

Deposition of CuInSe₂ Thin Films Using Stable Copper and Indium-selenide Precursors through Two-stage MOCVD Method

Jong Pil Park, Sin Kyu Kim, Jae-Young Park, Kang Min Ok, and Il-Wun Shim*

Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea. *E-mail: iwshim@cau.ac.kr

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Highly polycrystalline copper indium diselenide (CuInSe₂, CIS) thin films were deposited on glass or ITO glass substrates by two-stage metal organic chemical vapor deposition (MOCVD) at relatively mild conditions, using Cu- and In/Se-containing precursors. First, pure Cu thin film was prepared on glass or ITO glass substrates by using a single-source precursor, bis(ethylbutyrylacetate)copper(II) or bis(ethylisobutyrylacetate)copper(II). Second, on the resulting Cu films, tris(*N,N*-ethylbutyldiselenocarbamate)indium(III) was treated to produce CuInSe₂ films by MOCVD method at 400 °C. These precursors are very stable in ambient conditions. In our process, it was quite easy to obtain high quality CIS thin films with less impurities and uniform thickness. Also, it was found that it is easy to control the stoichiometric ratio of relevant elements on demands, leading to Cu or In rich CIS thin films. These CIS films were analyzed by XRD, SEM, EDX, and Near-IR spectroscopy. The optical band gap of the stoichiometric CIS films was about 1.06 eV, which is within an optimal range for harvesting solar radiation energy.

Key Words: CuInSe₂, CIS, Thin film, MOCVD, Solar cell

Introduction

The ternary ABC₂ chalcopyrites (A = Cu and Ag, B = In, Ga and Al and C = Se, S) form a large family of semiconducting materials with diverse optical, electrical and structural properties.¹ Among them, polycrystalline CuInSe₂, a ternary compound with a direct optical band gap of near 1.1 eV, is well-known to have a great potential as an absorption layer material for the application to the low cost, less toxic, and high-efficiency thin film solar cells.² This material can be easily produced in the form of very thin films with nanocrystalline structures.³ The high absorption coefficient of CIS materials allows them to be used as absorber layers in solar cells. Nearly 19% conversion efficiency has been reported for lab-scale CuInSe₂ (CIS)-based thin film solar cells.^{4,5} For these reasons, a high throughput technique that may provide a potentially scalable process has been requested for the fabrication of CuInSe₂ films. These films have been fabricated through a large variety of techniques⁶⁻¹⁴ such as RF sputtering,¹⁵ spray pyrolysis,¹⁶⁻¹⁸ chemical deposition,¹⁹ stacked elemental layer (SEL),²⁰⁻²² microwave-assisted solid-state reaction involving pure metal powders,²³ preparation of nanoparticles,²⁴ and metal organic chemical vapor deposition of organometallic precursors (MOCVD).²⁵⁻²⁷ Among them, MOCVD offers several advantages; through this method, it is relatively easy to obtain high quality thin films with less impurities and uniform thickness and to control the stoichiometric ratio of relevant elements.²⁶ However, the success of the MOCVD process depends on the availability of highly volatile and thermally stable precursors since these thermal properties are important to achieve uniform thickness and reproducible film growth.²⁷

We recently reported the preparation of CuInSe₂ thin films through two-stage MOCVD process, using Cu- and In/Se-containing single source precursors.^{26,28} As an In/Se precursor, di-μ-methylselenobis(dimethylindium) was used.²⁶ However,

this In/Se precursor was quite air sensitive and difficult to handle.

Therefore, we developed a stable In/Se precursors: tris(*N,N*-ethylbutyldiselenocarbamate)indium(III)²⁹ in ambient conditions. Herein, we report preparation of the CIS films by two-stage MOCVD method on glass or ITO glass substrates using those precursors.

Experimental Details

Reagents. Most of the reagents were purchased from Sigma-Aldrich Corporation except CSe₂. CSe₂ was prepared through the reaction with selenium powder and excess dichloromethane.³⁰ All solvents were refluxed over molecular sieves 3 Å (pellets, 3.2 mm) to remove water molecules and then distilled prior to use.

General Procedures. For the analyses of Cu, In₂Se₃, and CuInSe₂ thin films, Scintag XDS 2000 X-ray diffractometer, I.S.I.-DS 130, Philips XL 30S FEG scanning electron microscope equipped with a Phoenix Energy Dispersive X-ray spectrometer (EDX) field-emission scanning electron microscope (Hitach S-4700) were used. Scanning electron microscopic images were obtained at accelerating voltages of 10 or 15 kV and EDX results at accelerating voltage of 30 kV with a collection time of 1 minute. Magna 750 FT-IR spectroscopy was used to measure the band gap of CIS thin films in the 6000-14000 cm⁻¹.

Synthesis of bis(ethylisobutyrylacetate)copper(II), Cu(eiac)₂: This precursor, Cu(eiac)₂, was synthesized as our early paper²⁸ by reacting 0.2 mol of ethyl isobutyrylacetate and sodium metal, and 0.1 mol of CuCl₂ (Aldrich Chem. Co.) in a 30 mL tetrahydrofuran (THF) solution at room temperature. After 2 hours, the solvent was evaporated, and the resulting residue was dissolved in a pentane solution. The solution was filtered off to remove impurities and the dark green product was obtained after evaporation of the solvent. Cu(eiac)₂: yield

89%. Its melting point was found to be 98 °C and decomposition temperature was about 206 °C.

Synthesis of bis(ethylbutyrylacetato)copper(II), Cu(ebac)₂: Bis(ethyl butyrylacetato)copper(II), Cu(ebac)₂, was synthesized similarly as above by reacting CuCl₂ and corresponding sodium salts of β -diketonates at room temperature.²⁸ These dark green Cu precursors were very stable in ambient condition. Cu(ebac)₂: yield 85%. Its melting point was found to be 104 °C and decomposition temperature was about 196 °C.²⁸

Synthesis of tris(*N,N*-ethylbutyldiselenocarbamato)indium(III), In(ebdsc)₃: Tris(*N,N*-ethylbutyldiselenocarbamato)indium(III), In(ebdsc)₃, was obtained by the reaction of sodium *N,N*-ethylbutyldiselenocarbamate and InCl₃.²⁹ The sodium *N,N*-ethylbutyldiselenocarbamate was prepared by reacting sodium hydroxide (120.0 mg, 3 mmol), *N*-ethylbutylamine (0.410 mL, 3 mmol), and CSe₂ in dichloromethane (1.734 mL, 3 mmol); CSe₂ solution was slowly dropped into the ethanol (30 mL) solution of sodium hydroxide and *N*-ethylbutylamine at 0 °C for 1 hr. After the addition, the color of the solution turned transparent yellow. To this solution, InCl₃ (225.7 mg, 1 mmol) was slowly added. Then, yellow In(ebdsc)₃ product was immediately precipitated. This precipitate was filtered, dried under vacuum, and recrystallized. The yield of this light yellow product was 79%. Its melting point was found to be 165 °C and decomposition temperature about 276 °C.²⁹

CuInSe₂ film deposition: MOCVD experiments for CIS film deposition were carried out in a glass warm-wall reactor through two stage process.^{26,28,29} First, pure Cu thin film was prepared on glass or ITO glass substrates by using a single-source precursor, bis(ethylbutyrylacetate)copper(II) or bis(ethylisobutyrylacetate)copper(II) without using H₂ gas for reduction of Cu(II). Substrate temperature was controlled to 330 °C and feed temperature to 90 °C. Second, on the resulting Cu films, tris(*N,N*-ethylbutyldiselenocarbamato)indium(III) was treated to produce CuInSe₂ films by MOCVD method. Substrate temperature was controlled to 400 °C and bubbler temperature to 200 °C for deposition of In/Se precursor. Working pressure during deposition was maintained at about 7.5×10^{-4} Pa using argon for flowing gas.

Results and Discussion

Deposition of Cu films from the two Cu(II) precursors. The two Cu(II) precursor compounds, Cu(eiac)₂ and Cu(ebac)₂, were found to be excellent precursors for the preparation of highly pure cubic copper thin films^{29,31} using MOCVD method: they were very stable in ambient conditions and used at mild conditions such as low bubbler (≤ 120 °C) and substrate (≤ 400 °C) temperatures. Although no deposition was observed on a silicon substrate with Cu(ebac)₂ precursor, the Cu films prepared from those precursors revealed reasonably good adhesion ability on the most glass substrates. Deposition rates was about 12.5 Å/min and the average resistivity of the Cu films by four point probe method was 1.699 $\mu\Omega\cdot\text{cm}$, indicating that the films were composed of very pure copper metal.²⁸ Figure 1 shows XRD data of Cu film deposited on glass at 330 °C.

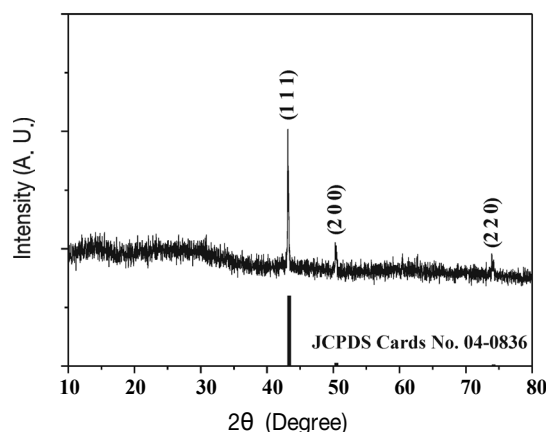


Figure 1. XRD pattern of pure Cu films at 330 °C.

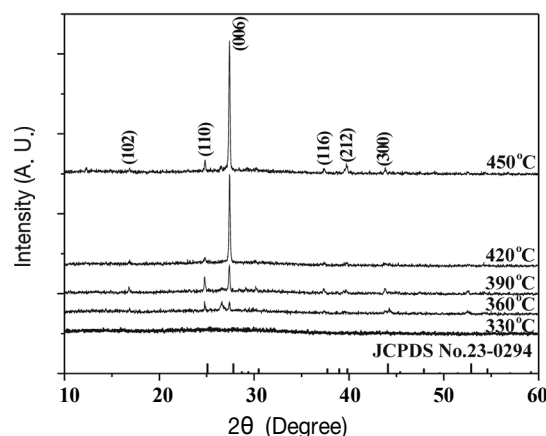


Figure 2. XRD patterns of In₂Se₃ films at different temperatures.

Deposition of In₂Se₃ films from the In/Se precursor. The In(ebdsc)₃ precursor was also quite stable in ambient conditions and had relatively low melting point with short decomposition temperature range (280–290 °C) in comparison to the known similar precursors, suggesting that it can be used in the MOCVD process under relatively milder conditions.²⁹

A separate experiment was carried out in order to test In(ebdsc)₃ as a MOCVD precursor: In₂Se₃ thin films were obtained by MOCVD method using In(ebdsc)₃, in which the bubbler temperature was 200 °C, and substrate temperature was about 330 °C. The X-ray diffraction pattern of the resulting red In₂Se₃ thin film on glass or ITO glass coincided well with that of the known hexagonal γ -In₂Se₃ (see Fig. 2). With the In₂Se₃ film growth, we were not able to observe any preference on the substrates.³² EDX analyses of these films showed an In/Se ratio of 2:3 in whole substrate temperature range, indicating the formation of In₂Se₃ without any appreciable amount of impurities such as carbon, oxygen and nitrogen. In addition, it is quite noteworthy that there were no other phases such as InSe, In₆Se₇ or In₂O₃.

Deposition of CuInSe₂ films using two precursors. The CIS films were successfully obtained by two-stage MOCVD process; First, Cu thin films were prepared on glass or ITO glass substrate at the described conditions. Second, on the

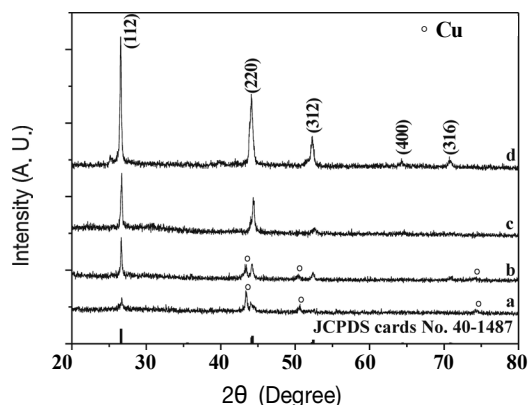


Figure 3. XRD patterns of CuInSe_2 films at different deposition time; a. 40 min., b. 50 min., c. 60 min., d. 70 min.

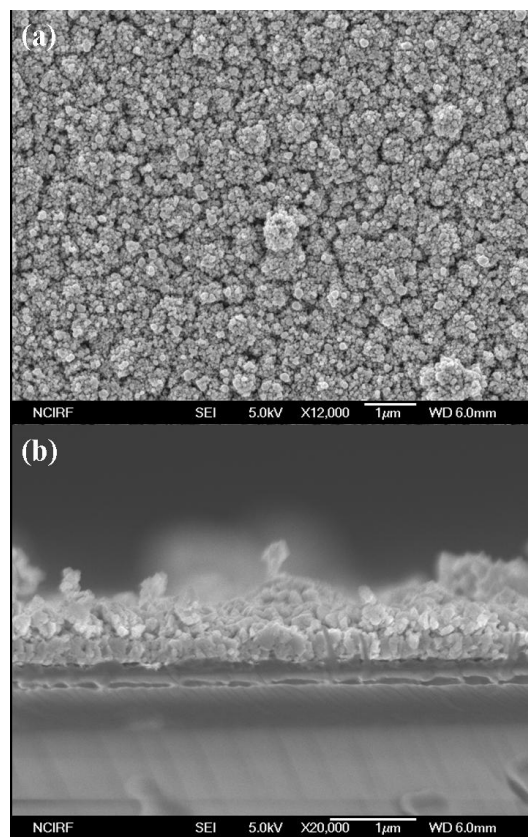


Figure 4. SEM images of CuInSe_2 films grown on glass at 400 °C for 60 min (a) top view image, (b) side view image.

resulting Cu films, the $\text{In}(\text{ebdsc})_3$ precursor was treated through MOCVD method. This process for the formation of CIS films can be seen in Figure 3; when $\text{In}(\text{ebdsc})_3$ is deposited on Cu thin film at 400 °C for 40 min, the (1 1 2) peak of CuInSe_2 appears and the peaks of Cu correspondingly decrease. After then, as the deposition time increases, the peaks of 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 literature³³ which is in tetragonal phase. Interestingly there are no other phases such as Cu_2Se , CuSe , InSe , In_2Se_3 , and $\text{CuIn}_{11}\text{Se}_{17}$.^{34,35}

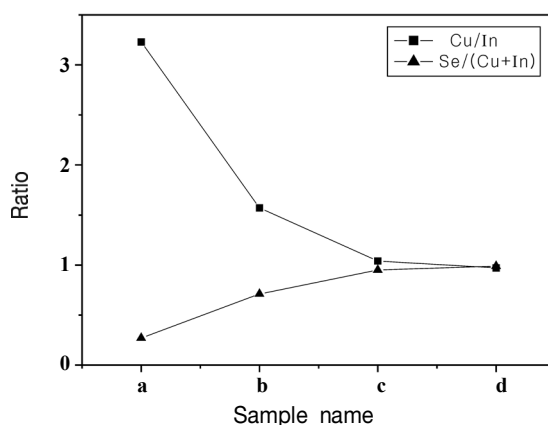


Figure 5. EDX data of the CIS films deposited on glasses at 430 °C at different deposition time; a. 40 min., b. 50 min., c. 60 min., d. 70 min.

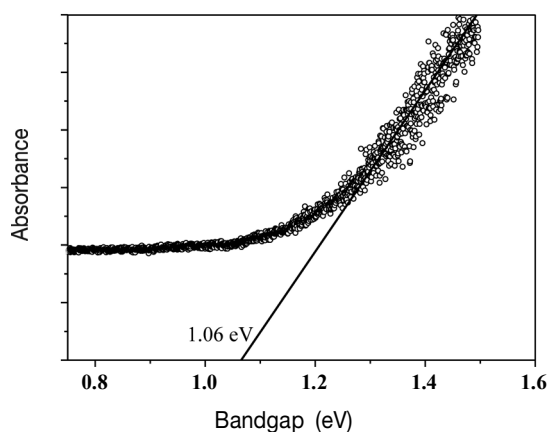


Figure 6. Plot of absorbance vs. band gap of CIS film deposited on glass at 400 °C for 1 hr.

Figure 4 shows the SEM images of the CIS films grown on glasses at 400 °C for 60 min; the average grain size is about 100 nm in diameter. Figure 5 indicates the EDX measurement results at different deposition time; the ratio of Cu, In, Se elements in the films is almost 1:1:2 after 60~70 min In/S deposition. This graph shows that the elemental ratio can be elaborately adjusted by controlling deposition conditions on demand. Also, it is interesting to note that the optical band gap of the prepared CIS films, based on Near-IR spectroscopy, ranges from 0.92 to 1.1 eV depending upon the deposition times and corresponding ratio of the elements: as the films become rich in In element, the corresponding band gap increases, which is in good agreement with those in literatures.^{34,35} As shown in Figure 6, when the ratio of Cu, In and Se elements becomes nearly 1:1:2, the optical band gap is 1.06 eV.

Conclusions

The CuInS_2 films were successfully prepared on glass or ITO glass substrates using two distinctive Cu single source precursors, $\text{Cu}(\text{eiac})_2$ or $\text{Cu}(\text{ebac})_2$, and a In/Se single source precursor, $\text{In}(\text{ebdsc})_3$. These precursors were stable at room

temperature and had excellent thermal properties for the MOCVD method. CuInSe₂ films were deposited by two-stage MOCVD. Also, it is noteworthy that the ratio of Cu, In, and Se elements can be adjusted on demand by controlling the deposition conditions. The optical band gap of those CIS films ranges from 0.9 to 1.1 eV depending upon the deposition time of In(ebdsc)₃ precursor. This band gap range may be one of the quite promising properties for their application to photovoltaic solar cells.³⁴

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