusions by the VLS growth mode was reported in the case of the Zn-Sn-P system. In order to investigate the difference in both systems, the reaction process in the Cd-Sn-P system was investigated and discussed based on the chemical potential diagrams. The experimental results and the chemical potential diagram suggested that Cd, Sn and P₄ directly reacted to form CdSnP₂, while ZnSnP₂ was formed via the reaction among Zn₃P₂, Sn and P₄ after Zn reacts with P₄ to produce Zn₃P₂. Therefore, it is concluded that direct reaction route to form CdSnP₂ results in the high growth rate and flat morphology in the fabrication of CdSnP₂ thin films.

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- 2 The authors wish to thank Assistant Prof. N. Hatada (Kyoto Univ.) for the provision of
- 3 Chesta, software for creating chemical potential diagrams. This work was financially
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■ Figure captions

Figure 1. XRD profiles of Cd-Sn thin films before and after phosphidation for 30 min at various temperatures.

Figure 2. SEM images of Cd-Sn thin films before and after phosphidation for 30 min at various temperatures.

Figure 3. Cross-sectional SEM images of Cd-Sn thin films (a) before and (b) after phosphidation at 350 °C.

Figure 4. XRD profiles of Cd-Sn thin films before and after phosphidation at 300 °C.

“Discontinued” indicates the sample discontinued on the way heating up to 300 °C.

Figure 5. SEM images of thin films (a) before phosphidation, (b) discontinued during heating up, and after phosphidation at 300 °C (c) 5 min and (d) 30 min.

Figure 6. Chemical potential diagrams of (a) Cd-Sn-P system at 300 °C and (b) Zn-Sn-P system at 450 °C.

■ Figures

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(a)

(b)

Fig. 6. Chemical potential diagrams of (a) Cd-Sn-P system at 300 °C and (b) Zn-Sn-P system at 450 °C.

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