

Preparation of CdS Thin Films through MOCVD Method, Using Cd-S Single-source Precursors

Seok Hwan Yoon, Seung Soo Lee, Kook Won Seo, and Il-Wun Shim*

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

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Thin films of cadmium sulfide (CdS) have been used as a hetero-junction window layer in the fabrication of semiconductor based solar cells such as CdTe, InP, $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$, and Cu_2S ¹⁻⁴ since CdS has a relatively wide band gap energy ($E_g = 2.42\text{--}2.45$ eV)⁵ and possesses n-type semiconductor characteristics. Recently, CdS is also applied to dye-sensitized photoelectrochemical cells to improve their performance.⁶ Numerous physical properties of CdS films notably depend on their deposition methods and the particular conditions of preparation processes. They can be prepared by chemical, physical and electrochemical methods such as molecular beam epitaxy (MBE); metal organic chemical vapor deposition (MOCVD); close-spaced sublimation (CSS); chemical bath deposition (CBD); electro-deposition; successive ionic layer adsorption and reaction (SILAR); screen printing; pulsed laser ablation; RF sputtering; and spray pyrolysis.⁷ Among them, the MOCVD technique has received much attention due to its great potential application to the fabrication of high-quality layers. Though there are several different kinds of precursors for MOCVD process, the use of a single-source precursor provides a novel approach to the deposition of CdS films with many benefits to reduce deposition temperatures and avoid the use of hazardous metal alkyls, H_2S , or alkyl sulfide.^{8,9} Also, the precursors containing dithiocarbamate ligands with asymmetrical dialkyl groups were interesting since they were found to have relatively lower melting and/or decomposition temperatures than those of symmetrical ones.⁸

In this work, new Cd-S single source precursors were synthesized with high purity and high yield. Using them, CdS thin films were successfully deposited through MOCVD method on various substrates such as glass, ITO/glass, $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS)/glass and TiO_2 /ITO/glass, and were characterized by various spectroscopic methods.

Experimental Section

General. NMR spectra were recorded on Varian Gemini 2000 NMR spectrometer, Infrared spectra were obtained on Jasco FT/IR-5300 spectrometer and mass spectra were obtained on Autospec EBE mass spectrometer. Thermal analyses including TGA and DSC were carried out with Setaram LABSYS for the characterization of synthesized precursors. For the analyses of CdS thin films, Scintag XDS 2000 x-ray diffractometer (XRD), I.S.I.-DS 130, and Philips

XL30S FEG scanning electron microscope equipped with a Phoenix energy dispersive x-ray spectrometer (SEM-EDAX) were used. The optical band gap energy was measured by UV/Vis spectroscopy (JASCO U-550).

Synthesis of CdS single source precursors: Three cadmium(II)dithiocarbamate precursors were synthesized by reacting cadmium hydroxide (10 mmol), three different secondary amines (20 mmol) and carbon disulfide (20 mmol) in a 100 mL boiling methanol solution, as described in other researches.¹⁰⁻¹² After a 1 hour reaction, ivory-colored precipitates was obtained. These precipitates were filtered by glass filter and recrystallized with cold methylene chloride and ethanol. The final product was dried under vacuum at room temperature.

Synthesis of Cd(*N,N*-diethyldithiocarbamate)₂: this precursor⁸ with symmetric alkyl groups was synthesized with diethyl amine (Aldrich, 1.47 g, 20 mmol) for a comparative study to those with asymmetric alkyl groups; yield 72%; white powder; EI-MS m/z (70 eV) 410 (M^+); ¹H NMR (300 MHz, CDCl_3) δ 1.34 (t, 6H), 3.93 (q, 4H); FT-IR (KBr pellet) ν (C-N) 1498, ν (N- CS_2) 1431, ν (C-S) 992 cm^{-1} ; elemental analysis (calcd. C 29.4, H 4.9, N 6.9%) C 29.0, H 4.8, N 6.8%.

Synthesis of Cd(*N,N*-ethylbutyldithiocarbamate)₂: this asymmetric precursor was synthesized with *N*-ethylbutyl amine (Aldrich, 2.04 g, 20 mmol); yield 90%; white powder; EI-MS m/z (70 eV) 466 (M^+); ¹H NMR (300 MHz, CDCl_3) δ 0.95 (t, 3H), 1.36 (m, 2H), 1.78 (m, 2H), 3.83 (t, 2H), 1.35 (t, 3H), 3.92 (q, 2H); FT-IR (KBr pellet) ν (C-N) 1503, 1493, ν (N- CS_2) 1425, ν (C-S) 996 cm^{-1} ; elemental analysis (calcd. C 36.2, H 6.1, N 6.0%) C 36.1, H 6.0, N 6.0%.

Synthesis of Cd(2-ethylpiperidinedithiocarbamate)₂: this cyclic asymmetric precursor was synthesized with 2-ethylpiperidine (Aldrich, 2.35 g, 20 mmol); yield 78%; white powder; EI-MS m/z (70 eV) 490 (M^+); ¹H NMR (300 MHz, CDCl_3) δ 0.95 (t, 3H), 1.58 (m, 2H), 1.65 (m, 2H), 1.72 (m, 2H), 1.81 (m, 2H), 3.14 (m, 1H), 5.19 (m, 1H), 5.35 (m, 1H); FT-IR (KBr pellet) ν (C-N) 1471, 1447, ν (N- CS_2) 1432, ν (C-S) 989 cm^{-1} ; elemental analysis (calcd. C 39.3, H 5.8, N 5.7%) C 38.7, H 5.7, N 5.6%.

Film depositions: CdS thin films were prepared with the three precursors through MOCVD method. The bubbler-type glass warm wall MOCVD reactor was used. In the case of $\text{Cd}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)]_2$ as a precursor, bubbler temperature was 170 °C, substrate temperature was 350-440 °C,

and deposition time was 1-4 hr. In the other case of $\text{Cd}[\text{S}_2\text{CN}(\text{C}_7\text{H}_{14})_2]_2$, bubbler temperature was 220 °C, substrate temperature was 330-410 °C, and deposition time was 2 hr. In each case, base pressure was 1 mtorr and working pressure was 100 mtorr. Both asymmetric precursors gave rise to CdS thin films with same quality. Ar gas was used for a carrier gas with 20 sccm flow rate. Various substrates such as glass, ITO/glass, TiO_2 /ITO/glass, and $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS)/glass were used to examine their applicability for the preparation to thin film solar cells.

Results and Discussion

The synthesized precursors, $\text{Cd}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)]_2$ and $\text{Cd}[\text{S}_2\text{CN}(\text{C}_7\text{H}_{14})_2]_2$, are air stable and also thermally stable without decomposition even at quite high temperature above their melting points. The results of thermo-gravimetric analyses (TGA) conducted at atmosphere pressure under an argon purge are listed in Table 1. It is noteworthy that the melting point range of $\text{Cd}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)]_2$ is quite lower than that of any other Cd-S single source precursors; it was even lower than that of $\text{Cd}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$. Such low melting is believed to arise from the asymmetric aliphatic groups of the precursor, resulting in less compact packing in solid state. In this respect, $\text{Cd}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)]_2$ could be better precursor that can be processed at lower operating condition. In the case of $\text{Cd}[\text{S}_2\text{CN}(\text{C}_7\text{H}_{14})_2]_2$ precursor, it has a relatively very low decomposition temperature than any other similar precursors. This result can be ascribed to its cyclic moiety, making the thermal decomposition process easier.¹³

XRD patterns and SEM images of prepared CdS thin films from $\text{Cd}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)]_2$ precursor on ITO/glass substrate were shown in Figure 1. These XRD patterns show that prepared CdS has a hexagonal crystal structure.¹⁴ In Figure 1, the intensities of the peaks of (002) and (103) and the particle sizes of the films increase as the substrate temperature increases. The film growth rate measured by the thickness of the films was 8 nm/min at 410 °C, indicating that the film growing process is very efficient. EDX analyses show that the ratios of S/Cd of deposited films vary from nearly 1.02 to 0.87 at the substrate temperature range of 350-410 °C. The Cd and S ratio was exactly 1 : 1 at the substrate temperature about 360 °C, revealing that the Cd/S ratio can be controlled by the substrate temperature. Also, there was

Table 1. Physical properties of synthesized CdS precursors

Precursors	State	Air and thermal stability	Melting point (°C)	Decomposition temperature (°C)
$\text{Cd}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$	white powder	stable	248-259	337
$\text{Cd}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)]_2$	white powder	very stable	111-123	340
$\text{Cd}[\text{S}_2\text{CN}(\text{C}_7\text{H}_{14})_2]_2$	white powder	stable	209-226	311

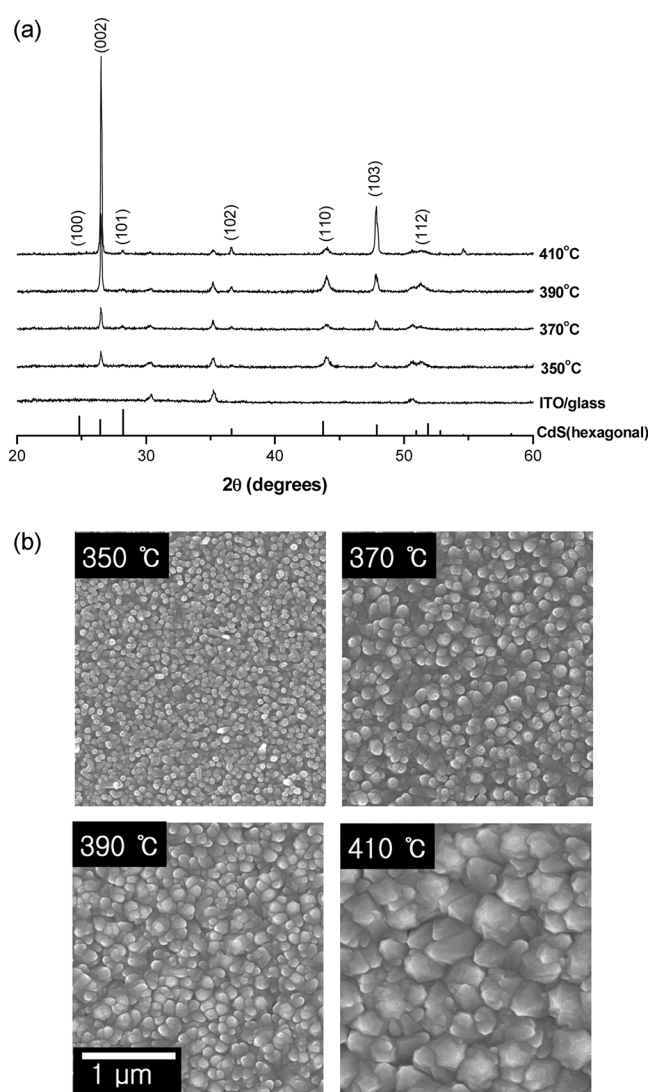


Figure 1. (a) X-ray diffraction patterns and (b) SEM images of CdS thin films on ITO/glass substrate at different substrate temperatures from $\text{Cd}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)]_2$ precursor.

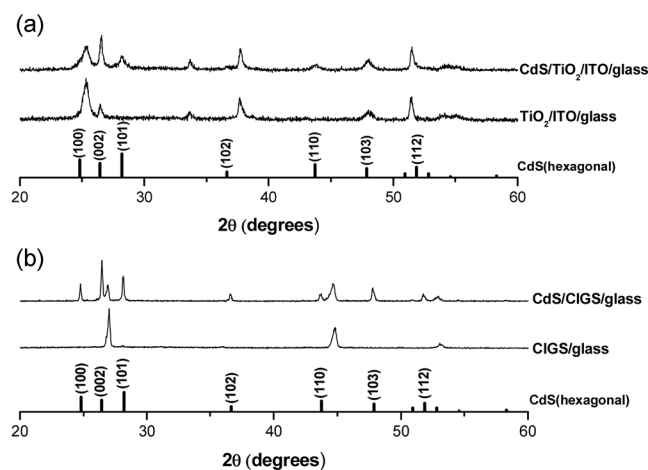


Figure 2. X-ray diffraction patterns of CdS thin films on (a) TiO_2 /glass substrate and (b) $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS)/glass substrate at 410 °C.

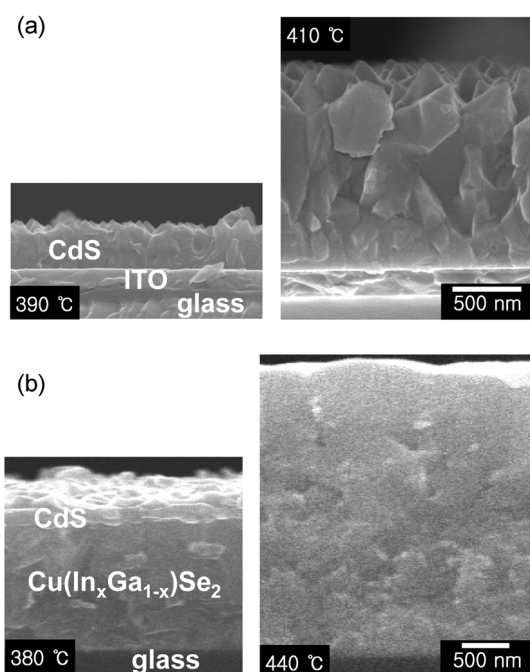


Figure 3. Cross section SEM images of CdS thin films on (a) ITO/glass substrate and (b) CIGS/glass substrate.

no evidence for the appreciable amounts of impurities such as carbide, nitride, and oxide in the films.

In addition, CdS thin films could be easily deposited on TiO₂ and CIGS film as shown in Figure 2. In the case of CIGS substrate, however, there was a significant intermixing between the two layers at above 440 °C as shown in Figure 3. Therefore, for the CIGS/glass substrate, the CdS film should be deposited below 440 °C.

CdS films with Cd[S₂CN(C₇H₁₄)₂]₂ were deposited on glass substrate at the bubbler temperature of 220 °C. The growth rate of CdS thin films was 3 nm/min when the substrate temperature was 370 °C. This result is interesting since, in the case of Cd[S₂CN(C₂H₅)(C₄H₉)₂], the growth rate of CdS thin film was 1 nm/min at the same condition. This relatively high growth rate is assumed to arise from the lower decomposition temperature of the precursor. Besides, it is noteworthy that though the Cd[S₂CN(C₂H₅)₂]₂ precursor was tried to make CdS thin film at the similar conditions as above, but the quality of films was very poor. At this stage,

the reason is not clear.

In conclusion, Cd[S₂CN(C₂H₅)(C₄H₉)₂] and Cd[S₂CN(C₇H₁₄)₂]₂ precursors were synthesized for bubbler type MOCVD process with high yields and characterized by various spectroscopic methods. Cd[S₂CN(C₂H₅)(C₄H₉)₂] with asymmetric ligand structure has the lowest melting point among the known Cd-S single source precursors. In the case of Cd[S₂CN(C₇H₁₄)₂]₂ having asymmetric cyclic ligand, its decomposition temperature were found to be quite low in comparison to the similar precursors. Using these precursors, highly pure CdS thin films were prepared on various substrates such as glass, ITO/glass and CIGS/glass substrates under relatively mild conditions with high growth rate. The optical band gap energy of the obtained CdS thin film was about 2.44 eV, suggesting that these precursors could be adopted as a polycrystalline CdS window layer through MOCVD process for the CIGS type solar cells.

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