

Deposition of cadmium sulfide and zinc sulfide thin films by aerosol-assisted chemical vapors from molecular precursors

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Abstract: New complexes with the general formula $[M(S_2CN^r Bu_2)_2]$ [where $M = Cd^{II}$ (**1**) and Zn^{II} (**2**)] were synthesized and used as single source precursors to deposit thin films of cadmium sulfide and zinc sulfide by the aerosol-assisted chemical vapor deposition technique. The single crystal X-ray structures of **1** and **2** are also reported. Thermogravimetric analysis of **1** and **2** showed that both precursors decompose cleanly in a single step to produce their respective metal sulfides. The deposition of thin films was carried out on soda glass substrates in the 350–450 °C temperature range under inert conditions. The as-deposited thin films were characterized by powdered X-ray diffraction and field emission scanning electron microscopy. Thin films of CdS deposited at low temperature (350 °C) consist of densely packed granular crystallites with an average size of ca. 150 nm, while at higher temperatures (400 and 450 °C) particles with varying sizes and mixed morphologies are observed. The ZnS thin films deposited at 400 °C showed rod-like structures, whereas dense globular-like structures were obtained at 450 °C. Energy dispersive X-ray analysis was performed to study the chemical composition of the thin films.

Key words: Thin films, AACVD, molecular precursor, single crystal/ZnS thin films

1. Introduction

Semiconductors have become the most important area of research during the past few decades, especially in the fields of electronic and optoelectronic technologies.^{1–3} Considerable work has been devoted towards the preparation of single source precursors (SSPs) for the deposition of thin films/nanoparticles of semiconductors.^{4–10} A number of methods are used to grow the thin films, including spray pyrolysis,¹¹ chemical bath deposition,¹² and chemical vapor deposition.^{13–19} Chemical vapor deposition (CVD) is an important technique to grow high quality thin films compatible with a wide range of substrates (silica, quartz, glass, plastics) for electronic and optoelectronic applications.^{6–8} Aerosol-assisted chemical vapors deposition (AACVD) is an important type of CVD used primarily for precursors soluble in volatile organic solvents under ambient conditions. AACVD offers an efficient and low cost way to grow multicomponent thin films with precise stoichiometric control.^{20–22} The

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composition of as-deposited thin films is the most critical parameter that can adversely affect characteristics of functional devices. Cadmium and zinc sulfide are well-established photoconducting materials^{23,24–27} that can be used as detectors, emitters, and modulators in optoelectronics and blue light emitting laser diodes.

In the present work, we prepared $[M(S_2CN^nBu_2)_2]$ [where $M = Cd^{II}$ (**1**) and Zn^{II} (**2**)] and their single crystal X-ray diffraction structures were also determined. After purification and characterization of these complexes, thin films were deposited on the glass substrates by AACVD. The deposited thin films exhibited good substrate adhesion and crystallinity.

2. Results and discussion

The synthesis of SSPs **1** and **2** was carried out according to the reported method.¹⁴ Both precursors were purified and recrystallized from toluene at room temperature after several days. They are air-, moisture-, and light-stable and can be stored at room temperature for several months. Both are soluble in common organic solvents like toluene, acetonitrile, and tetrahydrofuran. The single crystal X-ray analysis of precursor **1** and **2** was carried out and cif files have been deposited in the Cambridge Crystallography Database. The CCDC number of precursor **1** is 905773 and of **2** is 905772. Table 1 shows comparative characteristic parameters of SSP **1** and **2** determined by single crystal X-ray diffraction.

Table 1. Important structural refinement data of SSPs **1** and **2** determined from single crystal X-ray diffraction.

	1	2
Empirical formula	$C_{36}H_{72}Cd_2N_4S_8$	$C_{36}H_{72}N_4S_8Zn_2$
Formula weight	1042.26	948.20
Temperature (K)	100(2) K	100(2) K
Wavelength (Å)	0.71069	0.71073
Crystal system, space group	Monoclinic, C2/c	Monoclinic, C2/c
Unit cell dimensions	a = 23.340(5) Å alpha = 90° b = 16.194(5) Å beta = 127.414(5)° c = 15.876(5) Å gamma = 90°	a = 23.133(3) Å alpha = 90° b = 16.3310(19) Å beta = 127.875(2)° c = 15.938(2) Å gamma = 90°
Volume	4766(2) Å ³	4752.8(10) Å ³
Z, Calculated density	4, 1.453 Mg/m ³	4, 1.325 Mg/m ³
Absorption coefficient	1.272 mm ⁻¹	1.390 mm ⁻¹
F (000)	2160	2016
Theta range for data collection	1.67 to 25.02°	1.67 to 28.32°
Limiting indices	-27 ≤ h ≤ 27, -19 ≤ k ≤ 19, -18 ≤ l ≤ 18	-23 ≤ h ≤ 30, -19 ≤ k ≤ 21, -21 ≤ l ≤ 9
Reflections collected / unique	15,287 / 4199 [R(int) = 0.0918]	14,441 / 5545 [R(int) = 0.0896]
Max. and min. transmission	0.7850 and 0.7416	0.7685 and 0.6806
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.121	0.886
Final R indices [I > 2sigma(I)]	R1 = 0.1039, wR2 = 0.2305	R1 = 0.0807, wR2 = 0.2156

2.1. Single crystal X-ray structure of $[Cd(S_2CN^nBu_2)_2]$

The single crystal structure of **1** shows that there are 2 molecules in a unit cell (Figure 1). The structure is based on a monomer in which each cadmium is bonded to 4 sulfur atoms by 2 bidentate dithiocarbamate ligands. The geometry around the central metal atom is distorted square planar. The distortion in geometry

is evident from the bond lengths of cadmium to sulfur, which vary from 2.5 Å to 2.8 Å. Selected bond lengths and bond angles are shown in Table 2.

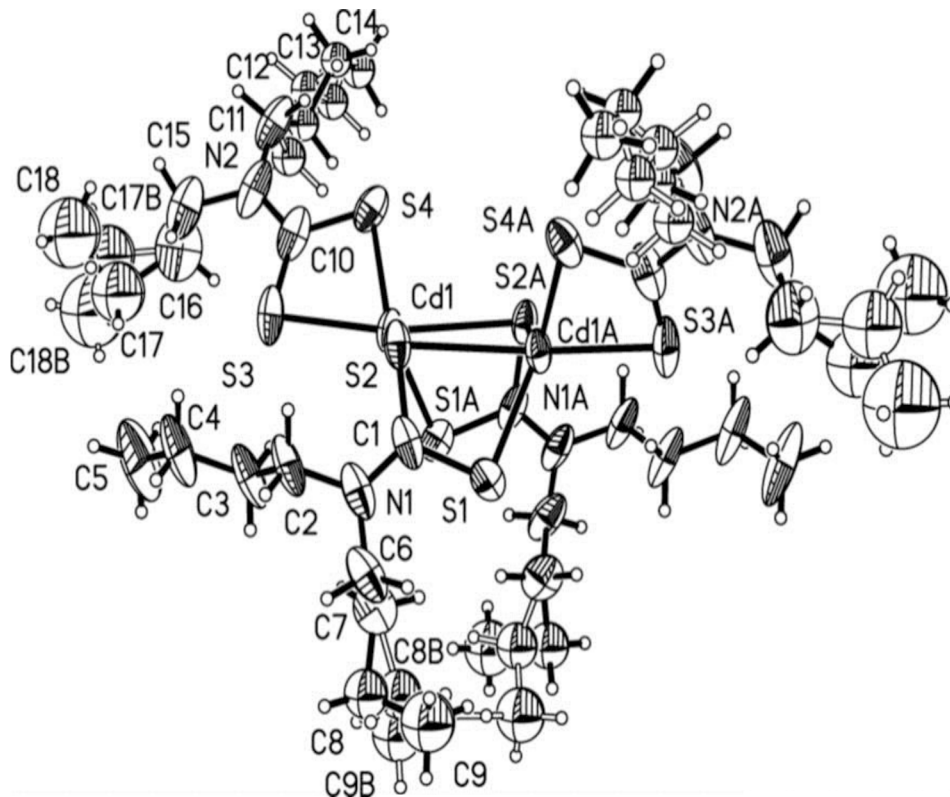


Figure 1. Molecular structure of **1** is shown with 50% ellipsoidal probability level.

Table 2. Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

Atoms	Bond lengths (Å)	Atoms	Bond angles (°)
Precursor 1			
Cd(1)-S(1)# 1	2.50(4) 2.53(4)	S(4)-Cd(1)-S(2)	120.30(13)
Cd(1)-S(4)	2.57(3) 2.60(4)	S(1)#1-Cd(1)-S(3)	112.91(14)
Cd(1)-S(2)	2.86(3) 2.50(4)	S(4)-Cd(1)-S(3)	69.91(15)
Cd(1)-S(3)	2.86(3)	S(2)-Cd(1)-S(3)	107.05(12)
Cd(1)-S(2)# 1	128.70(12)	S(1)#1-Cd(1)-S(2)#1	66.94(12)
S(1)-Cd(1)# 1	107.94(12)	S(4)-Cd(1)-S(2)#1	93.92(12)
S(2)-Cd(1)# 1			
S(1)#1-Cd(1)-S(4)			
S(1)#1-Cd(1)-S(2)			
Precursor 2			
S(1)-Zn(1)	2.308(12)	S(1)-Zn(1)-S(2)#1	111.95(5)
S(2)-Zn(1)# 1	2.364(14)	S(4)-Zn(1)-S(2)#1	118.46(5)
S(3)-Zn(1)	2.441(11)	S(1)-Zn(1)-S(3)	110.35(5)
S(4)-Zn(1)	2.335(13)	S(4)-Zn(1)-S(3)	75.54(4)
Zn(1)-S(2)# 1	2.364(15)	S(2)#1-Zn(1)-S(3)	107.93(5)
S(1)-Zn(1)-S(4)	124.30(5)		

2.2. Single crystal X-ray structure of $[\text{Zn}(\text{S}_2\text{CN}^n\text{Bu}_2)_2]$

Figure 2 depicts the single crystal X-ray structure of precursor **2** (CCDC-905772) in which Zn adopts a distorted tetrahedral geometry with S_2 donor sites. The 2 sulfur atoms are mutually *cis* in configuration and they produce a 6-membered ring with the unit $(\text{Zn NC}_2\text{S}_2\text{-Zn})$. The zinc atom is coordinated to 4 sulfur atoms, 2 from each alkyldithiocarbamato chelating ligand. The crystalline phase of the precursor belongs to the monoclinic system with space group C2/c . One sulfur atom $\text{S}(1)$ or $\text{S}(4)$ is closely attached to the zinc atom to form a relatively strong coordination bond, the average of the Zn–S distances being 2.321 Å. The sulfur atoms $\text{S}(2)$ or $\text{S}(3)$, however, make a weak bond and the average Zn–S distance is 2.402 Å. The S–Zn–S bond angle of **2** ranges from 75.54 to 124.30°. Other selected bond lengths and bond angles are given in Table 2.

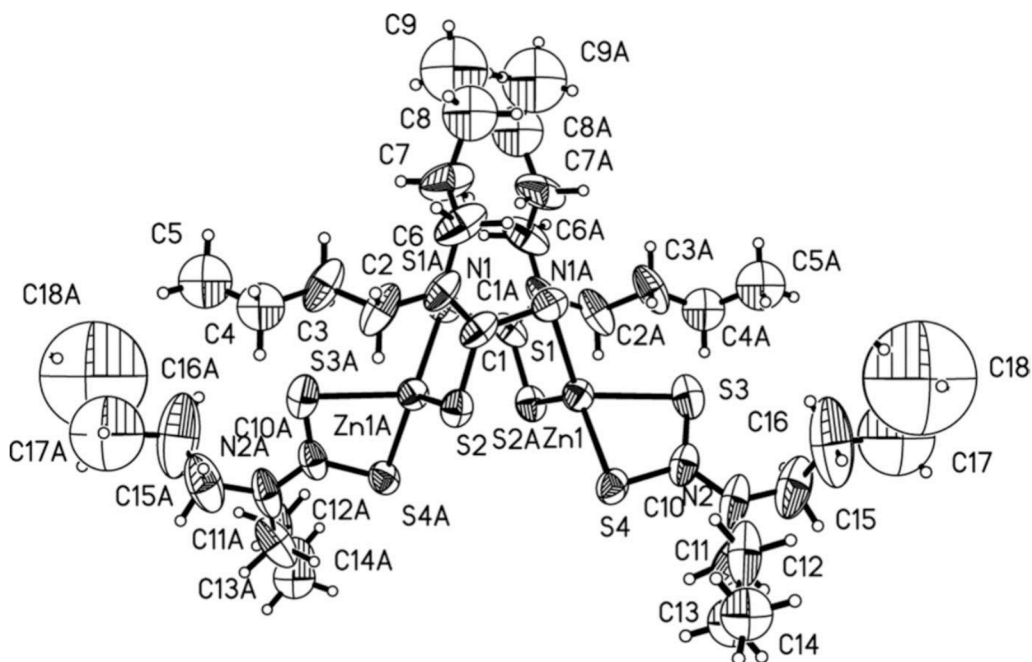


Figure 2. Molecular structure of **2** is shown with 50% ellipsoidal probability level.

Thermogravimetric analysis (TGA) of the precursors **1** and **2** was carried out in a temperature range of 25–500 °C at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. TGA studies show that both precursors decompose cleanly in one step (Figure 3). The decomposition of precursor **1** starts at 260 °C in comparison to precursor **2**, which begins to decompose at 245 °C; however, decomposition of **2** completes at 333 °C and of **1** at 350 °C. The solid decomposition residual amount is 22% for **1**, which is in good agreement with the calculated value of 27% for CdS. Similarly, precursor **2** yields a residual mass of 11% against 20% calculated for ZnS. In both precursors **1** and **2**, the obtained mass of residues (experimental) is less than the calculated (theoretical) probably due to the formation of decomposed volatile species (metal-alkyl), which are driven out with the stream of nitrogen gas.

Deposition of CdS films from $[\text{Cd}(\text{S}_2\text{CN}^n\text{Bu}_2)_2]$ (**1**) was carried out at 350–450 °C using 10 mL of 9.5 mM toluene solution with an argon flow rate of 160 sccm for 1 h. The as-deposited films were yellow transparent and very adherent to the glass surface. At higher growth temperature (450 °C), slightly dark yellow-brown films were deposited after 1 h of growth time.

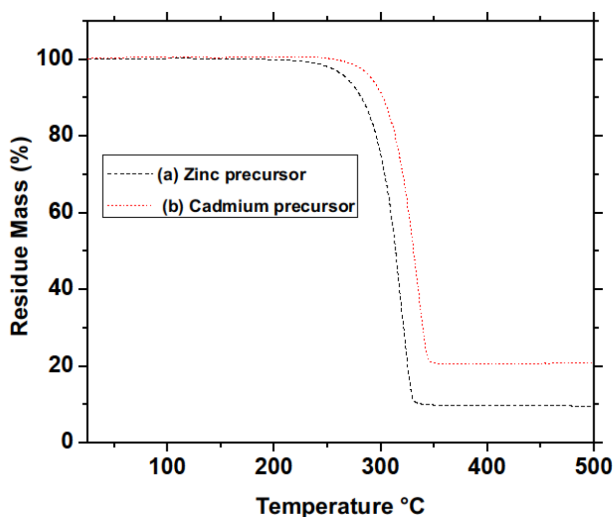


Figure 3. TGA of (a) zinc precursor **2** and (b) cadmium precursor **1** at 25–500 °C at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

The structural characterization of as-deposited CdS thin films was carried out by powdered X-ray diffraction (p-XRD) (Figure 4) at various temperatures, which confirmed the formation of the hexagonal phase of CdS (ICDD –2306). The diffracted peak at 2θ 25.1 corresponds to the [100] plane and that at 26.5 to the [200] plane, while that at 28.2 represents [101] planes. These are characteristic peaks of the hexagonal phase of CdS. The intensity of the diffraction peak along the [200] plane increased as the deposition temperature increased from 350 to 400 °C; however, the film deposited at 450 °C showed a marked decrease in the intensity of the [200] peak. The [100] plane peak showed the opposite trend and its intensity increased as deposition temperature was raised from 350 to 450 °C (Figure 5). A field emission scanning electron microscope (FE-SEM) showed that the films deposited at 350 °C consist of granular crystallites with the size of ca. 150 nm densely packed together (Figure 5a). The films deposited at 400 °C have a flake-like structure with an approximate size of 1 μ m (Figure 5b). At 450 °C, the as-deposited films of CdS showed 2 different morphologies. In the middle position of substrate, films exclusively consist of flake-like structures, while at the edges of substrate, the crystallites of film are predominantly spherical (Figures 5c and 5d). A high resolution SEM image is shown in the inset in Figure 5d.

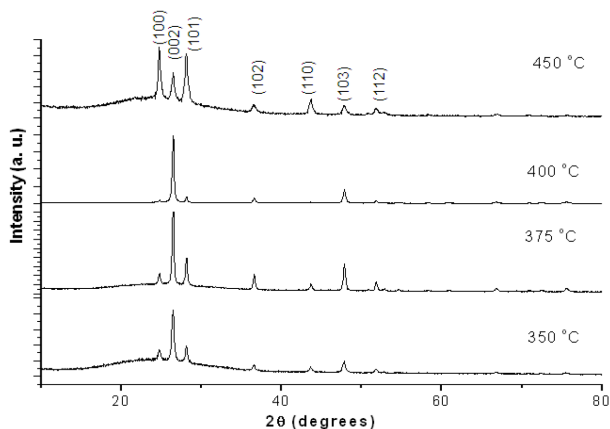


Figure 4. p-XRD patterns of CdS deposited films from $[\text{Cd}(\text{S}_2\text{CN}^n\text{Bu}_2)_2]_2$ by AACVD at 350 °C, 375 °C, 400 °C, and 450 °C.

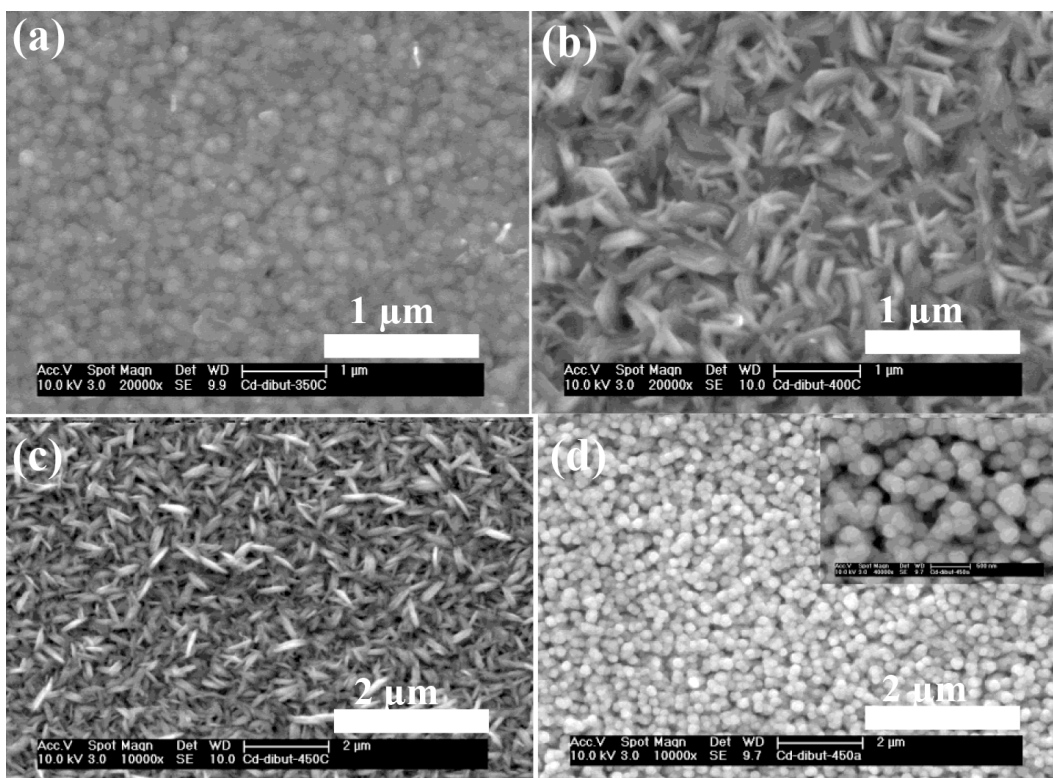


Figure 5. FE-SEM images of CdS deposited from $[\text{Cd}(\text{S}_2\text{CN}^n\text{Bu}_2)_2]_2$ by AACVD at (a) 350 °C, (b) 400 °C, (c, d) 450 °C.

The deposition of ZnS thin films from $[\text{Zn}(\text{S}_2\text{CN}^n\text{Bu}_2)_2]_2$ was carried out under similar conditions used for CdS thin films by AACVD. The as-deposited films were dark gray and very adherent to the glass substrates at 350 and 400 °C. No deposition occurred at 350 °C. In Figure 6 p-XRD of the films deposited at 400 °C shows the formation of hexagonal ZnS (JCPDS 80-0007). SEM showed the ZnS thin films deposited at 400 °C were compact and uniform and consisted of rod-like structures, but at 450 °C the morphology changes to globular-like structures that are densely packed (Figures 7a–7d). Energy dispersive X-ray (EDX) analyses of as-deposited thin films of CdS and ZnS from both precursors showed the presence of respective elements. A typical EDX graph of ZnS thin films deposited at 450 °C is shown in Figure 8.

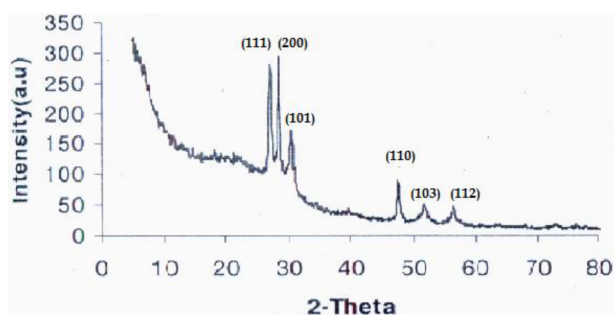


Figure 6. Typical p-XRD of zinc sulfide thin film deposited at 400 °C using precursor **2** by AACVD technique.

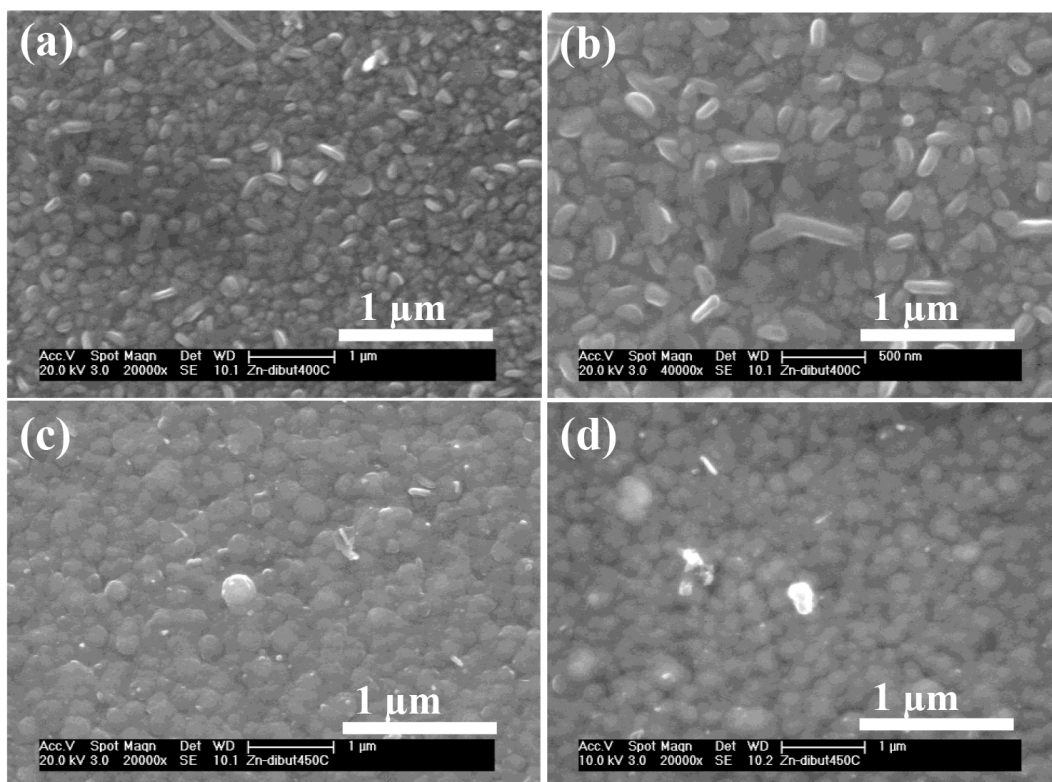


Figure 7. SEM images of ZnS deposited from $[Zn(S_2CN^n Bu_2)_2]_2$ by AACVD at (a, b) 400 °C (c, d) 450 °C.

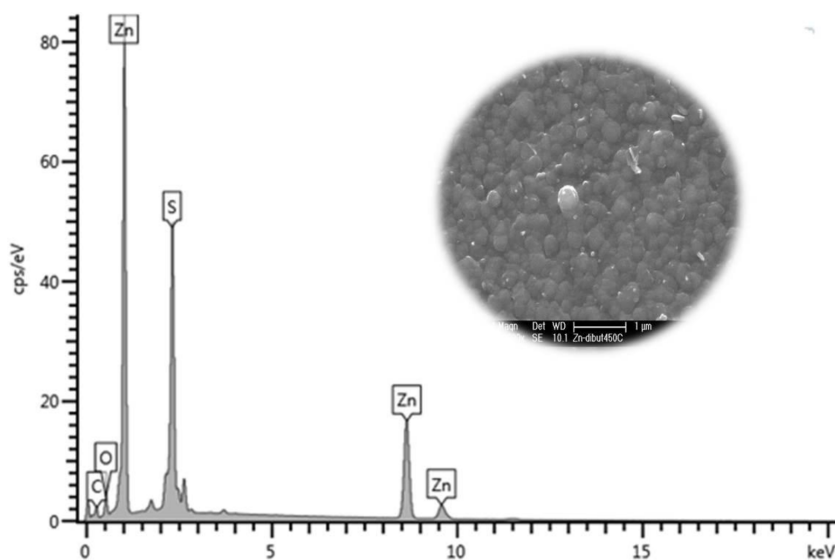


Figure 8. Energy dispersive X-ray graph of ZnS thin film deposited from $[Zn(S_2CN^n Bu_2)_2]_2$ by AACVD at 450 °C.

In conclusion, the complexes $[Cd(S_2CN^n Bu_2)_2]_2$ (**1**) and $[Zn(S_2CN^n Bu_2)_2]_2$ (**2**) were synthesized and characterized by NMR, elemental analysis, FTIR, and thermal studies. The single crystal X-ray structures of **1** and **2** were determined and showed dimeric structures. These complexes are soluble in most organic solvents and are stable in open air at room temperature for several months and hence are useful as precursors for the deposition of CdS and ZnS. Thin films of CdS and ZnS were deposited from using **1** and **2** by AACVD method

on glass substrates between 350 and 450 °C. The as-deposited thin films were smooth and adherent, and showed significant changes in the morphology and the size of crystallites depending on the growth temperature.

3. Experimental

All the reactions were performed under inert atmosphere conditions. All the chemicals were of reagent grade (Sigma-Aldrich) and used without further purification. Solvents were distilled prior to use.

Elemental analysis was performed using the Thermo Scientific Flash 2000 Organic Elemental Analyzer at the University of Manchester micro-analytical laboratory. The infrared absorption spectrum was recorded on a FTIR Bio-RAD Merlin (Varian) FTIR spectrometer in the range of 4000–200 cm^{-1} . PerkinElmer and Seiko thermal analyzers were used to obtain thermogravimetric analysis (TGA) data. A PIFCO ultrasonic humidifier (Model No. 1077) and a CARBOLITE furnace were used for AACVD. X-ray diffraction studies were performed on a Bruker AXS D8 diffractometer using $\text{Cu-K}\alpha$ radiation. The samples were mounted flat and scanned between 20 and 80° in a step size of 0.05 with a count rate of 9 s. Films were carbon coated using Edward's E306A coating system before carrying out SEM. SEM analysis was performed using a Philips XL 30FEG.

3.1. X-ray crystallography

Single-crystal X-ray diffraction data for the compounds were collected using graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker APEX diffractometer. The structure was solved by direct methods and refined by full-matrix least squares on F2. All non-H atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All calculations were carried out using the SHELXTL package.^{28,29} The structural refinement data for **1** and **2** are given in Table 1.

3.2. Synthesis of precursors

3.2.1. Synthesis of $[\text{Cd}(\text{S}_2\text{CN}^n\text{Bu}_2)_2]_2$ (**1**)

The complex was prepared by adding a solution of di-butylamine (3.39 mL, 0.020 mol) to the solution of NaOH (0.80 g, 0.020 mol) in methanol (20 mL) followed by cooling at ca. 10 °C in an ice bath. Carbon disulfide (1.20 mL, 0.02 mol) was added dropwise to the mixture with constant stirring. After removal of the ice bath, cadmium chloride solution (1.83 g, 0.01 mol in 10 mL of water) was added slowly to the reacting mixture with vigorous stirring. The white precipitate formed was filtered, washed with water, and dried at room temperature under vacuum. The product was further recrystallized in toluene. Transparent white crystals suitable for X-ray studies were obtained. Yield 83.5%. Micro elemental analysis: Calculated: C, 41.44; H, 6.90; N, 5.37; S, 24.63; Cd, 21.56) %. (Found: C, 41.39; H, 6.75; N, 5.33; S, 24.07; Cd, 20.93, FTIR: 2834 ν (C–H), 1408 ν (C–N), 987 ν (C–S) cm^{-1} . ^1H NMR δ ppm (CDCl_3): 3.10 (t, 8H, $J = 7.4$ Hz, $4\text{CH}_2\text{N}$), 1.91 (quint, 8H, $J = 7.4$ Hz $4\text{CH}_2\text{--CH}_2\text{--R}$), 1.22 (sext., 8H, $J = 7.4$ Hz, 4CH_2), 0.95 (t, 12H, $J = 7.4$, H 4- CH_3).

3.2.2. Synthesis of $[\text{Zn}(\text{S}_2\text{CN}^n\text{Bu}_2)_2]_2$ (**2**)

The complex was prepared by a method similar to that described above but ZnCl_2 (0.01 mol) in 20 mL of water was used. The product was recrystallized in toluene for further studies. Yield 86.2%. Micro elemental

analysis: Calculated: C, 45.56; H, 7.59; N, 5.90; S, 27.08; Zn, 13.37)%. (Found: C, 45.46; H, 7.57; N, 5.84; S, 26.74; Zn, 13.15. FTIR: 2780 ν (C–H), 1370 ν (C–N), 940 ν (C–S) cm^{-1} .

^1H NMR δ ppm (CDCl_3): 3.30 (t, 8H, $J = 7.4$, $4\text{CH}_2\text{N}$), 1.60 (quint, 8H, $J = 7.4$ Hz, 8H, $4\text{-CH}_2\text{R}$), 1.20 (sext., 8H, $J = 7.4$ Hz), 0.90 (t, 12H, $J = 7.4$ Hz, $4\text{CH}_3\text{R}$).

3.3. Deposition of thin films from SSPs (1) and (2)

Thin film deposition experiments were carried out in a homemade hot wall AACVD kit.⁶ This homemade aerosol-assisted chemical vapor deposition kit consists of a 2-necked flask, a PIFCO ultrasonic humidifier (Model No. 1077), and a CARBOLITE furnace. The experiments were carried out using 9.5 mM toluene solution of $[\text{Cd}(\text{S}_2\text{CN}^n\text{Bu}_2)_2]_2$ and 20 mM solution of $[\text{Zn}(\text{S}_2\text{CN}^n\text{Bu}_2)_2]_2$ precursor with an argon flow rate of 160 sccm at 350–450 °C. Seven glass substrates (1×1 cm) were placed inside the reactor tube. The carrier flow rate was controlled by Platon flow gauge. The solution in the 2-necked flask was placed in the water above the piezoelectric modulator of a humidifier, where aerosol droplets are generated. The aerosol droplets of the precursor thus generated were transferred into the hot wall zone of the reactor by carrier gas. Both the solvent and the precursor were evaporated and the precursor reached the heated substrate surface, where thermally induced reactions and films deposition took place.

Acknowledgments

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