

# Single-source Precursor Based ZnSe Thin Film Preparation through MOCVD Method

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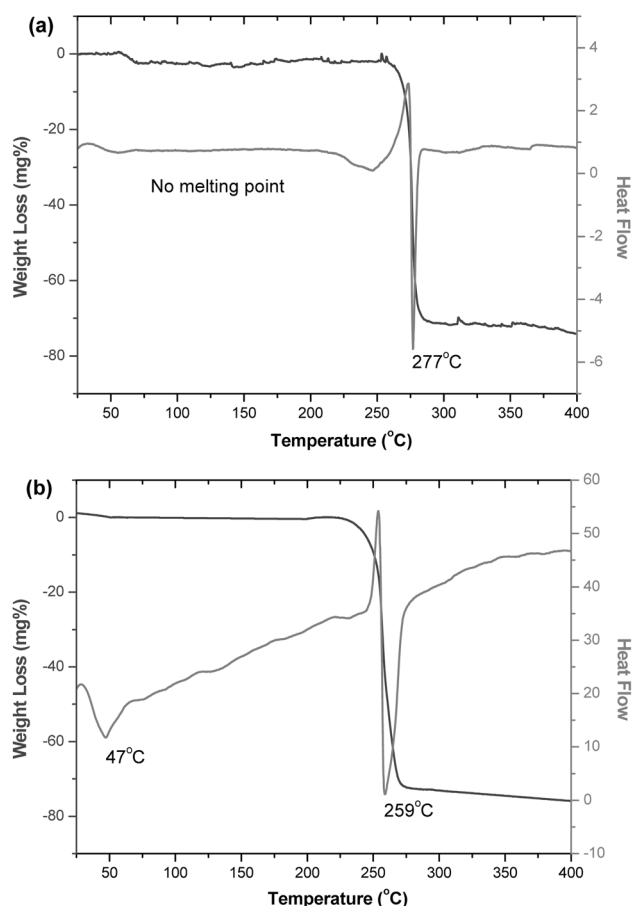
**Key Words :** Zinc selenide thin films, Zinc diselenocarbamate, MOCVD

ZnSe is a well-known II-VI n-type semiconductor material with a 2.7 eV band gap, which can be used for buffer layer for Cd-free CIS type solar cells,<sup>1-3</sup> light emitting diode,<sup>4</sup> and thin film transistors.<sup>5</sup> For these uses, various efforts to develop ZnSe films have been carried out using different methods such as chemical bath deposition (CBD),<sup>6,7</sup> atomic layer deposition (ALD),<sup>8</sup> successive ionic layer adsorption and reaction (SILAR),<sup>9</sup> pulse plating technique,<sup>10</sup> and metal organic chemical vapor deposition (MOCVD) methods.<sup>11</sup>

So, there have been many attempts to make ZnSe films through MOCVD since it is known as one of the reliable methods that can produce homogeneous and well-packed thin films. In the beginning, alkyl zinc and alkyl selenides were used,<sup>12,13</sup> but they were too reactive or very toxic to handle. Accordingly, various single-source precursors were developed to make ZnSe thin films.<sup>14</sup> Among them, diselenocarbamate type compounds were widely investigated for the preparation of ZnSe films after the research by O'Brian *et al.*<sup>15,16</sup> and especially, by adopting asymmetric alkyl groups, they could be used for ZnSe films through MOCVD under relatively milder conditions.<sup>11</sup>

In this study, to improve the thermal properties of the precursors, two new asymmetric diselenocarbamate deliberatives, Zn(N-ethylbutyldiselenocarbamate)<sub>2</sub> (designated as Zn(Se<sub>2</sub>CNEtBu)<sub>2</sub>) and Zn(2-ethylpiperidinediselenocarbamate)<sub>2</sub> (designated as Zn(Se<sub>2</sub>CNepp)<sub>2</sub>) were synthesized and characterized. Then, using them, ZnSe thin films were prepared through MOCVD on various substrates such as, glass, ITO/glass, and CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> (CIGS)/glass.

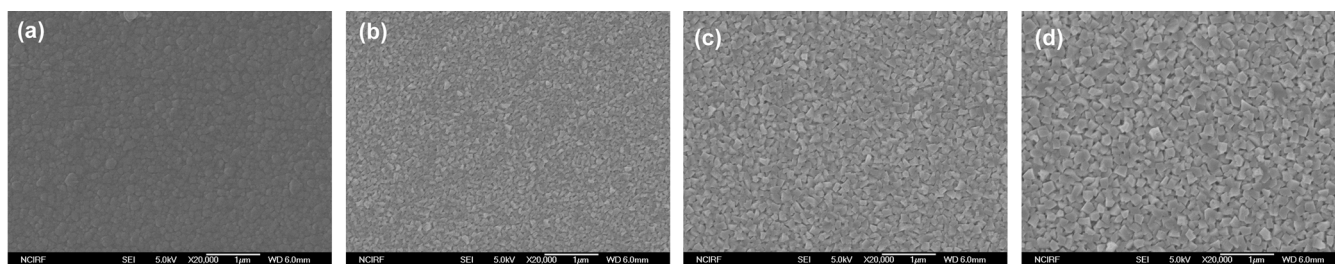
Surprisingly, Zn(Se<sub>2</sub>CNEtBu)<sub>2</sub> was in a liquid state at room temperature and Zn(Se<sub>2</sub>CNepp)<sub>2</sub> has a very low melting temperature of 47 °C. These results mean that these compounds have higher vapor pressure and can be better precursors in MOCVD process compared to any other known precursors for ZnSe thin films.<sup>11</sup> Also, thermo-gravimetric analyses conducted at atmospheric pressure under argon gas as shown in Figure 1 reveal that their decomposition temperatures are quite sharp and lower than 280 °C. This result is very important in that these compounds can be used as precursors to make a ZnSe window layer for CIGS type solar cells since the CIGS absorber material itself could be seriously damaged above about 320 °C during the window layer deposition process. Weight losses of these precursors, 76% for Zn(Se<sub>2</sub>CNEtBu)<sub>2</sub> and 78% for Zn(Se<sub>2</sub>CNepp)<sub>2</sub>, prove that quite stoichiometric ZnSe is formed after calcinations over their decomposition temperature without



**Figure 1.** TGA-DSC data for (a) Zn(Se<sub>2</sub>CNEtBu)<sub>2</sub> and (b) Zn(Se<sub>2</sub>CNepp)<sub>2</sub>.

leaving any impurity in the films.

Figure 2 shows the SEM images of ZnSe thin films on glass substrate made from Zn(Se<sub>2</sub>CNepp)<sub>2</sub> precursor; as the substrate temperature increases, the ZnSe particle size increases gradually from 100 nm to 250 nm and unexpectedly, their size distribution is quite narrow. When the substrate temperature is higher than 380 °C, well-packed dense ZnSe thin films are constructed. XRD data as shown in Figure 3 indicate that ZnSe thin film becomes more and more crystallized as the substrate temperature increases. But, at the substrate temperature over 420 °C, ZnSe thin film begins to change in their morphology from cubic to hexagonal. Accordingly, at 460 °C, both cubic and hexagonal phase ZnSe appear in the film at the same time. This result is

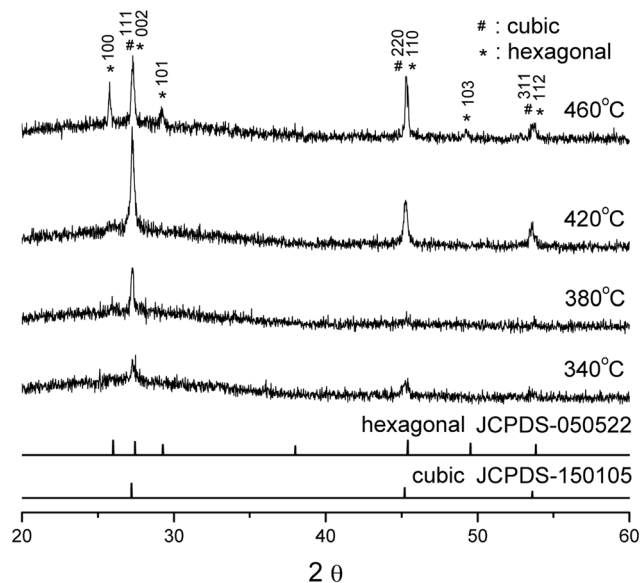


**Figure 2.** SEM images of ZnSe thin film using  $\text{Zn}(\text{Se}_2\text{CNepp})_2$  on glass for 2 hr at (a) 340 °C (b) 380 °C (c) 420 °C (d) 460 °C.

in accord with other related report.<sup>17</sup>

The growth rate of ZnSe films were measured on the basis of cross SEM images. As shown in Figure 4, ZnSe films are thickening as the deposition time increases, indicating that the film thickness can be easily controlled in this process. At fixed substrate temperature of 380 °C, the growth rate was approximately 150 nm/hr.

Figure 5 shows that highly polycrystalline and dense ZnSe films can be deposited on CIGS/glass layer and ITO/glass substrates. Especially, Figure 5(a) is striking in that even at 300 °C, the ZnSe film as a window layer can be successfully deposited on the CIGS substrate with a longer deposition time without damaging the CIGS layer.



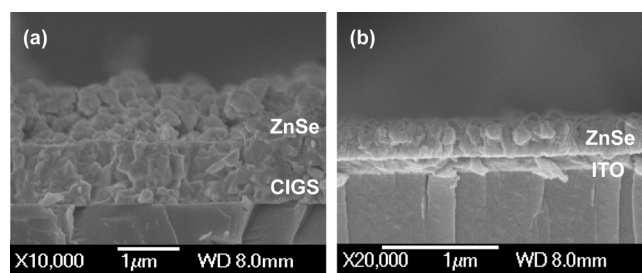
**Figure 3.** XRD data of ZnSe thin films using  $\text{Zn}(\text{Se}_2\text{CNEtBu})_2$  on glass for 2 hr.

According to EDX data, the composition of the films corresponds to the 1 : 1 stoichiometry between Zn and Se in this temperature range and there are no appreciable amounts of impurities such as carbide or oxide. UV-Vis spectroscopy for these films indicates that the band gap of ZnSe films for both precursors ranges from 2.65 eV to 2.8 eV, depending upon the deposition process. Thus, it is believed that the ZnSe films prepared in this study is very likely to replace CdS (band gap: 2.44 eV), which is quite harmful to the environment.

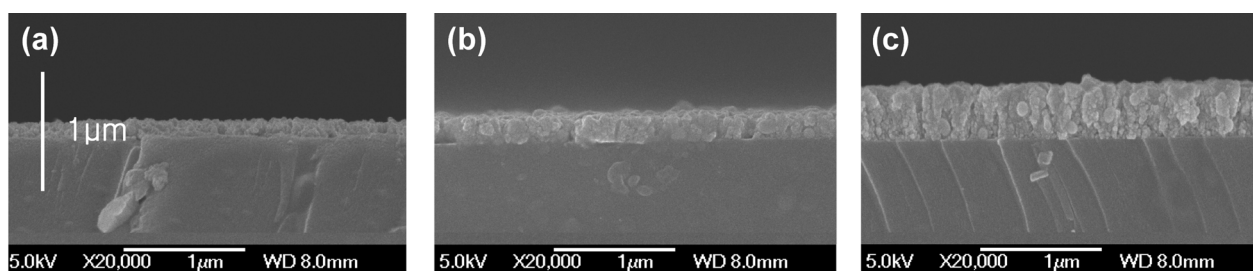
In conclusion, two new single-source precursors for ZnSe thin film were synthesized and characterized. Both precursors were found to have improved thermal properties of relatively very low melting and decomposition temperatures, which are quite suitable in their application to a window layer material through MOCVD method. Using these precursors, ZnSe thin films were successfully deposited on various substrates with a relatively large growth rate.

### Experimental Details

Nuclear magnetic resonance spectra were recorded on Varian Gemini 2000 NMR (300 MHz) spectrometer, using



**Figure 5.** Cross SEM image of ZnSe thin films on (a) CIGS/glass for 4 hr, (b) on ITO/glass for 2 hr, using  $\text{Zn}(\text{Se}_2\text{CNEtBu})_2$



**Figure 4.** Cross SEM images of ZnSe thin film using  $\text{Zn}(\text{Se}_2\text{CNepp})_2$  on glass at 380 °C for (a) 1 hr (b) 2 hr (c) 3 hr.

Si(CH<sub>3</sub>)<sub>4</sub> and CDCl<sub>3</sub> as an internal reference and solvent, respectively. Infrared spectra were obtained on Jasco FT/IR-5300 spectrometer within the range 4000-600 cm<sup>-1</sup> with a medium slit and a peak resolution of 2.0 cm<sup>-1</sup>, 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. 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 zinc sulfide 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 (EDX) were used. Scanning electron microscopic images were obtained at accelerating voltages of 15 or 5 kV and EDX results at accelerating voltage of 20 kV. For band gap energy analyses, JASCO U-550 UV/VIS spectroscopy was used.

**Synthesis of Precursors: Preparation of CSe<sub>2</sub>:** CSe<sub>2</sub> was obtained by the reaction with Selenium powder and dichloromethane.<sup>18</sup> The CSe<sub>2</sub> in this process was gathered with dichloromethane, but its concentration was too low. To enhance the concentration, it was collected through repeated evaporating and concentrating steps, resulting 20% CSe<sub>2</sub> solution.

**Zn(Se<sub>2</sub>CNEtBu)<sub>2</sub> Synthesis:** Sodium hydroxide (32 mmol) dissolved in methanol and the solution was stirred at 0 °C for 30 min. N-ethylbutylamine (30 mmol) was added to this solution and then left for 1 hour. Carbon diselenide (32 mmol) was slowly added to the mixture and was consistently stirred for 1 hour. Zinc chloride (16 mmol) dissolved in methanol was added to above slightly yellow mixture and then was stirred for 2 hours. Because the product was slightly soluble in methanol, methanol was evaporated and then dichloromethane was added. The dichloromethane solution was filtered and evaporated slowly. Yellow liquid was obtained. Yield 77%, yellow liquid, EI-MS m/z 606 (M<sup>+</sup>), <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 3.89 CH<sub>2</sub> (q, 2H), δ 3.81 CH<sub>2</sub> (t, 2H), δ 1.80 CH<sub>2</sub> (m, 2H), δ 1.39 CH<sub>2</sub> (m, 2H), δ 1.34 CH<sub>3</sub> (t, 3H), δ 0.96 CH<sub>3</sub> (s, 1H), IR 1506 cm<sup>-1</sup> (ν(Se<sub>2</sub>C-N)), 1443 cm<sup>-1</sup> (ν(N-C)), 970 cm<sup>-1</sup> (ν(C-Se)), Elemental analysis: Found C 28.12%, H 4.54%, N 4.78%, Calc. C 27.77%, H 4.66%, N 4.63%, TGA-DSC: decomposition temperature 277.

**Zn(Se<sub>2</sub>CNepp)<sub>2</sub> Synthesis:** Synthetic procedure for Zn(Se<sub>2</sub>CNepp)<sub>2</sub> was similar as above. Yellow powder product was obtained and was recrystallized by cold ethanol for several times. Yield 61%, yellow powder, EI-MS m/z 630 (M<sup>+</sup>), <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 5.20 (m, 1H), δ 5.02 CH (m, 1H),

δ 3.07 CH (m, 1H), δ 1.84 CH<sub>2</sub> (m, 2H), δ 1.76 CH<sub>2</sub> (m, 2H), δ 1.65 CH<sub>2</sub> (m, 2H), δ 1.54 CH<sub>2</sub> (m, 2H), δ 0.97 CH<sub>3</sub> (t, 3H), IR 1476 cm<sup>-1</sup> (ν(Se<sub>2</sub>C-N)), 1430 cm<sup>-1</sup> (ν(N-C)), 983 cm<sup>-1</sup> (ν(C-Se)), Elemental analysis: Found C 29.93%, H 4.44%, N 4.22%, Calc. C 30.52%, H 4.48%, N 4.45%, TGA-DSC: melting point 47 °C, decomposition temperature 259 °C.

**ZnSe Thin Film Fabrication:** ZnSe thin films fabrication was carried out in a warm-wall reactor as previously reported without flow gas.<sup>19,20</sup> ZnSe thin films deposited on soda lime glass, ITO glass, and CIGS film after normal cleaning procedures. The bubbler temperature was fixed as optimum condition, 150 °C for Zn(Se<sub>2</sub>CNEtBu)<sub>2</sub> and 190 °C for Zn(Se<sub>2</sub>CNepp)<sub>2</sub>, respectively. The substrate temperature was varied from 300 °C to 460 °C with 40 °C interval for both precursors.

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