Inorg. Chem. **2007**, *46*, 1013–1017

Inorganic Chemistry
Article

Deposition of $CuInS_2$ Thin Films Using Copper- and Indium/Sulfide-Containing Precursors through a Two-Stage MOCVD Method

Seung Soo Lee, Kook Won Seo, Jong Pil Park, Sin Kyu Kim, and Il-Wun Shim*

Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea

Received August 2, 2006

Copper indium disulfide ($CuInS_2$; CIS) films were deposited on various substrates by two-stage metal–organic chemical vapor deposition (MOCVD) at relatively mild conditions, using Cu- and In/S-containing precursors without toxic H_2S gas: first, a pure Cu thin film was prepared on glass or indium/tin oxide glass substrates by using a single-source precursor, bis(ethylbutyrylacetato)copper(II) or bis(ethylisobutyrylacetato)copper(II); second, on the resulting Cu film, tris(*N*,*N*-ethylbutyldithiocarbamato)indium(III) was treated to produce CIS films by a MOCVD method at 430 °C. In this process, their thicknesses and stoichiometries were found to be elaborately controlled on demand by adjusting the process conditions. The optical band gap of the stoichiometric CIS film was about 1.41 eV, which is in the near-optimal range for harvesting solar radiation energy.

Introduction

Polycrystalline copper indium disulfide ($CuInS_2$; CIS), a ternary compound with a direct optical band gap of 1.3−1.5 eV, has been well-known to have a great potential as an absorption layer material for application to low-cost, less toxic, high-efficiency thin-film solar cells; its typical absorption coefficient is about 10^5 cm^{-1} and its efficiency has been up to nearly 13% at present.[1−3] For these reasons, there have been many researches about the preparation of CIS films through chemical bath deposition,[4] chemical spray deposition,[5] radio-frequency reactive sputtering,[6] selenization/sulfurization of metallic alloys,[7] electrodeposition,[8] spray pyrolysis,[9] and other methods.[10,11] Among them, the metal−organic chemical vapor deposition (MOCVD) method has many practical benefits over other methods; especially, the composition, structure, and morphology of the thin films can be controlled properly if there is a suitable single-source precursor that is stable at ambient conditions with high volatility.[12] However, ternary or multinary single-source precursors with the correct Cu/In/S stoichiometry for CIS films[13,14] are relatively very rare simply because it is very difficult to synthesize heterometallic compounds with proper elements in the proper ratio. Besides, such single-source precursors containing Cu, In, and S or Se elements in one compound were usually found to have large molecular weight, high melting point, and low vapor pressure, not suitable for the typical MOCVD process.[13,14] In the case of aerosol-assisted CVD using a single-source precursor, the precursor was air- and moisture-sensitive and the growth rate was very low.[13] In addition, although CIS films were prepared through the many different methods as above, it was typically difficult to control the stoichiometric ratio of the relevant elements, and other further subordinate processes were required for acceptable results.[1−11]

Recently, we prepared highly polycrystalline copper indium diselenide ($CuInSe_2$) thin films on a Mo substrate

* To whom correspondence should be addressed. E-mail: iwshim@cau.ac.kr. Tel.: +822-820-5201. Fax: +822-825-4736.

(1) Störkel, U.; Aggour, M.; Murrell, C. P.; Lewerenz, H. J. *Thin Solid Films* **2001**, *90*, 182−184.
(2) Klaer, J.; Bruns, J.; Henninger, R.; Siemer, K.; Klenk, R.; Ellmer, K.; Braunig, D. *Semicond. Sci. Technol.* **1998**, *13*, 1456−1458.
(3) Ogawa, Y.; Uenishi, S.; Tohyama, K.; Ito, K. *Sol. Energy Mater. Sol. Cells* **1994**, *35*, 157−163.
(4) Pathan, H. M.; Lokhande, C. D. *Appl. Surf. Sci.* **2004**, *239*, 11−18.
(5) Hehemann, D. G.; Lau, J. E.; Harris, J. D.; Hoops, M. D.; Duffy, O. V.; Fanwick, P. E.; Khan, O.; Jin, M. H.-C.; Hepp, A. F. *Mater. Sci. Eng. B* **2005**, *116*, 381−389.
(6) He, Y. B.; Krämer, T.; Polity, A.; Hardt, M.; Meyer, B. K. *Thin Solid Films* **2003**, *431−432*, 126−130.
(7) Bekker, J.; Alberts, V.; Leitch, A. W. R.; Botha, J. R. *Thin Solid Films* **2003**, *431−432*, 116−121.
(8) Martinez, A. M.; Arriaga, L. G.; Fernández, A. M.; Cano, U. *Mater. Chem. Phys.* **2004**, *88*, 417−420.
(9) Krunks, M.; Kijatkina, O.; Rebane, H.; Oja, I.; Mikli, V.; Mere, A. *Thin Solid Films* **2002**, *403−404*, 71−75.
(10) Bini, S.; Bindu, K.; Lakshmi, M.; Kartha, C. S.; Vijayakumar, K. P.; Kashiwaba, Y.; Abe, T. *Renewable Energy* **2000**, *20*, 405−413.
(11) Lokhande, C. D.; Barkschat, A.; Tributsch, H. *Sol. Energy Mater. Sol. Cells* **2003**, *79*, 293−304.
(12) Kemmler, M.; Lazell, M.; O'Brien, P.; Otway, D. J. *Mater. Res. Soc. Symp. Proc.* **2000**, *606*, 147−152.
(13) Kelly, C. V.; Jin, M. H.-C.; Banger, K. K.; McNatt, J. S.; Dickman, J. E.; Hepp, A. F. *Mater. Sci. Eng. B* **2005**, *116*, 403−408.
(14) O'Brien, P.; Nomura, R. *J. Mater. Chem.* **1995**, *5*, 1761−1773.

10.1021/ic061445c CCC: $37.00 © 2007 American Chemical Society

Published on Web 12/30/2006

Table 1. Characterization Results for Two Cu Precursors ([M^+] = [$Cu(ebac)_2]^+$, [$Cu(eiac)_2]^+$)

precursor	yield (%)	MS [M^+] (m/z)	FT-IR bands ν (cm^{-1})	elem anal.: obsd value (calcd) C (%)	H (%)
$Cu(eiac)_2$	89	377	2971, 2932, 2872, 1606, 1586, 1534, 1509, 1366, 1326, 1263, 1178, 1093, 1045, 954, 797, 492, 469	51.85 (50.85)	7.32 (6.93)
$Cu(ebac)_2$	85	377	2983, 2960, 2931, 2872, 1596, 1529, 1368, 1302, 1258, 1172, 1054, 978, 776, 503	48.44 (50.85)	6.85 (6.93)

through a two-stage MOCVD method by using two precursors at relatively mild conditions.[15] First, a phase-pure InSe thin film was prepared on a Mo substrate by using a single-source precursor, di-μ-methylselenobis(dimethylindium). Second, on this InSe film, bis(ethylisobutyrylacetato)copper(II), designated as $Cu(eiac)_2$, was treated by MOCVD to produce $CuInSe_2$ films.

In this paper, to prepare the CIS films in a similar manner, we used three distinctive Cu- and In/S-containing precursors: first, pure Cu films were prepared on glass or indium/tin oxide (ITO) glass substrates by using a single-source precursor, bis(ethylbutyrylacetato)copper(II) [$Cu(ebac)_2$] or $Cu(eiac)_2$; second, on the resulting Cu film, tris(*N*,*N*-ethylbutyldithiocarbamato)indium(III), designated as In-(ebdtc)$_3$,[16,17] was treated to produce CIS films by a MOCVD method.

Experimental Section

All reagents used were from Sigma-Aldrich Corp. All solvents were refluxed over molecular sieves of 3 Å (pellets, 3.2 mm) to remove water molecules and then distilled before use. For analysis of the characteristics of precursors, infrared (IR) spectra were obtained on a Jasco FT/IR-5300 spectrometer within the range of 4000−600 cm^{-1} with a medium slit and a peak resolution of 4.0 cm^{-1}, using a 10-cm gas cell or KBr pellets. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Gemini 2000 NMR spectrometer, using $Si(CH_3)_4$ and $CDCl_3$ as the internal reference and solvent, respectively. Elemental analyses were performed with a Fisous EA-1110. Thermal analyses were carried out with a Setaram LABSYS at atmospheric pressure in Ar from room temperature to 500 °C at a heating rate of 10 °C/min. Mass spectrometry (MS) spectra were obtained on a Autospec EBE mass spectrometer through the standard electron impact procedure with electron beam energy of 70 eV at 150 °C in a vacuum. Foranalysis of Cu and CIS thin films, a Scintag XDS 2000 X-ray diffractometer, ISI-DS 130, and a Philips XL 30S FEG scanning electron microscope equipped with a Phoenix energy-dispersive X-ray (EDX) spectrometer were used. Scanning electron microscopic (SEM) images were obtained at accelerating voltages of 10 or 15 kV and EDX results at an accelerating voltage of 30 kV with a collection time of 1 min. A Jasco U-550 UV/vis spectrometer was used to measure the band gaps of CIS thin films.

Preparation of Bis(ethylisobutyrylacetato)copper(II). This precursor, designated as $Cu(eiac)_2$, was synthesized as in our early paper[16] by reacting 0.2 mol of ethyl isobutyrylacetate, sodium metal, and 0.1 mol of $CuCl_2$ (Aldrich Chemical Co.) in a 30-mL tetrahydrofuran solution at room temperature. After 2 h, the solvent was evaporated, and the resulting residue was dissolved in a pentane solution. The solution was filtered off to remove impurities, and the product was obtained after evaporation of the solvent. Its melting point was found to be 98 °C, and the decomposition temperature was about 206 °C.

Preparation of Bis(ethylbutyrylacetato)copper(II). Bis(ethylbutyrylacetato)copper(II), designated as $Cu(ebac)_2$, was synthesized similarly as above by reacting $CuCl_2$ and corresponding sodium salts of β-diketonates at room temperature.[16] The products were very stable in ambient conditions. Its melting point was found to be 104 °C, and the decomposition temperature was about 196 °C.[14] Table 1 shows the characterization results for these two Cu precursors.

Cu Film Deposition. Before deposition, the substrates, glass and ITO glass, were washed through the normal washing process with sonication; they were dipped in deionized water, 10% sulfuric acid, methanol, and acetone in order. Typical MOCVD experiments were carried out using the two Cu(II) precursors without H_2 gas for the reduction of Cu(II) species in a glass warm-wall reactor with silicon, glass, and ITO glass substrates. The substrate temperature was controlled in the 310−350 °C range and the feed temperature in the 90−110 °C range. The working pressure during deposition was maintained at about 7.5×10^{-4} Torr using Ar as the flowing gas.[16]

Preparation of Tris(*N*,*N*-ethylbutyldithiocarbamato)indium-(III). Sodium hydroxide (120.0 mg, 3 mmol) and *N*,*N*-ethylbutylamine (0.410 mL, 3 mmol) were dissolved in methanol (30 mL). In this solution, carbon disulfide (0.186 mL, 3 mmol) was slowly dropped at 0 °C for 1 h. After the solution was stirred, indium trichloride (221.2 mg, 1 mmol) was slowly added. Immediately, white precipitates were obtained. They were filtered, dried under a vacuum, and recrystallized. The product, designated as In(ebdtc)$_3$, was obtained with high yield, 89%.[17] Its melting point was found to be 140 °C and its decomposition temperature about 350 °C. Table 2 includes the characterization results for In(ebdtc)$_3$.

CIS Film Deposition. MOCVD experiments for CIS film deposition were carried out using the In(ebdtc)$_3$ precursor in a glass warm-wall reactor on Cu substrates from the above process. The substrate temperature was controlled to 430 °C and the feed temperature to 180 °C. The working pressure during deposition was maintained at about 7.5×10^{-4} Torr using Ar as the flowing gas.

Results and Discussion

The two Cu(II) precursor compounds were very stable in ambient conditions and were found to be excellent precursors for the preparation of highly pure metallic Cu films in the cubic phase[18] through a MOCVD method at mild conditions, as shown in Figure 1. Adhesion of the prepared Cu films to substrates was good, but it should be mentioned that, in the case of the $Cu(ebac)_2$ precursor, no deposition on Si

(15) Yoon, S. H.; Seo, K. W.; Lee, S. S.; Shim, I. W. *Thin Solid Films* **2006**, in press. Available online July 11, 2006.
(16) Kim, K. S.; Jeong, H. C.; Cho, J. Y.; Kang, D. H.; Kim, H. K.; Yoo, H. M.; Shim, I. W. *Bull. Korean Chem. Soc.* **2003**, *24*, 647−649.
(17) Lee, S. S.; Yoon, S. H.; Seo, K. W.; Shim, I. W. *Bull. Korean Chem. Soc.* **2005**, *26*, 1453−1456.
(18) Powder Diffraction File, Joint Committee on Powder Diffraction Standard, ICDD, Sept 1995, Card No. 04-0836, Version 1.10.

Table 2. Characterization Results for $In(ebdtc)_3$

precursor	yield (%)	^1H NMR δ (ppm)	MS $[In(ebdtc)_3]^+$ (m/z)	FT-IR bands ν (cm^{-1})	elem anal.: obsd value (calcd) C (%)	H (%)	N (%)
$In(ebdtc)_3$	89	3.84 (q, 2H, CH_2), 0.94 (t, 3H, CH_3), 3.73 (d, 2H, CH_2), 1.76 (m, 2H, CH_2), 1.34 (m, 2H, CH_2), 0.95 (t, 3H, CH_3)	643	2960, 2931, 2868, 1623, 1496, 1425, 1370, 1284, 1235, 1193, 1152, 1089, 997, 940, 856, 793, 736, 616, 581	38.27 (39.19)	6.5 (6.5)	6.4 (6.5)

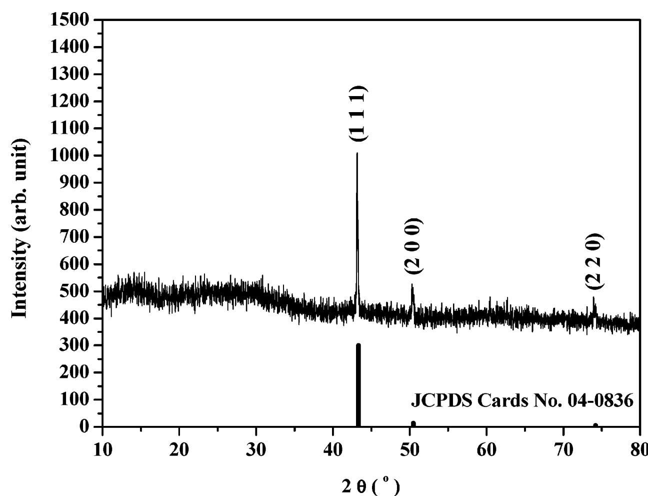

Figure 1. XRD data of the Cu thin film on glass.

substrates was observed. The deposition rate was about 12.5 Å/min, and the average resistivity of the Cu films by a four-point probe method was 1.699 $\mu\Omega$•cm, indicating that the films were composed of very pure Cu metal.[16]

The $In(ebdtc)_3$ precursor was also quite stable in ambient conditions and had a relatively lower melting point with a short decomposition temperature range in comparison to the known similar precursors, suggesting that it can be used in the MOCVD process under relatively milder conditions.[17]

A separate experiment was carried out in order to test $In(ebdtc)_3$ as a MOCVD precursor; In_2S_3 thin films were obtained by a MOCVD method using the precursor, in which the bubbler temperature was 180 °C and the substrate temperature was about 350 °C. The X-ray diffraction (XRD) pattern of the resulting dark-red film on glass or ITO glass coincided quite well with that of the known tetragonal In_2S_3 up to 450 °C without any dependence on the substrates.[19] It was transformed to a cubic β-In_2S_3 phase above 470 °C, as shown in Figure 2. EDX analyses of these films showed an In/S ratio of 2:3 in the whole substrate temperature range, indicating the formation of In_2S_3 without any appreciable amount of impurities such as C, O, and N. In addition, it was quite noteworthy that there were no other phases such as InS or In_3S_5. The optical band gap of these films ranged from 2.0 to 2.4 eV according to the grain size and thickness of the thin films. The growth rate of the In_2S_3 films was 2.8 nm/min on average at the temperature region near 370 °C.

(19) Powder Diffraction File, Joint Committee on Powder Diffraction Standard, ICDD, Sept 1995, Card No. 25-0390, Version 1.10.

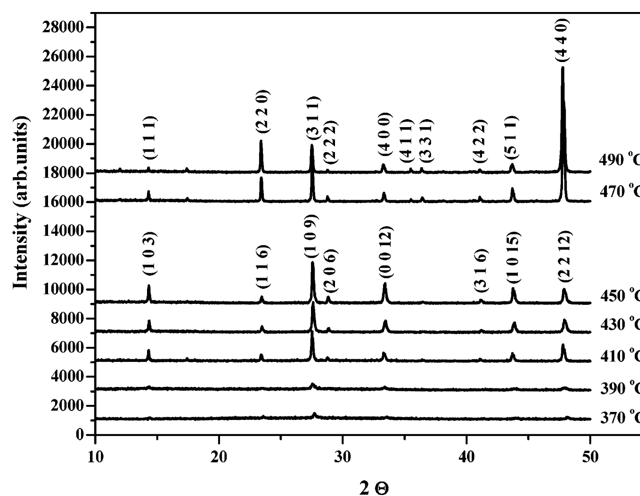

Figure 2. XRD pattern of the In_2S_3 thin films deposited at different temperatures on glass. The phase of the films was tetragonal from 370 to 450 °C and cubic above 470 °C.

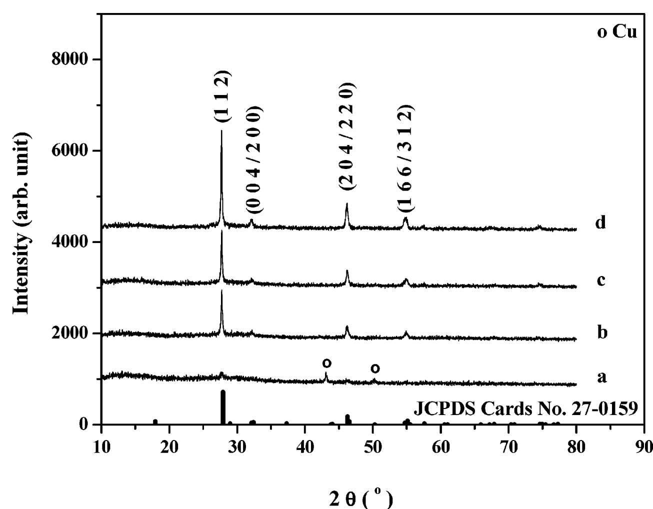

Figure 3. XRD data of the CIS films deposited on glass at 430 °C for different deposition times: (a) 40 min; (b) 50 min; (c) 60 min; (d) 70 min.

However, the rate notably increased to 43.3 nm/min at the higher temperature region of 490 °C.[17]

The CIS films were successfully obtained by a two-stage MOCVD process. First, Cu thin films were prepared on a glass or ITO glass substrate at the described conditions. Second, on the resulting Cu films, the $In(ebdtc)_3$ precursor was treated through a MOCVD method. This process for the formation of CIS films can be seen in Figure 3; when $In(ebdtc)_3$ is deposited on the Cu thin film at 430 °C for 40 min, the (112) peak of CIS appears and the peaks due to Cu correspondingly decrease. After that, as the deposition time

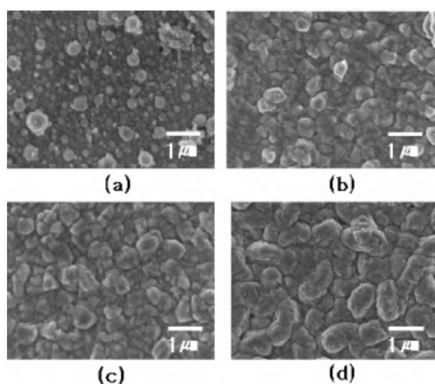

Figure 4. SEM images of the CIS films deposited on glass at 430 °C for different deposition times: (a) 40 min; (b) 50 min; (c) 60 min; (d) 70 min.

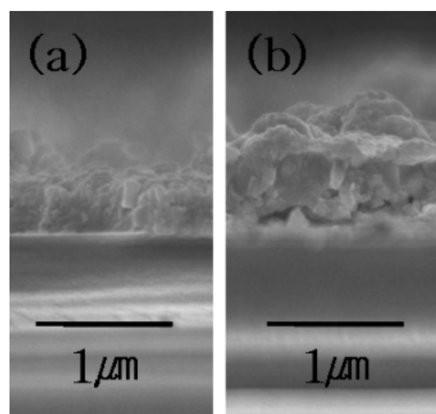

Figure 5. SEM cross images of the CIS films deposited on glass at 430 °C for different deposition times: (a) 50 min; (b) 60 min.

increases, the peaks due to Cu completely disappear and those from CIS gradually grow in their intensities. The XRD patterns of the prepared CIS films coincide quite well with that of the literature,[20] which is in the tetragonal phase and in which interestingly there are no other phases such as Cu_2S, CuS, In_2S_3, and $CuIn_{11}S_{17}$.[1,4] Figures 4 and 5 show the SEM images of the CIS films grown on glass at 430 °C for different deposition times as above; as the deposition time increases, the CIS films at each condition become quite dense and have relatively uniform grain size. At the same time, the grains gradually increase in their sizes; after 40 min of deposition of the $In(ebdtc)_3$ precursor on the Cu film, the average grain size is about 550 nm in diameter, but after 70 min, it increases to 1.2 μm. Figure 5 shows the SEM cross image of the CIS films after deposition times of 50 and 60 min at 430 °C. The thickness of each film is about 550 and 900 nm, respectively, revealing that the growth rate is about 13 nm/min. Figure 6 indicates the EDX measurement results at different deposition times; the ratio of Cu, In, and S elements in the films is almost 1:1:2 after 50−60 min of deposition time, but after that, the film becomes rich in the In element. This result means that, by the MOCVD method in this study, both n- and p-type CIS films can be prepared by controlling the MOCVD process.[10] In addition, the elemental ratio can be elaborately adjusted by controlling

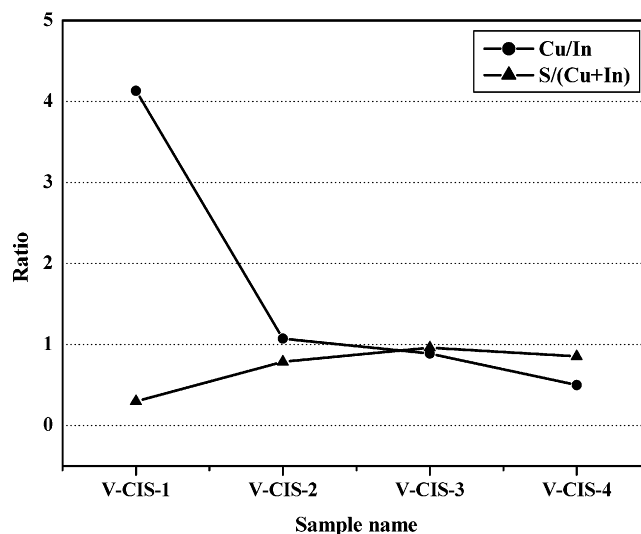

Figure 6. EDX data of the CIS films deposited on glass at 430 °C for different deposition times: (a) 40 min; (b) 50 min; (c) 60 min; (d) 70 min.

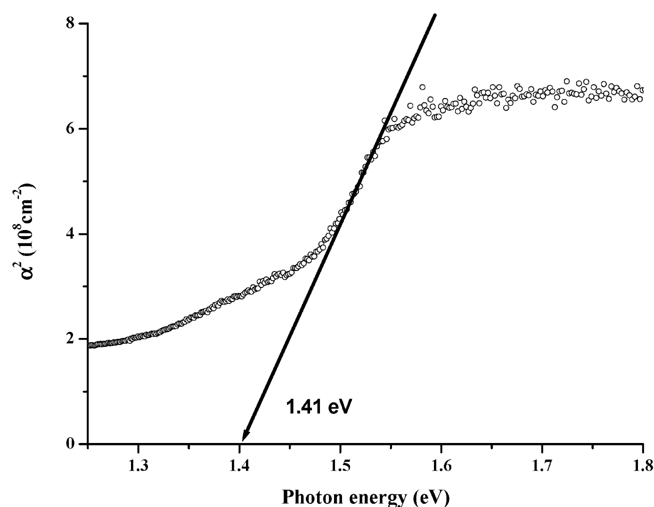

Figure 7. Typical plot of α^2 vs band gap of the CIS film deposited on glass at 430 °C for 1 h (α: absorption coefficient). The optical band gap of those CIS films ranges from 1.38 to 1.50 eV depending upon the deposition time of the $In(ebdtc)_3$ precursor.

the deposition conditions on demand. Thus, the Cu/In ratio is believed to be controlled to larger than 1, leading to a more efficient photovoltaic cell performance.[1]

Also, it is interesting to note that the optical band gap of the prepared CIS films, based on UV/vis spectroscopy, ranges from 1.38 to 1.50 eV depending upon the deposition time and corresponding ratio of the elements; as the films become rich in In elements, the corresponding band gap increases. These results are in good agreement with those in the literature.[6,10,21] As shown in Figure 7, when the ratio of Cu, In, and S elements becomes nearly 1:1:2, the optical band gap is 1.41 eV, which is quite similar to that of CuIn(S,Se) films (S; about 47 atom %).[7] However, in the case of an In/S-rich CIS film, prepared with a deposition time of 70 min, the band gap is about 1.50 eV.

(20) Powder Diffraction File, Joint Committee on Powder Diffraction Standard, ICDD, Sept 1995, Card No. 27-0159, Version 1.10.

(21) Antony, A.; Asha, A. S.; Yoosuf, R.; Manoj, R.; Jayaraj, M. K. *Sol. Energy Mater. Sol. Cells* **2004**, *81*, 407−417.

Conclusions

The CIS films were successfully prepared on glass or ITO glass substrates using two distinctive Cu single-source precursors, $Cu(eiac)_2$ or $Cu(ebac)_2$, and an In/S single-source precursor, $In(ebdtc)_3$. These precursors were stable at room temperature and had excellent properties for the MOCVD method. CIS films were deposited by a two-stage MOCVD method. Also, it is noteworthy that the ratio of Cu, In, and S elements can be adjusted on demand by controlling the deposition conditions. The optical band gap of those CIS films ranges from 1.38 to 1.50 eV depending upon the deposition time of the $In(ebdtc)_3$ precursor. This band gap range may be one of the quite promising characterisics for their application to photovoltaic solar cells.[22]

Acknowledgment. This work was partially supported by the Seoul R&BD Program 2006.

IC061445C

(22) Shay, J. L.; Tell, B.; Kasper, H. M.; Schiavone, L. M. *Phys. Rev. B* **1972**, *5*, 5003−5005.