

Preparation of ZnS Thin Film Using Zn(dithiocarbamate)₂ Precursors by MOCVD Method

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

Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea. *E-mail: iwshim@cau.ac.kr
Received June 3, 2005

Key Words : ZnS, Zinc sulfide thin film, Zinc dithiocarbamate, MOCVD, Buffer layer in solar cell

ZnS, a group II-VI semiconductor having a large direct band gap of 3.6 eV in near UV region and a refractive index of 2.35, is well known to be an important device material, which can be used for detector, emitter, and modulator in optoelectronics,^{1,2} and blue light emitting laser diode.³ Also, it can be applied to a transparent dielectric material,^{4,5} and a cadmium free buffer layer of CIGS based solar cell.^{6,7} For this wide variety of usage, it has been prepared by various methods such as chemical bath deposition (CBD),^{8,9} spray pyrolysis,^{10,11} solution growth technique,^{12,13} metal-organic chemical vapor deposition.¹⁴⁻¹⁶ Among them, MOCVD method is well known to obtain higher quality thin films with less impurities and uniform thickness. In the beginning, alkyl zinc and H₂S¹⁴ were used, but they were too reactive or very toxic. Accordingly, various single source precursors were developed and Zn(dialkyldithiocarbamate)₂ type compounds were widely studied for the preparation of ZnS thin films.¹⁵⁻¹⁸ By adopting asymmetric or neutral ligands, they could be used for the preparation of ZnS films through MOCVD under relatively milder conditions.^{19,20}

In this work, to improve thermal properties of the precursors by increasing their volatility and/or lowering decomposition temperature, two new single source precursors containing asymmetric aliphatic or cyclic ligands: Zn(N-ethylbutyldithiocarbamate)₂, designated as Zn(S₂CNEtBu)₂, and Zn(2-ethylpiperidinedithiocarbamate)₂, designated as Zn(S₂CNepp)₂ have been synthesized and characterized. Then, they are tested to make ZnS thin films on various substrates through MOCVD process.

Thermo-gravimetric analyses conducted at atmospheric pressure under argon show that Zn(S₂CNEtBu)₂ has relatively quite low melting point at the temperature range of 63-94 °C compared to those of other similar precursors having asymmetric aliphatic ligands (typically 116.9-186.5 °C range).¹⁹ But its decomposition temperature is close to those of Zn(S₂CNEtEt)₂ and Zn(S₂CNMeMe)₂,²³ revealing that it has more benefits in growth rate. In case of Zn(S₂CNepp)₂, although it has relatively high melting point (156-185 °C), it can be deposited on substrates at lower temperature because of its sufficiently low decomposition temperature (304.5 °C). Weight loss of 77 and 78% of these precursors at above the decomposition temperature indicates that exactly stoichiometric ZnS are formed on the substrates.

Figure 1 shows the SEM images of ZnS thin films grown on glass for 1.5 hour at substrate temperature range of 380-

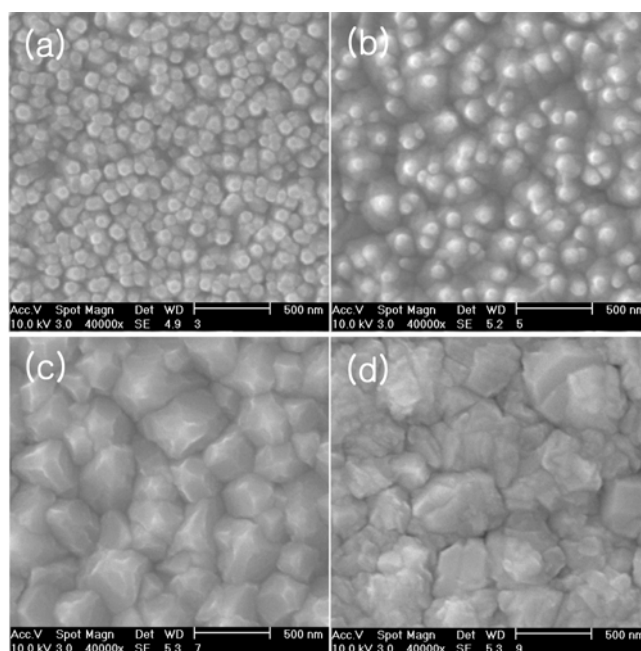


Figure 1. SEM image of ZnS thin films grown on glass using Zn(S₂CNEtBu)₂. (a) 380 °C, (b) 420 °C, (c) 460 °C, (d) 500 °C

500 °C, using Zn(S₂CNEtBu)₂ single source precursor. Average grain size increases from 100 nm to 500 nm in diameter as the substrate temperature increases. This result can be ascribed to their easy nucleation and followed crystal growing process.

Figure 2. shows the cross SEM images of ZnS films grown on glass depending on deposition time at fixed substrate temperature (460 °C) using Zn(S₂CNEtBu)₂ precursor. It shows that dense and well-arranged ZnS thin films are constructed. Approximate thickness of films is 500 nm after 30 min deposition; 1200 nm after 1 hour; and 2200 nm after 1.5 hour. This growth rate of about 1200 nm per hour is relatively very large compared to those of dimethyl and diethyl derivatives by about a factor of 7-25.^{17,23} This may be due to the substantial volatility of Zn(S₂CNEtBu)₂ containing asymmetric ligands. Similar result was observed in the case of Zn(S₂CNepp)₂ precursor. But, because of its high melting point, bubbler temperature was manipulated at 200 °C in order to get similar growth rate.

The X-ray diffraction pattern of ZnS thin films on glass using Zn(S₂CNepp)₂ is shown in Figure 3. As the substrate

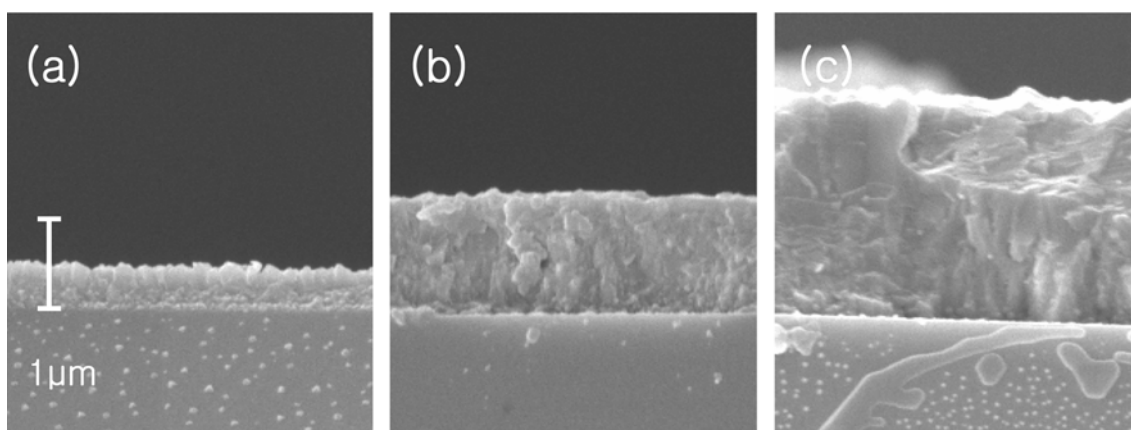


Figure 2. Cross view of ZnS films on glass at 460 °C using $\text{Zn}(\text{S}_2\text{CNEtBu})_2$ depending on deposition time (a) 30 min, (b) 1 hour, (c) 1.5 hour

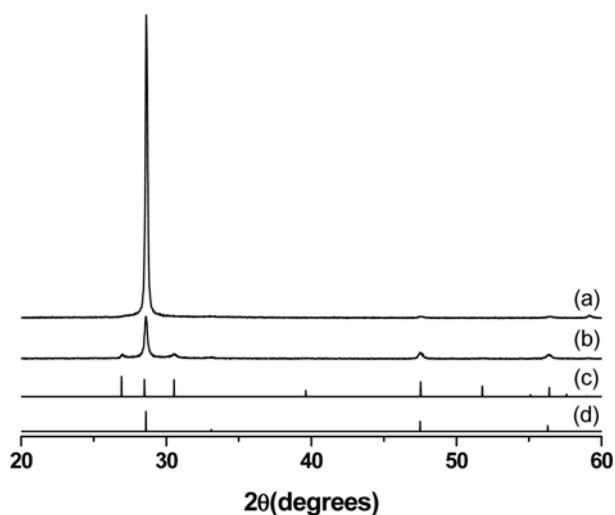


Figure 3. XRD pattern of ZnS/glass using $\text{Zn}(\text{S}_2\text{CNepp})_2$. (a) Substrate temperature 460 °C, (b) Substrate temperature 500 °C, (c) Hexagonal ZnS (JCPDS 05-0492), (d) Cubic ZnS (JCPDS 05-0566)

temperature increases, the intensity of X-ray diffraction data of cubic ZnS (111) peak (a) drastically increases, but the cubic ZnS (b) begins to change their phase to hexagonal. As reported in the literature, ZnS films showed mainly two different phases according to their preparation conditions.¹¹ In our study, substrate temperature is the only deciding factor for the phase. The same XRD pattern has been observed in the $\text{Zn}(\text{S}_2\text{CNEtBu})_2$ case. Figure 4 shows that ZnS thin films can be deposited on various types of substrates. Band Gap for ZnS film deposited at 460 °C on glass substrate based on UV-VIS spectroscopy is 3.62 eV. At all deposition temperature range, the band gap is ranged from 3.55 eV to 3.65 eV for both precursors.

According to EDX measurements with power source of 20 kV for above two precursors, the composition of the films corresponds to the stoichiometric 1 : 1 ratio between Zn and S at low temperature. But as the deposition temperature increases, slight sulfur deficiency was detected for both precursors.

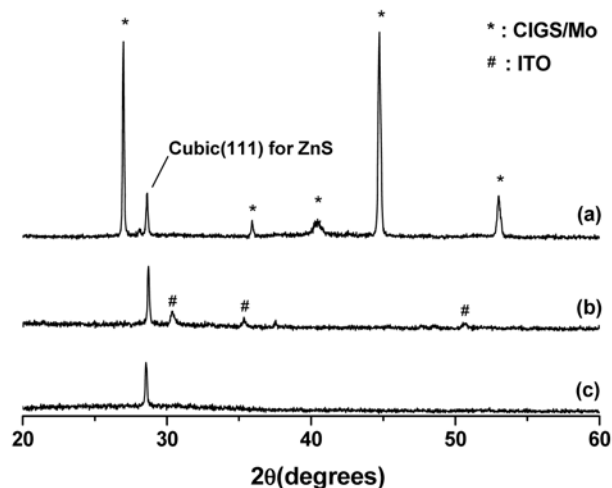


Figure 4. ZnS film on various substrate using $\text{Zn}(\text{S}_2\text{CNEtBu})_2$ at 380 °C substrate temperature. (a) on CIGS/Mo, (b) on ITO/glass, (c) on glass.

Thus, two new single source precursors for preparation of ZnS thin films: $\text{Zn}(\text{S}_2\text{CNEtBu})_2$ and $\text{Zn}(\text{S}_2\text{CNepp})_2$ have been synthesized and characterized. $\text{Zn}(\text{S}_2\text{CNEtBu})_2$ with asymmetric aliphatic ligands shows considerably low melting point, but $\text{Zn}(\text{S}_2\text{CNepp})_2$ with asymmetric cyclic ligands displays a decrease in decomposition temperature rather than a decrease in melting point. These are excellent precursors for the preparation of high quality ZnS thin films on various substrates such as soda lime glass, ITO/glass, and CIGS/Mo doped glass without any carrier gas under relatively mild conditions. X-ray diffraction patterns indicate that ZnS has phase change from cubic to hexagonal around 480-500 °C substrate temperature regions. Results from the scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) indicate that dense and pure ZnS films are constructed with high growth rate.

Experimental Detail

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 (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 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 (EDAX) were used. Scanning electron microscopic images were obtained at accelerating voltages of 10 or 15 kV and EDAX results at accelerating voltage of 20 kV. For band gap energy analysis, JASCO U-550 UV/VIS spectroscopy was used.

Synthesis of zinc sulfide precursors: Zn(S₂CNEtBu)₂: Sodium hydroxide (32 mmol, 1.35 g) dissolved in methanol and was stirred at 0 °C for 30 min. N-ethylbutylamine (30 mmol, 4.14 mL) was added to this solution and then left for 1 hour. Carbon disulfide (32 mmol, 1.93 mL) was slowly added to the mixture and was consistently stirred for 1 hour. Zinc chloride (16 mmol, 2.23 g) dissolved in methanol was added to above slightly yellow mixture and then was stirred for 2 hours. Because the product is slightly soluble in methanol, methanol was evaporated, and then dichloromethane was added. The dichloromethane solution was filtered and was evaporated slowly. White powder was obtained after 4 days from this solution. The white powder was washed by cold ethanol for several times.

Yield 82%, white powder, EI-MS m/z 416 (M⁺), ¹H-NMR (CDCl₃) δ 3.87 CH₂ (q, 2H), δ 3.78 CH₂ (t, 2H), δ 1.75 CH₂ (m, 2H), δ 1.36 CH₂ (m, 2H), δ 1.32 CH₃ (t, 3H), δ 0.96 CH₃ (s, 1H), IR 1506 cm⁻¹ (ν(S₂C-N)), 1431 cm⁻¹ (ν(N-C)), 994 cm⁻¹ (ν(C-S)), Elemental analysis: Found C 39.38%, H 6.68%, N 6.58%, Calc. C 40.38%, H 6.73%, N 6.73%, TGA-DSC: melting onset 68.5 °C, melting point 80.5 °C, decomposition temperature 349 °C.

Zn(S₂CNepp)₂: Synthesis procedure of Zn(S₂CNepp)₂ is exactly as same as above and white powder product was obtained. The white powder was recrystallized by cold ethanol for several times.

Yield 75%, white powder, EI-MS m/z 440 (M⁺), ¹H-NMR (CDCl₃) δ 5.19 (m, 1H), δ 5.01 CH (m, 1H), δ 3.11 CH (m, 1H), δ 1.86 CH₂ (m, 2H), δ 1.73 CH₂ (m, 2H), δ 1.64 CH₂ (m, 2H), δ 1.61 CH₂ (m, 2H), δ 0.96 CH₃ (t, 3H), IR 1476 cm⁻¹ (ν(S₂C-N)), 1438 cm⁻¹ (ν(N-C)), 989 cm⁻¹ (ν(C-S)), Elemental analysis: Found C 42.76%, H 6.36%, N 6.23%, Calc. C 43.44%, H 6.33%, N 6.33%, TGA-DSC: melting

onset 155 °C, melting point 172 °C, decomposition temperature 304.5 °C.

Preparation of zinc sulfide films: Chemical vapor deposition experiments of Zn(S₂CNEtBu)₂ and Zn(S₂CNepp)₂ were carried out in a glass warm-wall reactor, as we previously reported,^{21,22} on soda lime glass, ITO/glass, and CIGS/Mo doped glass without any carrier gas. Substrate temperature was controlled from 300 °C to 500 °C at 20 °C intervals. Bubbler temperature was fixed to 160 °C (Zn(S₂CNEtBu)₂) and 200 °C (Zn(S₂CNepp)₂) as a optimized temperature. Base pressure of these experiments was approximately kept at 10⁻² torr.

Acknowledgements. This research was supported by the Chung-Ang University Research Grant in 2005.

References

- Elidrissi, B.; Addou, M.; Regragui, M.; Bougrine, A.; Kachouane, A.; Bernede, J. C. *Mater. Chem. Phys.* **2001**, *68*, 175.
- Marquardt, E.; Optiz, B.; Scholl, M.; Henker, M. *J. Appl. Phys.* **1994**, *75*, 8022.
- Ymaga, S. *Physica B* **1993**, *185*, 500.
- Leftheriotis, G.; Yianoulis, P.; Patrikios, D. *Thin Solid Films* **1997**, *306*, 92.
- Liu, X.; Cai, X.; Mao, J.; Jin, C. *Appl. Surf. Sci.* **2001**, *183*, 103.
- Hariskos, D.; Spiering, S.; Powalla, M. *Thin Solid Films* **2005**, *480-481*, 99.
- Bhattacharya, R. N.; Ramanathan, K. *Solar Energy* **2004**, *77*, 679.
- Gangopadhyay, U.; Kim, K.; Mangalaraj, D.; Yi, J. *Appl. Surf. Sci.* **2004**, *230*, 364.
- Kundu, S.; Olsen, L. C. *Thin Solid Films* **2005**, *471*, 298.
- Ashour, A.; Afifi, H. H.; Mahmoud, S. A. *Thin Solid Films* **1994**, *248*, 253.
- Pike, R. D.; Cui, H.; Kershaw, R.; Dwight, K.; Wold, A.; Blanton, T. N.; Wernberg, A. A.; Gysling, H. J. *Thin Solid Films* **1993**, *224*, 221.
- Ndukwe, I. C. *Sol. Energ. Mat. Sol. C* **1996**, *40*, 123.
- Lee, J.; Lee, S.; Cho, S.; Kim, S.; Park, I. Y.; Choi, Y. D. *Mater. Chem. Phys.* **2002**, *77*, 254.
- Kashani, H. *Thin Solid Films* **1996**, *288*, 50.
- Byrom, C.; Malik, M. A.; O'Brien, P.; White, A. J. P.; Williams, D. J. *Polyhedron* **2000**, *19*, 211.
- Zhang, W.; Zhong, Y.; Tan, M.; Tang, N.; Yu, K. *Molecules* **2003**, *8*, 411.
- Tran, N. H.; Lamb, R. N.; Mar, G. L. *Colloids Surfaces A* **1999**, *155*, 93.
- Osasona, O.; Djebah, A.; Ojo, I. A. O.; Eleruja, M. A.; Adedeji, A. V.; Jaynes, C.; Ajayi, E. O. B. *Opt. Mater.* **1997**, *7*, 109.
- Motevalli, M.; O'Brien, P.; Walsh, J. R.; Watson, I. M. *Polyhedron* **1996**, *15*, 2801.
- Klevtsova, R. F.; Glinskaya, L. A.; Zemskova, S. M.; Larionov, S. V. *Polyhedron* **1999**, *18*, 3559.
- Kim, H. K.; Jeong, H. C.; Kim, K. S.; Yoon, S. H.; Lee, S. S.; Seo, K. W.; Shim, I. W. *Thin Solid Films* **2005**, *478*, 72.
- Kim, H. K.; Jeong, H. C.; Kim, K. S.; Yoon, S. H.; Lee, S. S.; Seo, K. W.; Shim, I. W. *Bull. Korean Chem. Soc.* **2004**, *25*, 1068.
- Lee, E. Y. M.; Tran, N. H.; Lamb, R. N. *Appl. Surf. Sci.* **2005**, *241*, 493.