CdSe Thin Films Grown by MOCVD Method Using New Single-source Precursors

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CdSe is one of the well known II-VI semiconductor materials having a band gap of 1.74 eV, suitable for photo-voltaic cell, light emitting diodes, and thin film transistors (TFTs).[1-3] Due to these variety of applications, various methods such as chemical bath deposition,[4] vacuum evapo-ration,[5] sputtering,[6] and chemical vapor deposition[7,8] have been adopted to prepare CdSe thin films. Among them, MOCVD method is known to have many benefits in produc-ing thin film layers with less contaminations and controlling proper stoichiometry, thickness, and the growth rate of the films.

Typical precursors to fabricate CdSe films in earlier study[9] were alkyl metal and Group VI hydrides. But, because these materials are very toxic and hard to handle, a number of efforts have been exerted to obtain stable single-source precursors, such as selenocarbamates,[8,10] silicon based system (Cd(SeSi(CH$_3$)$_3$)$_2$),[11] cadmium mixed alkyl diseleno-imidodiphosphinate.[12] In these precursors, selenocarbamates have been reliable precursors for not only in the construction of CdSe thin films,[13,14] but also in the preparation of CdSe nanoparticles.[15,16] Also, the precursors containing diseleno-carbamate 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.[13-15]

In this study, we synthesized two new derivatives of selenocarbamates containing asymmetric aliphatic or cyclic ligands: Cd(*N,N*-ethylbutyldiselenocarbamate)$_2$ and Cd(2-ethylpiperidinediselenocarbamate)$_2$, designated as Cd(Se$_2$CNEtBu)$_2$ and Cd(Se$_2$CNepp)$_2$, respectively. Using them, CdSe thin films were prepared at 300-450 °C substrate temperature range.

Figure 1 shows the thermo-gravimetric analysis data of those precursors conducted at atmospheric pressure under an argon flow. Cd(Se$_2$CNEtBu)$_2$ has a melting point of 127-137 °C and decomposes at 272 °C; Cd(Se$_2$CNepp)$_2$ melts at 193-205 °C and decomposes at 268 °C. The melting point of Cd(Se$_2$CNEtBu)$_2$ is lower than methyl hexyl derivative[8] and the decomposition temperature of Cd(Se$_2$CNepp)$_2$ is lower than those of any other known similar derivatives. Because of their lower melting and decomposition temperatures which are very important factors in MOCVD process, both Cd(Se$_2$CNEtBu)$_2$ and Cd(Se$_2$CNepp)$_2$ are quite likely to be appropriate single-source precursors to fabricate CdSe thin film. Also, their weight losses of 71 and 72% at above conditions indicate that exactly stoichiometric CdSe could
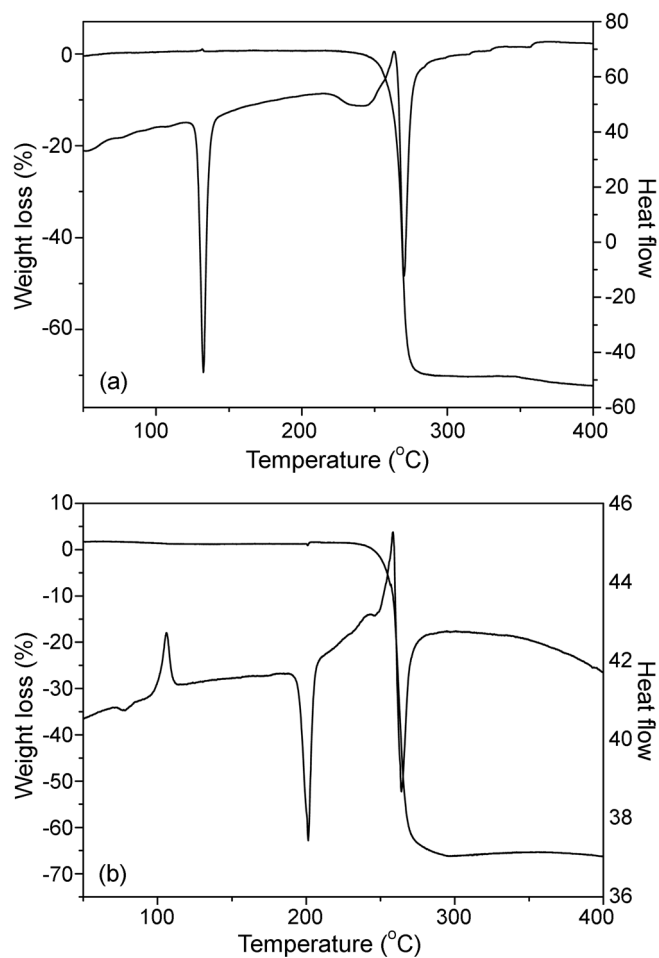

Figure 1. Thermo-gravimetric data for (a) Cd(Se$_2$CNEtBu)$_2$ and (b) Cd(Se$_2$CNepp)$_2$.

be formed on the substrates after thermal decomposition reactions.

As shown in Figure 2 and 3, highly crystalline and phase-pure CdSe thin films were obtained by using those two precursors through MOCVD and they were in hexagonal phase.[1,13] For both precursors, there was no phase change at this substrate temperature range of 300-450 °C. But, as the substrate temperature increases, (002), (102), and (103) peaks show relatively large increases in their intensities.

Figure 3 shows the top views of manufactured CdSe thin films using Cd(Se$_2$CNEtBu)$_2$ at various substrate temper-atures. As the substrate temperature increased, the crystalli-

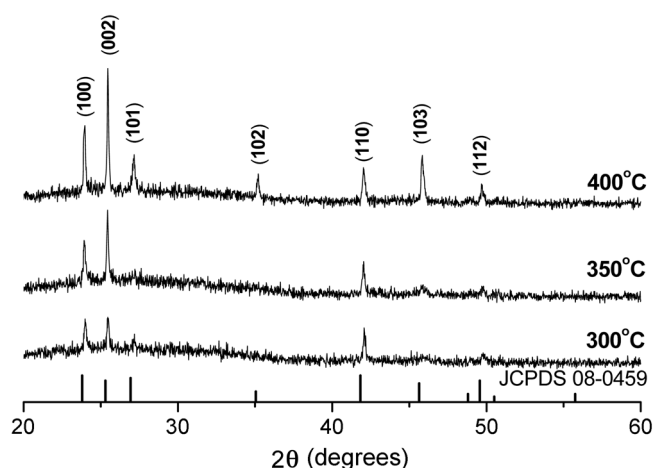**Figure 2**. X-ray diffraction patterns of CdSe films from the Cd(Se₂CNepp)₂ precursor depending on the different substrate temperature for 1 hour.

Figure 4. Cross sections of fabricated CdSe thin films using Cd(Se₂CNepp)₂ for 1.5 hours depending on the substrate temperature at (a) 320 °C, (b) 360 °C, (c) 400 °C at T_{source} = 180 °C.

nity and size of CdSe particles increased; when the substrate temperature was 300 °C, the average particle size was about 100 nm. But it increased to about 490 nm at 400 °C. Thus, the CdSe thin films were able to be successfully prepared even at 300 due mainly to the low decomposition temperatures of the two precursors. Therefore, these precursors are thought to be a good candidate for the preparation of CdSe buffer layers in CIGS solar cell without causing severe damage on CIGS layer since the CIGS layer is expected to be damaged if it is processed at over 300 °C.[17]

Figure 4 shows the cross sections of CdSe thin films grown using Cd(Se₂CNepp)₂ precursors. Although films were constructed at the source temperature of 180 °C, lower than its melting point, its growth rate (about 550 nm/hour) was very high even at low substrate temperature (320 °C). This seems to arise from their relatively low decomposition temperature. In case of the films fabricated using Cd(Se₂CNEtBu)₂ precursor, the growth rate was much higher to approximately 1.5 μm/hour at similar conditions. Considering its relatively lower melting point, this result is thought to be quite reasonable.

EDAX data for these films show that almost 1 : 1 stoichiometric ratio between Cd and Se although there is slightly deficiency of selenium as the substrate temperature
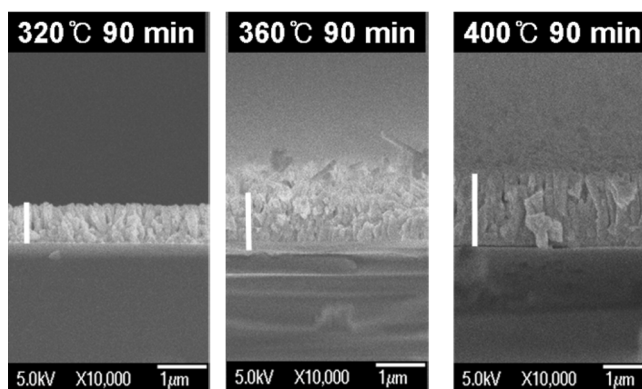
increases over 400 °C for a long period. Direct band gap analysis based on UV-VIS spectroscopy for these films shows that the CdSe films have a band gap of 1.74 eV and this result agrees quite well with the literature data,[8] revealing that this CdSe film could be adopted as an absorber material in various types of dye-sensitized solar cells.[21]

In conclusion, two new diselenocarbamate single-source precursors were synthesized and characterized. Using these precursors, hexagonal CdSe thin films were obtained at the various substrate temperatures and deposition time. Due to the merits coming from the synthesized precursors, phase-pure CdSe thin films were able to be deposited on glass even at low temperature with high growth rate.

Experimental Details

Nuclear magnetic resonance spectra were recorded on Varian Gemini 2000 NMR (300 MHz) spectrometer, using Si(CH₃)₄ and CDCl₃ as an internal reference and solvent, respectively. Infrared spectra were obtained on Jasco FT/IR-5300 spectrometer within the range 4000-600 cm⁻¹ with a medium slit and a peak resolution of 2.0 cm⁻¹, using KBr pellets. Mass spectra were obtained on Micromass Autospec EBE mass spectrometer through the standard electron impact procedure. Elemental analysis was carried out by 240XA CHN Analyzer of Control Equipment Corporation
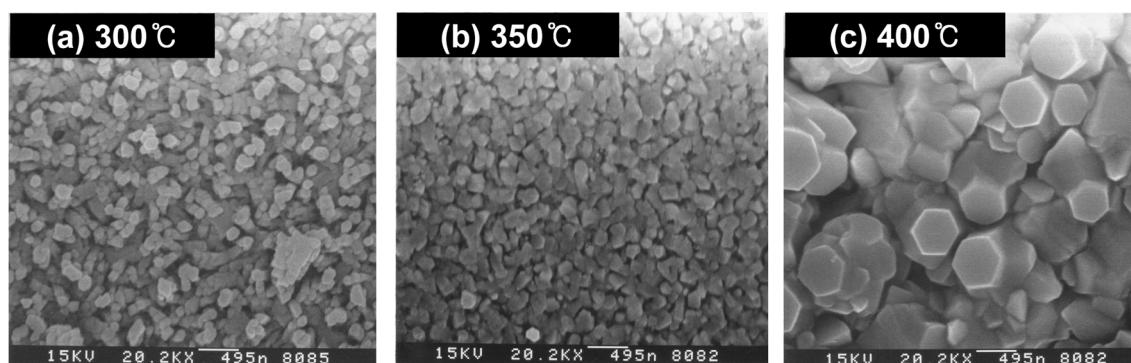

Figure 3. SEM images for CdSe on glass using Cd(Se₂CNEtBu)₂ at (a) 300, (b) 350, (c) 400 °C for 1 hour.

(U.S.A). Thermal analyses were carried out by Setaram LABSYS at atmospheric pressure in argon atmosphere from room temperature to 500 °C at a heating rate of 5 °C/min. For the X-ray analyses of CdSe thin films, Scintag XDS 2000 X-ray diffractometer, I.S.I.-DS 130, and Philips XL30S FEG scanning electron microscope equipped with a Phoenix energy dispersive X-ray spectrometer (EDAX) were used. Scanning electron microscopic images were obtained at accelerating voltages of 15 or 5 kV and EDAX results at accelerating voltage of 20 kV. For band gap energy analysis, JASCO U-550 UV/VIS spectroscopy was used.

Preparation of CSe₂. All reagents were used from Sigma-Aldrich-Corporation except CSe₂. CSe₂ was obtained through the reaction with Selenium powder and dichloromethane.[18] However, the prepared CSe₂ in this process was gathered with dichloromethane, and its concentration was too low. To enhance of the concentration of CSe₂, it was collected through repeated evaporating and concentrating steps, resulting in 20% CSe₂ solution. Ethanol was refluxed over molecular sieves 3 Å (pellets, 3.2 mm) to remove water molecules and distilled before using it.

Synthesis of Cd(*N,N*-ethylbutyldiselenocarbamate)₂. Cadmium hydroxide (10 mmol) dissolved in methanol and was stirred at 0 °C for 30 min. *N*-ethylbutylamine (18 mmol) was added to this solution and then left for 1 hour. Carbon diselenide (20 mmol) was added to the mixture by drop-wise and the solution was consistently stirred for 1 hour. Solvent was dried off, and then dichloromethane was added. The dichloromethane solution was filtered and was evaporated slowly. The pale yellow powder was obtained and recrystallized by ethanol for several times.

Yield 72%, pale yellow powder, EI-MS m/z 654 (M⁺), ¹H-NMR (CDCl₃) δ 3.94 CH₂ (q, 2H), δ 3.84 CH₂ (t, 2H), δ 1.83 CH₂ (m, 2H), δ 1.37 CH₂ (m, 2H), δ 1.34 CH₃ (t, 3H), δ 0.97 CH₃ (s, 3H), IR 1509, 1497 cm⁻¹ (ν(Se₂C-N)), 1441 cm⁻¹ (ν(N-C)), 982 cm⁻¹ (ν(C-Se)), Elemental analysis: Found C 25.6%, H 4.3%, N 4.2%, Calc. C 25.7%, H 4.3%, N 4.3%, TGA-DSC: melting onset 127 °C, melting point 132 °C, decomposition temperature 272 °C.

Synthesis of Cd(2-ethylpiperidinediselenocarbamate)₂. Synthetic procedure of Cd(Se₂CNepp)₂ was exactly same as above except 2-ethylpiperidine and the same colored product was obtained. The powder was recrystallized by cold ethanol for several times.

Yield 63%, pale yellow powder, EI-MS m/z 678 (M⁺), ¹H-NMR (CDCl₃) δ 5.36 (m, 1H), δ 5.18 CH (m, 1H), δ 3.09 CH (m, 1H), δ 1.85 CH₂ (m, 2H), δ 1.76 CH₂ (m, 2H), δ 1.68 CH₂ (m, 2H), δ 1.62 CH₂ (m, 2H), δ 0.98 CH₃ (t, 3H), IR 1475 cm⁻¹ (ν(Se₂C-N)), 1428 cm⁻¹ (ν(N-C)), 949 cm⁻¹

(ν(C-Se)), Elemental analysis: Found C 28.5%, H 4.3%, N 4.3%, Calc. C 28.3%, H 4.1%, N 4.1%, TGA-DSC: melting onset 193 °C, melting point 201 °C, decomposition temperature 268 °C.

CdSe thin films preparation. Using above precursors, the MOCVD experiments on glass substrates were carried out without any carrier gas in a glass warm wall reactor as described earlier our study.[19,20] Substrate temperature was controlled to 300-450 °C at 50 °C intervals using Cd(Se₂CNEtBu)₂ and 320-440 °C at 40 °C intervals using Cd(Se₂CNepp)₂. Bubbler temperature was fixed to 180 °C for both precursors and processing pressure of this MOCVD system was kept at about 10⁻¹ torr.

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