Fabrication of ZnSnP₂ thin films by phosphidation

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Abstract

ZnSnP₂ is a promising candidate as a solar absorbing material consisting of earth-abundant and low-toxic elements. In this study, the phosphidation method, where co-sputtered Zn-Sn thin films react with phosphorus gas, was adopted for fabricating ZnSnP₂ thin films. To establish the conditions for producing ZnSnP₂ thin films, we investigated the influence of phosphidation temperature on the product phases, and interpreted the experimental results using chemical potential diagrams of the Zn-Sn-P system. ZnSnP₂ thin films with a single phase were obtained by phosphidation at 500 °C under a phosphorus vapor pressure of 10⁻² atm. However, formation of ZnSnP₂ protrusions was observed on the surface of the thin films. Based on the experimental results and the chemical potential diagrams, it is indicated that un-reacted liquid Sn particles reacted with Zn and phosphorus gas to form ZnSnP₂ protrusions in a manner similar to the Vapor-Liquid-Solid growth mode.

1. Introduction

In recent years, various types of solar cells have been investigated due to increasing energy demand and low cost. Among them, thin film devices have made remarkable progress in a short time. In particular, $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ and CdTe show high conversion efficiencies of 20.8% [1] and 20.4% [1], respectively, while it is undesirable to use toxic elements (Cd and Te) or rare elements (In and Ga). With these considerations in mind, solar absorbing materials consisting of earth-abundant and low-toxic elements have been pursued and a solar cell using $\text{Cu}_2\text{ZnSnS}_{4-x}\text{Se}_x$ has achieved a conversion efficiency of 12.6% [2].

In this report, ZnSnP_2 with a chalcopyrite structure is investigated as an alternative candidate for a solar absorber. ZnSnP_2 consists of safe and abundant elements and its bandgap is 1.66 eV [3]. According to the Shockley-Queisser limit [4] under the AM 1.5 spectrum, the theoretical conversion efficiency of ZnSnP_2 single-junction solar cells achieves about 30% [5]. In addition, a high absorption coefficient of around 10^5 cm^{-1} was reported for visible light [5, 6]. For electrical properties, it was reported that ZnSnP_2 showed a p-type conduction with the carrier concentration of $10^{16} \sim 10^{17} \text{ cm}^{-3}$ and mobility of $\sim 50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [3]. Thus, ZnSnP_2

1 is a promising material for low-cost and high efficiency solar cells.

2 Preparation of ZnSnP_2 thin films was reported by several methods such as
3 co-evaporation [6], chemical vapor deposition (CVD) [7], molecular beam epitaxy
4 (MBE) [8] and liquid phase epitaxy (LPE) [9]. The co-evaporation method has
5 difficulties in controlling the composition at the stoichiometric ratio of ZnSnP_2 . The
6 CVD and MBE methods use PH_3 gas, which is toxic to humans. The LPE method
7 requires a high temperature to grow ZnSnP_2 , which is not suitable for fabricating
8 thin films on a glass substrate. We therefore adopted a phosphidation method for
9 fabricating ZnSnP_2 thin films as an analogy of selenization, in which Cu-In-Ga films
10 react with selenium gas or selenium hydride gas to form $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ [10]. In the
11 phosphidation method, Zn-Sn precursor thin films prepared on a substrate react with
12 phosphorus gas and this method is considered suitable for an industrialized process.
13 However, there have been no reports on fabricating ZnSnP_2 thin films by this
14 method.

15 In this study, we tried to establish phosphidation conditions to obtain thin films
16 having a single ZnSnP_2 phase. In particular, the influence of phosphidation
17 temperature on the product phases and morphology was investigated and interpreted

1 from thermodynamics based on the chemical potential diagram of the Zn-Sn-P
2 system.

3 4 **2. Experimental**

5 **2.1. Preparation of Zn-Sn thin films**

6 Zn-Sn precursor thin films with the thickness of 0.5 μm were prepared on
7 Mo-coated soda lime glass substrates by magnetron sputtering with Zn and Sn
8 targets. Zn and Sn were co-sputtered for 60 min under an Ar atmosphere with the
9 pressure of 8×10^{-1} Pa. The substrates were rotated at 12 rpm without heating. The
10 power densities for Zn and Sn targets were fixed at 1.0 and 1.6 W cm^{-2} , respectively.
11 The Zn-Sn thin films prepared by co-sputtering were heated for the reaction with
12 phosphorus gas. The atomic ratio of Zn/Sn in precursor thin films was controlled to
13 be about 1.2, considering the higher vapor pressure of Zn compared with Sn because
14 the phosphidation experiments were carried out 350 ~ 500 $^{\circ}\text{C}$ as described later. The
15 thickness and composition were measured by inductively coupled plasma atomic
16 emission spectroscopy (SII Nano Technology SPS3520UV). Morphology of the
17 films was observed by field emission scanning microscopy (FE-SEM, HITACHI

High Technologies SU6600) and elemental mappings were carried out by energy dispersive X-ray spectroscopy (EDX, Oxford Instruments X-MAX20) using Zn K and Sn L with the operating voltage of 20 kV.

2.2. Phosphidation of Zn-Sn thin films

For processing thin films by phosphidation, we chose a phosphorus source with two phases, Sn and Sn₄P₃, because of the difficulties in controlling phosphorus vapor pressure from red phosphorus [11]. The molar ratio of Sn/Sn₄P₃ was set at about 3, which corresponds to 30 at.% P in the Sn-P binary system, and the total amount was about 2 g. The phosphorus gas was transported to Zn-Sn thin films using Ar carrier gas and the partial pressure of phosphorus was controlled by heating temperature of the phosphorus source. The equilibrium is shown in equation (1).

In this study, the phosphorus source was heated at 500 °C. The partial pressure of phosphorus gas was estimated to be about 10⁻² atm based on the weight loss of the phosphorus source, which approximately corresponds to the value calculated from the pressure-temperature curve reported by Arita et al [12].

The phosphidation apparatus is shown in Fig. 1. A furnace with two heating zones was used in order to control the temperatures of Zn-Sn thin films and the phosphorus source individually. Before phosphidation, the Zn-Sn thin film and the phosphorus source were located at out of the heating zones in the quartz tube. Initially, the quartz tube was evacuated to 10^{-1} Pa and purged with Ar. The furnace was then heated to predetermined temperatures under Ar gas flow of 20 sccm and the background pressure of Ar was atmospheric pressure. Subsequently, the phosphorus source was moved into the heating zone. After 15 min to achieve stability, the Zn-Sn thin film was inserted into the heating zone and reacted with phosphorus gas. The Zn-Sn thin film after phosphidation was cooled down in the furnace by turning off the heater, or quenched outside the heating zone. In the phosphidation experiments, Ar gas was deoxidized by passing through a furnace at 900 °C containing Ti sponge, as shown in Fig. 1. Morphologies and compositions of the thin films before and after phosphidation were analyzed by scanning electron microscopy (SEM, KEYENCE VE-7800), FE-SEM and EDX (EDAX VE-9800 and Oxford Instruments X-MAX20) with the operating voltage of 20 kV. For the analysis of composition, Zn K, Sn L and P K were used. The product phases were identified by X-ray diffraction (XRD,

PANalytical X'Pert-ProMPD) where CuK α ($\lambda = 1.5406 \text{ \AA}$) was used as an X-ray source (45kV, 40 mA) in a Bragg-Brentano configuration.

3. Results

3.1. Zn-Sn precursor thin films fabricated by co-sputtering

Figure 2 shows the surface and cross-sectional SEM images of Zn-Sn thin film and the corresponding EDX elemental mappings of Zn and Sn. In addition, overlay images of SEM and EDX mappings are also displayed in Fig. 2. From these images, it is observed that Zn and Sn grains were spatially separated from each other and the Sn grains were larger than those of Zn. We attribute the morphology of thin film with Zn and Sn separated to the fact that the Zn-Sn system is described by a eutectic phase diagram.

3.2. Influence of phosphidation temperature

In order to determine the fabrication conditions for ZnSnP₂ thin films with a single phase, the phosphidation experiments were carried out at various temperatures. In the experiments, the phosphidation time was fixed at 30 min. Each sample was

1 cooled in the furnace after phosphidation. Figure 3 shows XRD profiles of the thin
2 films before and after phosphidation. In the samples prepared at lower phosphidation
3 temperatures, e.g., 350 and 400 °C, both Zn_3P_2 and Sn_4P_3 were identified as
4 secondary phases in addition to ZnSnP_2 . The thin film after phosphidation at 450 °C
5 contains only Zn_3P_2 besides ZnSnP_2 . In contrast, a single ZnSnP_2 phase was obtained
6 in the sample prepared at 500 °C.

7 From the SEM image of each sample shown in Fig. 4, particles were observed on
8 the surface of thin films prepared at lower temperatures, while protrusions formed at
9 higher temperatures. The samples after phosphidation were analyzed at several
10 locations using EDX. The average and standard deviation of their compositions are
11 summarized in Table 1. The compositions of particles and protrusions were
12 measured by point analysis and those of surface regions were determined by area
13 analysis. In the sample prepared at 500 °C, the compositions of the protrusions and
14 the surface are close to the stoichiometric ratio of ZnSnP_2 . This is consistent with the
15 results of XRD shown in Fig. 3. The composition of the protrusions observed in the
16 sample prepared at 450 °C is similar to those at 500 °C. In contrast, the composition
17 of the surface is Zn-rich compared to the stoichiometric ratio of ZnSnP_2 . This is

1 attributed to the presence of Zn_3P_2 as a secondary phase. On the other hand, the
2 compositions of particles observed in samples prepared at 350 and 400 °C are
3 Zn-deficient. Considering the results of XRD, it is indicated that particles are mainly
4 composed of Sn_4P_3 . The particles in the sample of 350 °C has higher Zn composition
5 than those of 400 °C. The difference might be attributed to the size of particles. In
6 other words, the particles in the sample of 350 °C are small and the contribution
7 from the underlying layer should be considered. While, the compositions of surface
8 regions in the samples of lower temperatures are Sn-deficient, which is consistent
9 with the fact that the particles are mainly composed of Sn_4P_3 . From XRD profiles
10 and EDX analysis, it is considered that these surfaces consist largely of ZnSnP_2 and
11 Zn_3P_2 .

13 3.3. Time dependence of phosphidation

14 Protrusions and particles on the surface of thin films are obstacles to fabricate
15 photovoltaic devices using ZnSnP_2 . Hence, their growth mechanism should be
16 understood in order to improve the surface morphology. Here, we carried out
17 phosphidation of the Zn-Sn thin film for 5 min at 450 °C to investigate the change of

product phases and morphology. This sample was quenched by moving it outside the heating zone in the quartz tube. After the 5 min phosphidation, ZnSnP_2 , Zn_3P_2 and Sn were identified from the XRD profile in Fig. 5, while Zn was not observed. Finally, almost single phase of ZnSnP_2 were observed after 30 min phosphidation. The change of phases between the 5 and 30 min samples can be understood from the reaction among $\text{Zn}_3\text{P}_2(\text{s})$, Sn (l) and $\text{P}_4(\text{g})$ to produce ZnSnP_2 , described by equation (2).

The production of $\text{Zn}_3\text{P}_2(\text{s})$ observed in the initial stage occurs according to equation (3),

$\text{ZnSnP}_2(\text{s})$ was also identified in 5 min sample which was due to the reaction of a part of Zn_3P_2 or Zn with Sn (l) and $\text{P}_4(\text{g})$. Thermodynamic considerations in the phosphidation reaction route will be discussed later.

Figure 6 and Table 2 show the SEM images and the EDX analysis of the samples for 5 and 30 min phosphidation, respectively. Some particles were observed on the surface of the thin film prepared for 5 min. From the EDX analysis, the composition

of the particles is Sn-rich. The morphology of this sample is similar to the thin film prepared at lower phosphidation temperatures, such as 350 and 400 °C, shown in Fig. 4. In comparison, protrusions of ZnSnP_2 were observed in the sample prepared for 30 min. From these changes, it is expected that the particles with a high concentration of Sn changed to ZnSnP_2 protrusions during phosphidation.

4. Discussion

4.1. Thermodynamic consideration of the phosphidation reaction using chemical potential diagrams

Here, we consider the reaction route where ZnSnP_2 thin films with a single phase were obtained to investigate conditions for fabricating thin films without protrusions. The experimental results are discussed from the viewpoint of thermodynamics using the chemical potential diagram. The review on a chemical potential diagram is summarized by Yokokawa [13]. A chemical potential diagram represents a stable potential region of various substances using chemical potentials of constituent elements as axes. In this work, the chemical potential diagram of the Zn-Sn-P system was created using the software Chesta 3.2.6.9 developed by Hatada. For drawing the

potential diagram, thermodynamic database edited by Barin [14] and data reported by Arita and Kamo [12] were used. And we calculated the standard Gibbs energy of formation of ZnSnP_2 using the enthalpy and entropy reported by our group [15]. In this study, Zn-Sn alloy was not considered for simplification.

Figure 7 shows the chemical potential diagrams at various temperatures. The axes are the logarithms of the partial pressures of Zn (g), Sn (g), and P_4 (g), which represent their chemical potentials. The dotted line shows the partial pressure of P_4 (g) in the experiments of this study. We here consider the phosphidation behavior at a temperature for simplicity, although the Zn-Sn thin films were inserted into a furnace that was already heated and the temperature at the thin films was increasing for a time during the actual experiments.

We discuss the phosphidation of Zn-Sn thin films at 450 °C as an example. Before phosphidation, the thermodynamic coordinates of the Zn-Sn thin film specify the point A in Fig. 7 (c). The chemical potential of phosphorus increases as phosphidation proceed and Zn (l) reacts with P_4 (g) to produce Zn_3P_2 at the point B, following equation (3). At this point, Zn (l), Sn (l) and Zn_3P_2 (s) thermodynamically coexist. The chemical potential of phosphorus then increases along the line between

Sn (l) and Zn_3P_2 (s), and ZnSnP_2 (s) forms at point C, following equation (2). At this point in the diagram, ZnSnP_2 (s) is in equilibrium with Zn_3P_2 (s) and Sn (l), which we experimentally observed (see Fig. 5) in the 5 min phosphidation sample as shown in Fig. 5. As phosphidation proceeds from point C, there are two possible routes. ZnSnP_2 (s) is in equilibrium with Zn_3P_2 (s), when Sn (l) is consumed by the ZnSnP_2 formation reaction, given by equation (2). Alternatively, excessive Sn (l) leads to the coexistence of ZnSnP_2 (s) and Sn (l). Finally, the chemical potential of P_4 (g) reaches 10^{-2} atm, shown in point D, maintaining the equilibria of ZnSnP_2 (s) and Zn_3P_2 (s) in the former route. In contrast, ZnSnP_2 (s) is in equilibrium with Sn_4P_3 (s), shown in point E, where Sn_4P_3 is more stable than Sn (l) at the phosphorus potential of 10^{-2} atm in the latter case. In this study, the composition of Zn-Sn thin films was Zn-rich, which corresponds to the former case. As shown in the XRD data of Fig. 5, the experimental results of phosphidation at 450 °C are consistent with the above thermodynamic considerations from the chemical potential diagram. However, a single-phase ZnSnP_2 thin film was obtained in phosphidation at 500 °C, in spite of the Zn-rich composition in the precursor thin films. In this case, it is expected that evaporation of Zn occurred due to the high phosphidation temperature, and residual

Zn₃P₂ was not identified, although the same reaction route is considered possible at 450°C from the chemical potential diagram. On the other hand, Zn₃P₂ and Sn₄P₃ were experimentally observed as secondary phases in the phosphidation samples at lower temperatures, however ZnSnP₂ (s), Zn₃P₂ (s) and Sn₄P₃ (s) are not in equilibrium in the chemical potential diagram. This inconsistency results from the driving force for Sn₄P₃ formation, which is represented by the difference between the equilibrium potential of Sn/Sn₄P₃ and the phosphorus potential of 10⁻² atm, being higher at lower phosphidation temperatures. Therefore, it is concluded that Sn (l) reacted with P₄ (g) to produce Sn₄P₃ (s) prior to formation of ZnSnP₂ (s), while the reaction between Sn₄P₃ (s), Zn₃P₂ (s) and P₄ (g) might be kinetically difficult because it involves two solid state phases.

4.2. Growth mechanism of protrusions and particles

To improve the morphology of thin films after phosphidation, the detailed mechanism of protrusion formation must be understood. We thus propose a growth mechanism shown in Fig. 8, based on the experimental results and the reaction route considered using the chemical potential diagram.

As previously mentioned, Zn and Sn grains are spatially separated in as-sputtered Zn-Sn thin films, and the Sn grains are larger than those of Zn, as illustrated in Fig. 8 (a). In the initial stage of phosphidation, Zn preferentially reacts with P_4 to produce Zn_3P_2 , and some Sn reacts with Zn_3P_2 (or Zn) and P_4 to form $ZnSnP_2$. Considering the densities of Zn_3P_2 [16], $ZnSnP_2$ [3], Zn and Sn, the molar volumes per a cation (Zn or Sn) of phosphides are twice compared with that of Zn or Sn. Consequently, the compressive stress due to phosphides acts on un-reacted Sn, as illustrated in Fig. 8 (b). In the intermediate stage (Fig. 8 (c)), it is extruded to the thin film surface, relieving the compressive stress. This behavior is similar to the formation of Sn whiskers observed in Sn thin films electroplated on Cu [17]. In this case, the relieving of the compressive stress caused by formation of intermetallic compounds is the driving force for whisker formation. Finally, Sn particles on the surface react with Zn, which might be in the gas stage generated from $Zn_3P_2(s)$ and $P_4(g)$, to produce $ZnSnP_2$ in the form of protrusions similar to the Vapor-Liquid-Solid growth mode [18], as shown in Fig. 8 (d). In the cases of lower temperatures, although it is possible that Sn particles react with $P_4(g)$ to form Sn_4P_3 due to the large driving force, Sn_4P_3 are kinetically unreactive with Zn_3P_2 as previously discussed. Therefore,

protrusions were not observed. Consequently, it is concluded that the formation of ZnSnP_2 protrusions is attributed to Sn particles formed on the surface of thin films. Based on the proposed mechanism, Zn-Sn thin films with spatial-homogeneity should be prepared to suppress the coarsening of Sn grains and obtain a smooth ZnSnP_2 surface.

5. Conclusions

In this study, thin films with a single phase of ZnSnP_2 were fabricated by phosphidation of co-sputtered Zn-Sn thin films at 500 °C under a phosphorus vapor pressure of 10^{-2} atm. Zn_3P_2 and Sn_4P_3 were formed as secondary phases during phosphidation at lower temperatures (such as 350 and 400 °C), and thin films prepared at 450 °C contained Zn_3P_2 in addition to ZnSnP_2 . These experimental results are able to be interpreted based on the chemical potential diagrams of the Zn-Sn-P system. In the initial stage of phosphidation, Zn preferentially reacts with phosphorus gas to produce Zn_3P_2 . Then, Sn reacts with Zn and P_4 to form ZnSnP_2 for the higher phosphidation temperatures (450 and 500 °C). In contrast, the driving force for formation of Sn_4P_3 is larger at lower phosphidation temperatures (350 and

400 °C). The experimental evidence and thermodynamic considerations indicate that Sn reacted with phosphorus gas to produce Sn_4P_3 before the formation of ZnSnP_2 , while Zn_3P_2 and Sn_4P_3 remained un-reacted due to the slow kinetics at lower phosphidation temperatures. Although thin films with a single phase of ZnSnP_2 were obtained, some protrusions were observed on the surface of the thin films after phosphidation. From experimental results during the initial stage of phosphidation, it was clarified that particles with high concentration of Sn were produced on the surface of thin films, due to release of compressive stress created by the phosphides. Then, the particles reacted with Zn_3P_2 and phosphorus gas to form ZnSnP_2 protrusions, which is a similar mechanism to the Vapor-Liquid-Solid growth mode. These considerations interpret the reaction route from the initial through final stages, based on the experimental results and the chemical potential diagrams. It is thus concluded that the formation of the protrusions were attributed to the morphology of the Zn-Sn thin film produced as a starting point for ZnSnP_2 production, where Zn and Sn grains were spatially separated and Sn grains are larger than those of Zn. Therefore, Zn-Sn thin films with a spatially homogeneous composition are needed to improve the surface morphology of thin films after phosphidation.

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1 **Table Captions**

2 **Table 1.** EDX composition of thin films after phosphidation at various temperatures.

3 **Table 2.** EDX composition of thin films after phosphidation for specified times.

4

5 **Figure Captions**

6 Figure 1. Schematic illustration of phosphidation apparatus.

7 Figure 2. SEM images and elemental mappings of Zn-Sn precursor before
8 phosphidation. (a) Surface and (b) cross-sectional images. The right figures
9 show the overlay images of Zn and Sn mappings.

10 Figure 3. XRD profiles of Zn-Sn thin films before and after phosphidation for 30
11 min at various temperatures.

12 Figure 4. SEM images of thin films (a) before and after phosphidation at (b) 350, (c)
13 400, (d) 450, and (e) 500 °C

14 Figure 5. XRD profiles of Zn-Sn thin films before and after phosphidation at 450 °C
15 for 5 and 30 min

16 Figure 6. SEM images of thin films (a) before and after phosphidation at 450 °C for
17 (b) 5 min and (c) 30 min.

1 Figure 7. Chemical potential diagrams of Zn-Sn-P system at (a) 350, (b) 400, (c) 450,
2 and (d) 500 °C. In this study, Sn_3P_4 and SnP_3 are not considered for the
3 construction of the diagram because thermodynamic data have not been
4 reported.

5 Figure 8. Growth mechanism of ZnSnP_2 protrusion. (a) Before phosphidation, (b)
6 initial and (c) intermediate stages of phosphidation, and (d) after
7 phosphidation.

Table 1. Composition of thin films after phosphidation at various temperatures.

Sample		Composition / at. %		
Temperature / °C	Region	Zn	Sn	P
350	Particles	10.3 ± 2.0	38.7 ± 2.5	51.0 ± 0.5
	Surface	35.2 ± 2.6	14.4 ± 1.8	50.4 ± 0.8
400	Particles	6.6 ± 2.2	46.7 ± 1.6	46.8 ± 1.2
	Surface	37.6 ± 1.1	16.7 ± 0.8	45.7 ± 0.4
450	Protrusions	22.7 ± 1.2	21.5 ± 0.9	55.8 ± 0.8
	Surface	29.4 ± 0.9	22.0 ± 0.5	48.6 ± 0.5
500	Protrusions	23.0 ± 1.7	21.2 ± 1.7	55.8 ± 1.8
	Surface	24.4 ± 0.7	23.2 ± 0.6	52.4 ± 1.2

Table 2. EDX composition of thin films after phosphidation for 5 and 30 min.

Sample		Composition / at. %		
Time / min	Region	Zn	Sn	P
5	Particles	7.0 ± 4.9	63.1 ± 13.3	29.9 ± 14.4
	Surface	45.5 ± 2.5	30.5 ± 3.0	24.0 ± 0.5
30	Protrusions	22.7 ± 1.2	21.5 ± 0.9	55.8 ± 0.8
	Surface	29.4 ± 0.9	22.0 ± 0.5	48.6 ± 0.5

Fig.1

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(a)

(b)

Fig.2

Nakatsuka et al.

Fig.3

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(a)

(b)

(c)

(d)

(e)

Fig.4

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Fig.5

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(a)

(b)

(c)

Fig.6

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(a)

(b)

(c)

(d)

Fig.7

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Fig.8

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