

Preparation and Characterization of Zinc Sulfide Thin Films by Solution Pyrolysis of Tailored Organometallic Precursors

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Zinc complexes having both thiolato and dithiocarbamate ligands [Zn(SR)(S₂CNR'R''), where (R, R', R'') = (Pr, Et, Et), (Prⁱ, Et, Et), (Prⁱ, Me, CH₂CH₂OH), (Prⁱ, Me, CH₂CH₂CN), (Prⁱ, CH₂CH₂OH, CH₂CH₂OH), (Bu, Et, Et), (Bu^t, Et, Et), (Oct, Et, Et), (Ph, Et, Et)] were synthesized. Bulky thiolato analogues (R=Prⁱ, Bu^t) are stable and form cyclic trimers of (ZnS)₃ six-membered ring. Where the bidentate dithiocarbamate ligand prevents disproportionation of the complex *via* intermolecular Zn-S linkages. These complexes are soluble in general organic solvents and are poorly volatile. Solution pyrolysis of Zn(SPrⁱ)(S₂CNEt₂) and Zn(SBu^t)(S₂CNEt₂) on a Si(111) gave ZnS(Wurtzite) thin films even at 250°C.

Key words: II-VI compound semiconductors, zinc sulfide, thin films, solution pyrolysis.

Introduction

II-VI compound semiconductors have attracted much attention over the past few years due to their great potential for optoelectronic applications.¹⁻⁴ We have already proposed several single-source precursor system for the growth of II-VI semiconductor thin layers.⁵ For example, we have succeeded epitaxial growth of cubic ZnS layers on Si(111) substrates through MOCVD using zinc(II) bis(diethyldithiocarbamate) as a single-source precursor.⁶ While the solution pyrolysis (printing-pyrolysis) process is known as the most economical process to prepare semiconducting layers of wide area.^{5,7} The dithiocarbamate complexes are, however, poor precursor for this purpose because of their high volatility.⁶ In this paper, we will report new single-source precursors for preparation of zinc sulfide thin films *via* solution pyrolysis technique.

Experimental

Syntheses of the complexes. A typical procedures are as following. Diethylzinc (5 mmol) and 2-propanethiol (5 mmol) were stirred in diethyl ether (20 ml) under N₂ for 2 h. Then a cold solution of diethylamine (5 mmol) and CS₂ (5 mmol) in ether (10 ml) were added dropwise to the solution, and the mixture was further stirred at room temperature for 20

h. Insolubles were removed by filtration, and the ether was evaporated under vacuum. Crystallization of the residue from DMF (dimethylformamide) / methanol gave transparent crystals of Zn(SPrⁱ)(S₂CNEt₂) with yield of 56% based on diethylzinc. Similarly, other eight complexes were synthesized. All complexes obtained in this study [Zn(SR)(S₂CNR'R''), where (R, R', R'') = (Pr, Et, Et), (Prⁱ, Et, Et), (Prⁱ, Me, CH₂CH₂OH), (Prⁱ, Me, CH₂CH₂CN), (Prⁱ, CH₂CH₂OH, CH₂CH₂OH), (Bu, Et, Et), (Bu^t, Et, Et), (Oct, Et, Et), (Ph, Et, Et)] gave satisfactory elemental analyses and their selected spectral data are summarized in Table I.

Table I Selected spectral data of Zn(SR)(S₂CNR'R'')

Compound	IR ν (C-N)	¹³ C-NMR δ (N ¹³ CS ₂)
PrSZnS ₂ CNEt ₂	1496.7	202.7
Pr ⁱ SZnS ₂ CNEt ₂	1502.7	202.5
Pr ⁱ SZnS ₂ CN(CH ₃) ₂ H ₄ OH	1499.8	205.1
Pr ⁱ SZnS ₂ CN(CH ₃) ₂ H ₄ CN	1506.3	207.1
Pr ⁱ SZnS ₂ CN(C ₂ H ₄ OH) ₂ H ₄ OH	1490.2	206.3
BuSZnS ₂ CNEt ₂	1496.7	202.7
Bu ^t SZnS ₂ CNEt ₂	1500.7	202.7
OctSZnS ₂ CNEt ₂	1496.7	202.7
PhSZnS ₂ CNEt ₂	1501.4	202.4

Among these complexes, $\text{Zn}(\text{SPr}^{\text{I}})(\text{S}_2\text{CNEt}_2)$ and $\text{Zn}(\text{SBU}^{\text{I}})(\text{S}_2\text{CNEt}_2)$ are stable but other complexes readily decompose through disproportionation into the corresponding zinc dithiolate and zinc dithiocarbamate during further purification by recrystallization. Thus we selected these two complexes having bulky thiolato ligands as candidate of single-source precursor.

Crystal Structure. Intensity data were collected at 298 K on a Rigaku AFC7R diffractometer operating in a ω - 2θ scan mode, with graphite-monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The structure was solved in the monoclinic space group Cc (#9) or $\text{P}2_1/\text{c}$ (#14) using direct methods (SIR91⁸ or SIR92⁹) to locate the first Zn position. Further details concerning data collection are given in Table II.

Table II. Crystal data and structure refinement of $[\text{Zn}(\text{SPr}^{\text{I}})(\text{S}_2\text{CNEt}_2)_3]$ and $[\text{Zn}(\text{SBU}^{\text{I}})(\text{S}_2\text{CNEt}_2)_3]$

	$[\text{Zn}(\text{SPr}^{\text{I}})(\text{S}_2\text{CNEt}_2)_3]$	$[\text{Zn}(\text{SBU}^{\text{I}})(\text{S}_2\text{CNEt}_2)_3]$
Formula	$\text{C}_{24}\text{H}_{21}\text{N}_3\text{S}_9\text{Zn}_3$	$\text{C}_{27}\text{H}_{27}\text{N}_3\text{S}_9\text{Zn}_3$
Formula weight	866	908
Crystal system	monoclinic	monoclinic
Space group	Cc(#9)	$\text{P}2_1/\text{c}$ (#14)
a/ \AA	22.452(1)	12.4984(9)
b/ \AA	11.229(1)	17.2417(9)
c/ \AA	17.535(1)	20.2971(9)
$\beta/^\circ$	115.088(5)	93.418(5)
V/ \AA^3	4003.8(6)	4366.1(4)
Z	4	4
Dcalc/ g cm^{-3}	1.437	1.382
Crystal size (mm)	0.20x0.20x0.20	0.05x0.10x0.10
Diffractometer	Rigaku AFC7R	
Radiation	Cu $\text{K}\alpha$ ($\lambda = 1.54178 \text{ \AA}$)	
Monochromator	graphite	
F(000)	1800.00	1896.00
Data collection range, $2\theta/^\circ$	25 (59.3-60.0)	25 (59.1-59.9)
Total reflections	3252	7079
Independent reflections	2770	5123
$I > 3\sigma(I)$		
Temperature	25.0 $^\circ\text{C}$	
R	0.037	0.077
Rw	0.040	0.068

Preparation of zinc sulfide thin films by solution pyrolysis.

The silicon substrates in a dimension of 20 mm \times 20 mm were prepared by cutting from a silicon wafer of 5

inches in diameter (Shin-Etsu Semiconductor, Co. Ltd., Japan). Washing the surface of the substrates was conducted by a previously reported procedure¹⁰. The following printing solutions were prepared and used; $\text{Zn}(\text{SPr}^{\text{I}})(\text{S}_2\text{CNEt}_2) / \text{DMF}$ (5 wt-%) and $\text{Zn}(\text{SBU}^{\text{I}})(\text{S}_2\text{CNEt}_2) / \text{benzene}$ (4 wt-%).

Whole surface of the substrate was covered by the printing solution by tipping and then the substrates were heated at the temperature just below the boiling points of the solvents for 2 h in a quartz tube furnace as shown in Figure 1. Then the substrates were further heated at the prescribed temperatures for 2 h. The detailed growth conditions are summarized in Table III and Figure 2.

Characterization. IR and ^{13}C and ^1H NMR spectra were recorded on a Shimadzu FT-IR DR8000 spectrophotometer and a Varian Unity 300 spectrometer, respectively. MS spectra were measured with a JEOL JMS-DX303 spectrometer. Surface morphology (SEM) and crystalline phases and structures (XRD) of thin films were obtained with a JEOL JSM-840 (acceleration voltage 10 kV) and a Rigaku RINT2000L diffractometer ($\text{CuK}\alpha$), respectively.

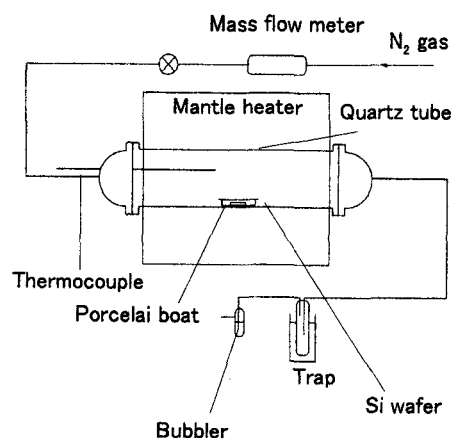


Figure 1 A set-up of the heater

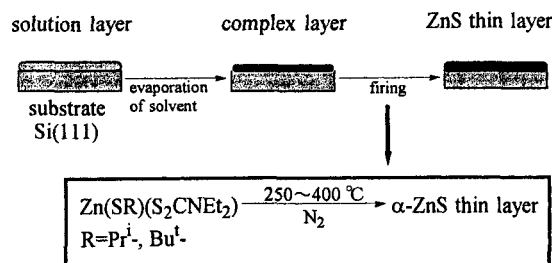


Figure 2 Procedure of solution pyrolysis

Table III Growth conditions of ZnS thin layers by solution pyrolysis

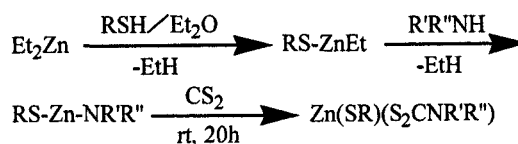
	Zn(SPr ⁱ)(S ₂ CNEt ₂)	Zn(SBu ^t)(S ₂ CNEt ₂)
solvent / concn	DMF(5-wt%)	benzene(4-wt%)
solvent evaporation temperature and time	150 °C, 2h	80 °C, 2h
pyrolysis temperature and time	250~400 °C, 4h	250~400 °C, 4h
N ₂ gas flow rate	0.1 Lmin ⁻¹	0.1 Lmin ⁻¹

Results and Discussion

Nine zinc complexes having both thiolato and dithiocarbamate ligands were prepared as shown in Scheme 1. Among these complexes, two complexes having bulky thiolato ligands such as PrⁱS and Bu^tS are stable and suitable for single-source precursors for growth of ZnS layers by solution pyrolysis, because other complexes readily decomposed through disproportionation into the corresponding zinc dithiocarbamates and zinc dithiolates as mentioned above.

From a result of crystallography, two bulky thiolate complexes form trimers of (ZnS)₃ six-membered ring (Figure 3) and the bidentate dithiocarbamate ligands exist at the exo-positions. On the other hand, the trimeric structure already contain a prototype of ZnS-frame in ZnS. Thus, releasing of any organic residues from the (ZnS)₃ six-membered ring and accumulation of them can easily form zinc sulfide framework. Consequently these two complexes seem to be an excellent candidate as the single-source precursor for low-temperature processing of ZnS.

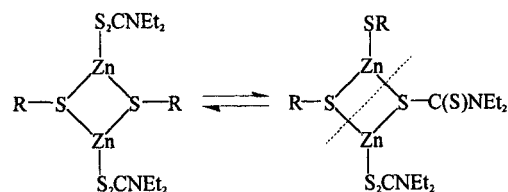
In contrast, other complexes such as Zn(SR)-(S₂CNEt₂) of R=Pr, Bu, Oct and Ph readily disproportionate into the corresponding zinc dithiocarbamates and zinc dithiolates. These complexes perhaps form a dimer of (ZnS)₂ four-membered ring and can undergo disproportionation from one of the isomeric conformation as shown in Scheme 2. Because of the existence of such a disproportionation, these complexes were not so good as precursors for ZnS.



(R,R',R'') = (Pr,Et,Et), (Prⁱ,Et,Et), (Prⁱ,Me,CH₂CH₂OH), (Prⁱ,Me,CH₂CH₂CN), (Prⁱ,CH₂CH₂OH,CH₂CH₂OH), (Bu,Et,Et), (Bu^t,Et,Et), (Oct,Et,Et), (Ph,Et,Et)

Scheme 1 Synthetic route of the complexes.

R=Ph, Pr, Bu, Oct



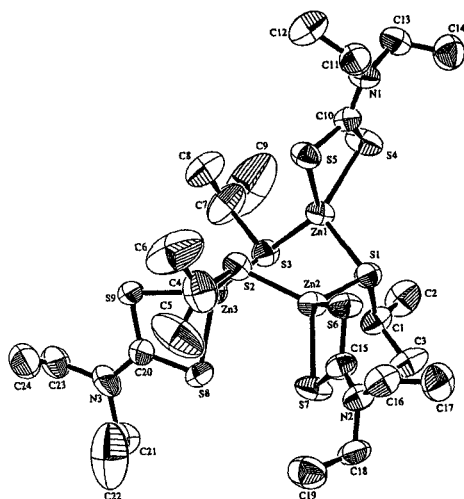
Scheme 2 Disproportionation path.

Stable complexes, Zn(SPrⁱ)(S₂CNEt₂) and Zn(SBu^t)(S₂CNEt₂) have both sufficient solubilities to general organic solvents and low volatility if compared with zinc bis(*N,N*-diethyldithiocarbamate). The static pyrolysis of these complexes actually gave ZnS powders under N₂ even at 250°C.

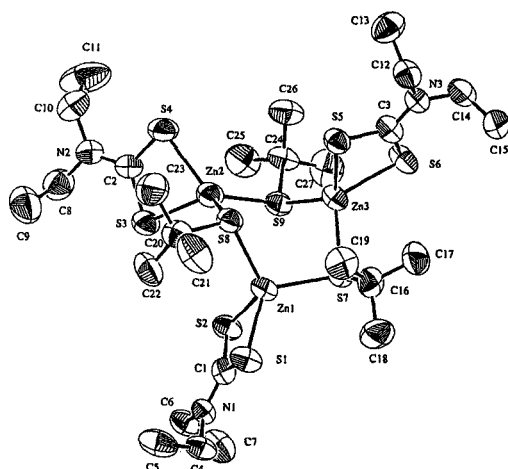
Then we attempted to prepare ZnS thin films by solution pyrolysis technique using these two complexes. Solutions of Zn(SPrⁱ)(S₂CNEt₂) in DMF(5 wt-%) and Zn(SBu^t)(S₂CNEt₂) in benzene(4 wt-%) were used as printing solutions. Thus solution pyrolysis of Zn(SPrⁱ)(S₂CNEt₂) on Si(111) substrate gave α-ZnS (Wurtzite or zincite) thin films at above 250°C. The film

deposited showed smooth surface morphology and XRD observations showed that Wurtzite type ZnS were obtained even at 250°C. Wurtzite phase deposition may be ascribed to the (ZnS)₃ six-membered ring structure of the precursor molecule.

(a)



(b)



Conclusion

In this work, we synthesized zinc alkylthiolato-dithiocarbamate complexes as a novel single-source precursor of zinc sulfide. Among them, the complexes having bulky thiolato ligands, such as Zn(SPrⁱ)(S₂CNEt₂) and Zn(SBu^t)(S₂CNEt₂) exhibited high solubility and low volatility. Therefore we successfully prepared zinc sulfide thin films *via* solution pyrolysis of these complexes and it was concluded that zinc alkylthiolatodithiocarbamate complexes were excellent precursors.

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Figure 3 ORTEP drawings of [Zn(SPrⁱ)(S₂CNEt₂)]₃ (a) and [Zn(SBu^t)(S₂CNEt₂)]₃ (b)