Growth and Optical Absorption of CoIn_2S_4 Thin Films by Spray Pyrolysis Method

Received 5 February, 2021; revised 23 April, 2021; accepted 30 April, 2021

Chang-Dae Kim^{a,*}

^aDepartment of Physics, Mokpo National University, Chonnam 58554, Republic of Korea

*Corresponding author E-mail: kimcd@mokpo.ac.kr

ABSTRACT

CoIn_2S_4 thin films were grown onto glass substrates by a spray pyrolysis method. For the growth, the substrate temperature was varied between 250 and 320 °C, and the spray rate was fixed at 6 ml/min. The grown thin films were characterized X-ray diffraction (XRD), field-emission scanning electron microscope (FE-SEM), and optical spectroscopy. The XRD analysis showed that the thin films grown at 320 °C were well crystallized in cubic spinel structure. The FE-SEM results demonstrated that the thin films have a uniform and homogeneous surface. The direct band gap energy was first obtained from the measurement of optical absorption spectra near the fundamental absorption edge at 292 K, and was founded to be 1.59 eV. We also observed two group absorption bands in the near-infrared region, which originate in cobalt ions of the constituent elements of CoIn_2S_4 . The absorption bands were well assigned as due to the crystal-field transitions of Co^{2+} ions occupying tetrahedral sites of the cubic spinel CoIn_2S_4 host lattice.

Keywords:

CoIn_2S_4 , Thin films, Optical absorption, Band gap, Tetrahedral Co^{2+} , Spray pyrolysis method

1. Introduction

CoIn_2S_4 , one of the type- AB_2X_4 ($A = \text{Co, Mn, Fe}$; $B = \text{Al, Ga, In}$; $X = \text{O, S, Se}$), is a ternary compound semiconductor with potential application in optoelectronic devices [1–3]. CoIn_2S_4 is also expected as an interesting material with magnetic properties due to the cobalt constituent elements. It has been reported that the cobalt constituent elements of CoGa_2S_4 has an influence on the magnetic behavior [4]. In addition, the constituent transition metals or the doped transition metals in semiconductors introduce localized states such as sensitizing and luminescent centers in the forbidden band gap. These desirable properties make this compound useful materials for more applications in optoelectronic devices, such as the $\text{II}_{1-x}\text{M}_x\text{VI}$ ($M = \text{Co, Fe, Mn, etc.}$) diluted magnetic semiconductors [5–7]. A few studies of CoIn_2S_4 have been made on the structural and magnetic properties of this material [8, 9]. Also, a few information of CoIn_2S_4 has been appeared in the systems of $\text{Co}_x\text{Cd}_{1-x}\text{In}_2\text{S}_4$ [10], $\text{Co}_x\text{Zn}_{1-x}\text{In}_2\text{S}_4$ [11–14], CoGaInS_4 [15,16], $\text{CoIn}_2\text{S}_4 - \text{CoIn}_2\text{Se}_4$ [17], and $\text{CoIn}_{2-2x}\text{Cr}_{2x}\text{S}_4$ [18]. However, there has been no information on band gap and optical properties of CoIn_2S_4 . In addition, there has been no study yet on the influence of cobalt, a constituent element of CoIn_2S_4 , on the optical properties of this material. In the previous work [19], we have studied the effects of cobalt constituent element in $\text{Co}_x\text{Cd}_{1-x}\text{Ga}_2\text{Se}_4$ mixed crystals on their optical properties. In order to further enhance the applicability of CoIn_2S_4 , therefore, more information about the influence of cobalt constituent element including band gap of this material is needed. And the spray pyrolysis technique for the thin film growth of the material should be established. Among a variety of methods for thin film growth, the spray pyrolysis technique is used for several compound semiconductors because of a simple and low-cost method enabling large-area production with highly uniform [20].

In the present paper, we report on the thin film growth of CoIn_2S_4

by the spray pyrolysis technique. The grown thin films were characterized by X-ray diffraction and field-emission scanning electron microscope measurements. The band gap energy at 292 K was first obtained by optical absorption spectroscopy measurements. Also, we discuss the absorption bands observed in the near-infrared region, which are originated in cobalt ions of the constituent elements of CoIn_2S_4 . These absorption bands are analyzed in connection with $d-d$ optical transitions of tetrahedral Co^{2+} ions in the CoIn_2S_4 lattice.

2. Experimental details

CoIn_2S_4 thin films were grown by the spray pyrolysis method [21]. A spraying solution was prepared by dissolving CoCl_2 (GA, Alfa Products), InCl_3 (5N, Alfa Products) and thiourea (GA, Alfa Products) in 1:1 solvent solution composed of methanol (Merck-Analysis) and distilled water to give 0.2 molar solutions of each solute. Then these solutions were mixed in a volume ratio of 1:2:4, and at the same time an excess thiourea solution of 20 % was added in order to compensate the loss of sulphur caused by vaporization during the deposition. The final mixture of the solutions was magnetically stirred at 70 °C for 30 min. Then this solution has sprayed on a slide glass (Corning-2948) with a fixed spray rate of $6 \text{ ml} \cdot \text{min}^{-1}$ under ambient air. The substrate temperature was varied from 250 to 320 °C for film deposition.

The structural properties such as surface morphology and layer thickness of the grown thin films were characterized by using field-emission scanning electron microscope (FE-SEM, Hitachi, S-4800), and their crystalline phases and qualities were studied by X-ray diffraction (XRD, X'pert pro MPD) measurements. Also, the band gaps of CoIn_2S_4 and the $d-d$ optical transitions of Co^{2+} ions were investigated by the measurements of optical absorption spectra in the wavelength region of 250 to 3200 nm at 292 K using a UV-VIS-NIR spectrophotometer (Hitachi, U-3501).

3. Results and discussion

Figure 1 shows the XRD patterns of the CoIn_2S_4 thin films depending on the substrate temperature. The XRD patterns for the thin films grown at 250 °C of Fig. 1(a) shows a broad and weak peak near 2θ angle of 20~30°, which is considered to be typical of amorphous thin films. As the substrate temperature increases, the XRD peaks become intense. For the thin films grown at the substrate temperature of 320 °C, as shown in Fig. 1(c), the XRD pattern shows a lot of planes (111), (220), (311), (400), (511), (440), (531), (533), and (444) of cubic spinel, except for the diffraction peak with a relatively weak intensity at $2\theta = 22.336$ originated from In_2O_3 . It is in good agreement with that in JCPDS 03-065-5369 for CoIn_2S_4 crystals. The strong and sharp diffraction peaks suggest that the grown thin films were well crystallized. Also, the FE-SEM micrographs of surface and cross-section of the CoIn_2S_4 thin films grown at 320 °C are given in Fig. 2. The result depicts that the morphological features of the CoIn_2S_4 thin films have almost a uniform and homogeneous surface, and a thickness of 1.90 μm .

Figure 3 depicts optical absorption spectrum of the CoIn_2S_4 thin films in the wavelength range of 250 to 3200 nm at 292 K. In Fig. 3 we can see some characteristics, i.e., a rapid rise in absorption near the regions of 780 and 2700 nm, and a relatively sharp absorption band in the wavelength range of 600 to 850 nm and a broad absorption band in the wavelength range of 1200 to 2400 nm. Among them, the rapid absorption near the 2700 nm-wavelength region originates in a slide glass used as a substrate, and also the arising of abrupt absorption near the 780 nm-wavelength region refers to the fundamental absorption. And the two absorption bands observed in the wavelength range of 650 to 850 nm and 1200 to 2400 nm are concerned with the $d-d$ transitions of Co^{2+} ions. In order to obtain the band gap of the CoIn_2S_4 thin films, firstly, we examined the absorption spectrum in the wavelength range of 500 to 680 nm near the fundamental absorption edge. However, unfortunately the fundamental absorption is influenced by the $d-d$ transitions of Co^{2+} ions. Thus, we extracted the absorption effects due to Co^{2+} ions from the optical absorption spectrum near the

Figure 1. XRD patterns of CoIn_2S_4 thin films grown at (a) 250, (b) 280, and (c) 320 °C.

Figure 2. SEM micrographs of (a) surface and (b) cross-sectional of CoIn_2S_4 thin films grown at 320 °C.

fundamental absorption edge. The corrected absorption spectrum is shown as a dotted line in Fig. 3, and is used for plotting of the relation between the optical absorption coefficient α and the incident photon energy $h\nu$. Figure 4 shows the relation $(\alpha h\nu)^2$ for a direct band gap, assuming that the CoIn_2S_4 has a direct band gap in consideration of a characteristic of a rapid absorption near the fundamental absorption edge for the case of direct band-to-band transitions. The direct band gap is then obtained by extrapolation of the plot to $(\alpha h\nu)^2 = 0$ in Fig. 4 from the relation $(\alpha h\nu)^2 = A(h\nu - E_g)$ for a direct band gap [22], and is found to be 1.59 eV. It is considered that the obtained band gap energy is a reasonable value considering the absorption edges for the crystals of $x = 0.46$ in $\text{Co}_x\text{Zn}_{1-x}\text{In}_2\text{S}_4$ ($0.07 \leq x \leq 0.46$) mixed crystals [14].

Now, we discuss the $d-d$ transitions of Co^{2+} ions in CoIn_2S_4 . Two absorption bands in Fig. 3 are assigned as the $d-d$ transitions between the ground state $^4\text{A}_2(^4\text{F})$ and the excited states $^4\text{T}_1(^4\text{F})$, $^4\text{T}_1(^4\text{P})$ of Co^{2+} ions, as shown in the schematic energy-level diagram inserted in Fig. 3. The relatively sharp absorption band, which corresponds to the transition $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{P})$ in the wavelength range of 600 to 850 nm, shows three split absorption bands as shown in Fig. 5. The triplet structure is assigned as the transitions of Co^{2+} ions from the ground state $^4\text{A}_2(^4\text{F})$ to the split states $\Gamma_7 + \Gamma_8$, Γ_8 , and Γ_6 of the excited $^4\text{T}_1(^4\text{P})$ under the spin-orbit interaction. On the other hand, the broad absorption band, which corresponds to the transition $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{F})$ in the wavelength range of 1200 to 2400 nm, is observed to be not resolved, and it gives the crystal-field splitting $18 Dq$. The Dq -value is then obtained by 348 cm^{-1} , which is close to $Dq \approx 400 \text{ cm}^{-1}$ for tetrahedral Co^{2+} ions [23]. This implies that the observed absorption bands are originated from Co^{2+} ions with the tetrahedral sites of the CoIn_2S_4 lattice. However, our results are compared to those of $\text{Co}_x\text{Cd}_{1-x}\text{In}_2\text{S}_4$ by Porta *et al.* [10]. The authors reported three group

Figure 3. Absorption spectrum in the wavelength range of 250 to 3200 nm at 292 K.

bands due to both octahedral and tetrahedral Co^{2+} in reflectance spectra of $\text{Co}_x\text{Cd}_{1-x}\text{In}_2\text{S}_4$ ($0.0 \leq x \leq 1.0$) crystals, which is a different appearance from our results due to only tetrahedral Co^{2+} . Also, Fiorani *et al.* [8] reported that the Co^{2+} ions of the spinel CoIn_2S_4 are distributed between octahedral (63 %) and tetrahedral (37 %) sites of the lattice. In our works, nevertheless, a characteristic of absorption bands due to octahedral Co^{2+} was not observed, but only absorption bands due to tetrahedral Co^{2+} were observed. It is possible that these results may be come from an occurrence of an accidental breaking of the true site symmetry of Co^{2+} ions in the CoIn_2S_4 . However, its origin is not clear at present. In Table I, our observed absorption bands due to tetrahedral Co^{2+} are summarized.

4. Conclusions

CoIn_2S_4 thin films have been successfully grown on a slide glass at an optimal substrate temperature of 320 °C and a spray rate of 6 $\text{ml}\cdot\text{min}^{-1}$ by the spray pyrolysis method. The XRD analysis revealed that the films grown at 320 °C are well crystallized in single-phase cubic spinel structure. The FE-SEM micrographs depicted that the films have a uniform and homogeneous surface.

The nature and the magnitude of band-to-band transitions of the CoIn_2S_4 thin films were determined from the optical absorption spectrum analysis near the fundamental absorption edge in which the absorption effect due to the cobalt ions of the constituent elements was extracted. The result gives the direct band gap of 1.59 eV. Also, the two absorption bands observed in the near-infrared regions, which

Table I. Observed absorption bands due to the $d-d$ transitions of tetrahedral Co^{2+} in CoIn_2S_4 .

Observed absorption bands				
Notation	nm	eV	cm^{-1}	Assignments
P	A	702	1.77	14245
	B	754	1.65	13263
	C	796	1.56	12563
F	1596	0.78	6266	$4A_2(^4F) \rightarrow 4T_1(^4F)$

Figure 4. Plots of $(\alpha h\nu)^2$ and band gap energy at 292 K.

are originated in cobalt ions of constituent elements, are well assigned as due to the crystal-field transitions of Co^{2+} ions with the tetrahedral sites of the CoIn_2S_4 lattice. However, our results due to only tetrahedral Co^{2+} are somewhat different from those due to both octahedral and tetrahedral Co^{2+} reported in reflectance spectra of CoIn_2S_4 for $x = 1.0$ of $\text{Co}_x\text{Cd}_{1-x}\text{In}_2\text{S}_4$ crystals [10]. The origin of the differences

Figure 5. Triplet absorption bands of the transition $4A_2(^4F) \rightarrow 4T_1(^4P)$.

in the results of each other is not clear at present. In order to clarify these results, further crystallographic studies on this material should be needed.

Acknowledgements

This research was supported by Research Funds of Mokpo National University in 2019.

References

- [1] C. Zeng and Y. Hu, *Nanotechnology* 31, 505711 (2020).
- [2] P. He, X. Li, T. Wang, W. Chen, H. Zhang, and W. Chen, *Inorg. Chem. Front.* 7, 2621 (2020).
- [3] S. Ge, Z. Shui, Z. Zheng, and L. Zhang, *Optical Materials* 33, 1174 (2011).
- [4] E. Agostinelli, L. Gastaldi, and S. Viticoli, *J. Phys. Chem. Solids* 46, 1345 (1985).
- [5] Q. Mahmood, A. Javed, G. Murtaza, and S. M. Alay-e-Abbas, *Mat. Chem. & Phys.* 162, 831 (2015).
- [6] A. A. Maksimov, D. R. Yakovlev, J. Debus, I. I. Tartakovskii, A. Waag, G. Karczewski, T. Wojtowicz, J. Kossut, and M. Bayer, *Phys. Rev. B* 82, 035211 (2010).
- [7] D. Ferrand, A. Wasiela, S. T. Tatarenko, J. Cibert, G. Richter, P. Grabs, G. Schmidt, L. W. Molenkamp, and T. Dietl, *Solid State Commun.* 119, 237 (2001).
- [8] D. Fiorani, L. Gastaldi, and S. Viticoli, *Solid State Commun.* 48, 869 (1983).
- [9] T. Kanomata, H. Ido, and T. Kaneko, *J. Phys. Soc. Jpn.* 34, 554 (1973).
- [10] P. Porta, A. Anichini, and M. C. Campa, *J. Solid State Chem.* 114, 524 (1995).
- [11] D. Fiorani, L. Gastaldi, and S. Viticoli, *Solid State Commun.* 48, 865 (1983).
- [12] C. Battistoni, L. Gastaldi, A. Lapicciarella, G. Mattogno, and S. Viticoli, *J. Phys. Chem. Solids* 47, 899 (1986).
- [13] C. Battistoni, G. Mattogno, and S. Viticoli, *Solid State Commun.* 63, 273 (1987).
- [14] A. Borghesi, G. Guizzetti, and L. Nosenzo, *Solid State Commun.* 64, 1187 (1987).
- [15] C. Battistoni, L. Gastaldi, G. Mattogno, M. G. Simeone, and S. Viticoli, *Solid State Commun.* 61, 865 (1987).
- [16] H. Haeuseler, H. J. Stork, and W. Cordes, *J. Solid State Chem.* 87, 15 (1990).
- [17] A. Memo, W. Kwarteng-Acheampong, and H. Haeuseler, *Mat. Res. Bull.* 38, 1057 (2003).
- [18] G. E. Delgado and V. Sagredo, *Chalcogenide Lett.* 6, 641 (2009).
- [19] C. D. Kim, *Appl. Sci. Converg. Technol.* 28, 24 (2019).
- [20] J. B. Mooney and S. B. Radding, *Ann. Rev. Mater. Sci.* 12, 81 (1982).
- [21] A. A. Akl, I. M. El Radaf, and A. S. Hassanien, *Optik*, 227, 165837 (2021).
- [22] J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1975) p. 35.
- [23] D. L. Wood and J. P. Remeika, *J. Chem. Phys.* 46, 3595 (1967).