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Aerosol assisted chemical vapor deposition (AACVD) of CdS thin films from heterocyclic cadmium(II) complexes



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Sixberth Mlowe^a, Linda D. Nyamen^b, Peter T. Ndifon^b, M. Azad Malik^c, James Raftery^c, Paul O'Brien^c, Neerish Revaprasadu^{a,*}

^a Department of Chemistry, University of Zululand, Private Bag X1001, Kwa-Dlangezwa 3886, South Africa ^b Department of Inorganic Chemistry, University of Yaoundé I, P.O. Box 812, Yaoundé, Cameroon ^c School of Materials, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom

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ABSTRACT

Cadmium dithiocarbamato complexes of piperidine (1) and tetrahydroquinoline (2) were synthesized and characterized by elemental analysis, FT-IR spectroscopy, NMR and TGA analyses. The X-ray single crystal structure of bis(piperidinedithiocarbamato)cadmium(II) complex (1) was determined. The synthesized compounds were used as single source precursors to deposit CdS films on glass substrates at 350, 400 and 450 °C using the aerosol assisted chemical vapor deposition (AACVD) method. The surface morphology and the size of the CdS films were determined by AFM and SEM analyses; the crystalline phases by *p*-XRD analyses and the elemental composition by EDX measurements. The particle sizes were found to be in the range between 50–110 nm and 100–220 nm for complex (1) and (2), respectively. The electronic properties of the CdS films were analyzed by UV-Vis and Raman spectroscopic methods. Results revealed that the morphology, size and composition of the films are influenced by the deposition temperature.

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1. Introduction

Binary metal chalcogenides as thin films, or particulates in mono-dispersed form, especially II-VI semiconductors and in particular cadmium or zinc chalcogenides (CdS, CdSe, CdTe, ZnS, ZnSe) have attracted considerable attention [1–5]. They have high symmetry axis distinguished from all the other axes which serves as the directional axis for the asymmetric growth for the synthesis of nanorods [6–8]. Their properties and potential for applications in photovoltaic technologies which employ the use of cheap and widely available elements is important [10–12].

Cadmium sulfide is a group II-VI semiconductor with a direct band gap of 2.42 eV. CdS thin films have been used for a wide variety of technological applications, including photovoltaic cells, electro-optic modulators, sensors, electroluminescent and photo luminescent devices, and antireflection coatings [13–15]. The route used to prepare or deposit a material can profoundly affect the phase composition, thermal stability, and morphology, which in turn can influence the functional behavior of the material. Many techniques such as spray pyrolysis [16], chemical bath deposition [17], sol-gel [18], and metal-organic chemical vapor deposition (MOCVD) [19-23], has been used to deposit phase pure films of CdS.

The MOCVD technique employing precursors is a well established giving high-quality thin films. The use of single-source precursors (SSPs) can potentially provide several key advantages over other routes due to the existence of preformed bonds which can lead to a material with fewer defects and better stoichiometry [24]. In this work, the aerosol-assisted CVD (AACVD) technique was used because it could lead to the deposition of nanosized thin films under soft processing conditions where the volatility of the precursor is no longer crucial as in the case conventional CVD [25].

The nature, morphology and composition of the final product can be affected by the single source precursor used to deposit the materials [26,27]. As initially reported the use of single source precursor for CdS has also provided an efficient route to high quality crystalline monodispersed nanoparticles of semiconductors [28,29]. Various classes of single source precursors have been identified and developed including dialkyldithiocarbamates [21,20,30,31], xanthates [19,32], N-alkyl thioureas [33], and dithioimidodiphosphinates [34,35], for the preparation of CdS thin films and nanoparticles.



^{*} Corresponding author. Tel.: +27 35 902 6152; fax: +27 35 902 6568.

We have recently demonstrated that heterocyclic piperidine and tetrahydroquinoline dithiocarbamato metal complexes can be used as single source precursors for the preparation of high quality ZnS, PbS and CdS nanoparticles [8–10,36–38]. The variation of some reaction parameters such as the temperature, the monomer concentration and the capping molecule showed an effect on the size and the morphology of the synthesized nanoparticles. The precursors used for the decomposition were air and moisture stable at room temperature. The AACVD of CdS thin films using the pyridine adduct of *bis*(piperidinedithiocarbamato) cadmium(II) complex was also reported [39]. In this work, we report the use of piperidine (1) and tetrahydroquinoline (2) dithiocarbamato cadmium(II) complexes as single source precursors for the deposition of CdS thin films at different temperatures by AACVD. The single crystal X-ray structure of the *bis*(piperidinedithiocarbamato)cadmium(II) complex is also reported.

2. Experimental

2.1. Chemicals

Cadmium chloride 99%, acetonitrile, 1,2,3,4, tetrahydroquinoline 98% (Aldrich). Piperidine 99% (Sigma–Aldrich). Petroleum ether, methanol 99.5%, dichloromethane, carbon disulfide 99.5%, chloroform, sodium hydroxide 98%, and acetone (Merck) were used as purchased without any further purification.

2.2. Instrumentation

Microanalysis was performed on a Perkin-Elmer automated model 2400 series II CHNS/O analyser. Infrared spectra were recorded on a Bruker FT-IR tensor 27 spectrophotometer directly on small samples of the compounds in the range 200–4000 cm⁻¹. Thermogravimetric analysis was carried out at 20 °C min⁻¹ heating rate using a Perkin Elmer Pyris 6 TGA up to 600 °C in a closed perforated aluminium pan under N₂ gas flow. Optical absorption measurements were carried out using a Varian Cary 50 UV–Vis spectrophotometer. A Perkin-Elmer LS 55 spectrofluorimeter was used to measure the photoluminescence of the CdS thin films. Both measurements were done at room temperature. Raman spectra were recorded using Horiba Jobinyvon Raman spectrometer using 514.5 nm lasers at room temperature.

Atomic force microscopy (AFM) analysis (Contact mode) of the CdS thin films was carried by a Bruker Inova instrument using Nano Drive Software and the images were processed using Nanoscope analysis. Scanning electron microscopy (SEM) and EDX measurements were carried out by carbon coating the films by using Edward's E306A coating system before carrying out SEM and EDX analyses. SEM analysis was performed using a Philips XL 30FEG and EDX was carried out using a DX4 instrument. Powder X-ray Diffraction (p-XRD were recorded in the high angle 2θ range of 20–60° using a Bruker AXS D8 Advance X-ray diffractometer, equipped with nickel filtered Cu K α radiation (λ = 1.5406 Å) at 40 kV, 40 mA and at room temperature.

X-ray crystallographic analysis: Single crystal X-ray diffraction data for complex (**1**) were collected using graphite monochromated Cu K α radiation (λ = 1.54178 Å) on a Bruker APEX diffractometer. The structure was solved by direct methods and refined by full-matrix least squares on F^2 . 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 [40]. Crystal data and structural refinement parameters are presented in Table 1. (CCDC reference number 1008839).

		Table	1
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Crystal data and structural refinement parameters for complex (1).

Formula	$C_{24}H_{40}Cd_2N_4S_8$
Mr	865.88
Crystal system	triclinic
Space group	ΡĪ
a (Å)	8.7196(4)
b (Å)	12.5000(9)
c (Å)	15.9023(8)
α (°)	80.328(5)
β (°)	89.921(4)
γ (°)	72.778(5)
V (Å ³)	1629.86(16)
$Z, D_{\text{calc}} (\text{Mg m}^{-3})$	2, 1.764
T (K)	100(2)
Refinement method	full-matrix least-squares on F ²
Reflections collected/unique	9866/5919, [<i>R</i> _{int} = 0.0566]
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0613, wR_2 = 0.1649$
R indices (all data)	$R_1 = 0.0751, wR_2 = 0.1736$
Largest difference in peak and hole ($e Å^{-3}$)	2.189 and -1.473
Goodness-of-fit (GOF)	1.101

2.3. Preparation of the ligands

Carbon disulfide (0.1 mol, 6.0 mL) was added in small portions to an equimolar solution mixture of sodium hydroxide (4.0 g, 0.1 mol) and the corresponding amine (piperidine, tetrahydroquinoline, 0.1 mol), cooled in an ice bath at 0 °C. After 15 min, a precipitate was formed which was then dried in air and re-crystallized in a mixture of acetone/petroleum ether. The final product was collected, washed with chloroform and suction dried.

Na(pip-dtc), Yield: 92.5%. Significant IR bands: $v_{(O-H)}$: 3370 cm⁻¹, $v_{(C=S)}$: 949 cm⁻¹, $v_{(C=N)}$: 1439 cm⁻¹. *Anal.* Calc. for C₆H₁₀NS₂Na·H₂O: C, 35.80; H, 6.01; N, 6.96. Found: C, 35.90; H, 6.13; N, 6.98%.

Na(thq-dtc), Yield: 61%. Significant IR bands: $v_{(O-H)}$: 3250 cm⁻¹, $v_{(C=S)}$: 968 cm⁻¹, $v_{(C=N)}$: 1481 cm⁻¹. *Anal*. Calc. for C₁₀H₁₀NS₂Na-2H₂O: C, 44.93; H, 5.28; N, 5.24. Found: C, 45.43; H, 5.09; N, 5.25%.

2.4. Preparation of the cadmium complexes

Cadmium chloride (5.0 mmol) was dissolved in distilled water (25.0 mL) and added drop-wise to the corresponding solution of the dithiocarbamate ligand (10.0 mmol). The reaction mixture was stirred for 1 h, and the precipitate formed was filtered, washed with excess distilled water and dried overnight in an oven at 70 °C.

[Cd(pip-dtc)₂], (**1**) (pip = piperidinyl, dtc = dithiocarbamato), Yield: 86%. IR (cm⁻¹, ATR): 967, ν (C=S); 1485, ν (C=N); 388, ν _(Cd-S). Anal. Calc. for C₁₂H₂₀N₂S₄Cd: C, 33.29; H, 4.66; N, 6.47. Found: C, 33.47; H, 4.55; N, 6.43%. m.p. 331%.

[Cd(thq-dtc)₂], (**2**) (thq = tetrahydroquinoline, dtc = dithiocarbamato), Yield: 69%. IR (cm⁻¹, ATR): 972, ν (C=S); 1492, ν (C=N); 397, ν (Cd–S). *Anal*. Calc. for C₂₀H₂₀N₂S₄Cd: C, 45.40; H, 3.81; N, 5.29. Found: C, 44.88; H, 3.61; N, 4.95%. m.p. 320 °C.

2.5. Deposition of films by AACVD

In a typical deposition, 0.2 g (0.4 mmol) of the precursor was dissolved in 20 ml of acetonitrile in a two-necked 100 ml roundbottom flask with a gas inlet that allowed the carrier gas (argon) to pass into the solution to aid the transport of the aerosol. This flask was connected to the reactor tube by a piece of reinforced tubing. The argon flow rate was controlled by a Platon flow gauge. Seven glass substrates (approx. 1×2 cm were placed inside the reactor tube, which is placed in a Carbolite furnace. The precursor solution in a round-bottom flask was kept in a water bath above the piezoelectric modulator of a Pifco ultrasonic humidifier (Model No. 1077). 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 vapor reached the heated substrate surface where thermally induced reactions and film deposition took place. The reaction temperatures were varied between 350 and 450 °C.

3. Results and discussion

3.1. Characterization of the ligand and the complexes

The purity of piperidine/tetrahydroquinoline dithiocarbamate ligands and the corresponding cadmium complexes were



Fig. 1. Thermogravimetric analysis (TGA) plots of complexes (1) and (2) at a heating rate of $10 \degree C \min^{-1}$ under nitrogen atmosphere.



Fig. 2. Single X-ray crystal structure of *bis*(piperidinedithiocarbamato)cadmium(II) complex.

Table 2	2
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Selected	bond	lengths	(Å)) and	angles	(°)	for	complex	(1).
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confirmed by elemental analysis, IR, NMR and TGA. The complexes were obtained in good yield with a simple reaction route. The piperidine dithiocarbamate and its complex were white while tetrahydroquinoline dithiocarbamate and its complex were yellow. The complexes are air and moisture stable at room temperature for periods of several months.

The TGA thermograms show decomposition in single step for both complexes at 331 and 319.80 °C, displaying a weight loss of 64.9% and 70.9% (calc = 66.6% and 72.7%) for piperidine and tetrahydroquinoline complexes, respectively (Fig. 1). The final residues 35.1% and 29.1% were close to 33.4% and 27.3%, higher than the calculated values for CdS obtained from complexes (1) and (2) respectively. The final TGA residue were analyzed by EDX and found to consist of small amount of carbon contamination, which attributes to the higher experimental values because of bulky alkyl organic moiety of the ligands.

The ORTEP view of the crystal structure of *bis*(piperidinedithiocarbamato)cadmium(II) [C₂₄H₄₀Cd₂N₄S₈] is shown in Fig. 2 while the crystal data are shown on Table 1 and selected bond parameters shown on Table 2. The compound is found to crystallise in the triclinic crystal system, with space group $P\bar{1}$ and Z = 2. The structure shows a dimeric compound with each of the cadmium center chelated to two dithiocarbamate ligands through their Satoms. Two S-atoms from two different dithiocarbamate ligands form two μ_3 -S bridges between the two Cd atoms and a C-atom of each of the ligands, thus forming a square pyramidal geometry around each Cd center as shown in Fig. 2. The Cd–S bond lengths range from 2.513 to 2.971 Å. The short Cd-S bond distances (2.513-2.515 Å) lie in the range consistent to Cd-S bond distances in pentacoordinate complexes (range 2.511-2.518A) [41], shorter than values reported for four-coordinate complexes (2.5274 Å) and for six-coordinate complexes (Cd–S range 2.558–2.810Å), thus supporting the involvement of Cd in electron delocalization [41,42]. The longer Cd–S bond lengths involving the μ_3 -S are longer than those observed for six-coordinate complexes. The *bis*(tetrahydroquinolinedithiocarbamato)cadmium(II)complex (2) did not give the crystals of good enough quality for X-ray single structure elucidation.

3.2. Optical properties of CdS thin films

The room temperature UV–Vis absorption spectra of the CdS samples (Fig. 3) in the wavelength range of 320–800 nm, using glass substrate as a reference, were recorded to calculate the energy band gap (Eg) from the Tauc plot (Inset Fig. 3). The blue shift in absorption edge is clearly observed from the UV–Vis absorption spectra, when CdS thin films were deposited using complex (1). The UV–Vis absorption results indicate that, with increasing the annealing temperature from 350 to 450 °C, band gap changes one insignificant. The band gap energy of the films was estimated to be 2.38 ± 0.04 eV from the Tauc plot [43]. These observations are similar to those of CdS thin films deposited when complex (2) was used as single source precursor, however the

Cd(1)-S(2)	2.513 (2)	S(2)-Cd(1)-S(3)	130.86 (9)	S(7)-Cd(2)-S(5)	135.70 (9)
Cd(1)-S(3)	2.514 (2)	S(2)-Cd(1)-S(1) #1	104.79 (8)	S(7)-Cd(2)-S(8) #2	102.53 (8)
Cd(1)-S(1) #1	2.576 (2)	S(3)-Cd(1)-S(1) #1	121.58 (8)	S(5)-Cd(2)-S(8) #2	119.90 (8)
Cd(1)-S(4)	2.640 (2)	S(2)-Cd(1)-S(4)	112.54 (8)	S(7)-Cd(2)-S(6)	110.91 (8)
Cd(1)-S(1)	2.971 (2)	S(3)-Cd(1)-S(4)	70.60 (7)	S(5)-Cd(2)-S(6)	70.00(7)
Cd(2)-S(7)	2.514 (2)	S(1) #1-Cd(1)-S(4)	106.96 (7)	S(8) #2-Cd(2)-S(6)	107.20(7)
Cd(2)-S(5)	2.515 (2)	S(2)-Cd(1)-S(1)	65.70 (7)	S(7)-Cd(2)-S(8)	66.31 (7)
Cd(2)-S(8) #2	2.568 (2)	S(3)-Cd(1)-S(1)	97.91 (7)	S(5)-Cd(2)-S(8)	97.20(7)
Cd(2)-S(6)	2.677 (2)	S(1) #1-Cd(1)-S(1)	88.86 (7)	S(8) #2-Cd(2)-S(8)	93.35 (6)
Cd(2)-S(8)	2.917 (2)	S(4)-Cd(1)-S(1)	163.67 (7)	S(6)-Cd(2)-S(8)	159.19 (7)



Fig. 3. UV–Vis absorption spectra of CdS films deposited on glass substrate using complex (1) at (i) 350 °C, (ii) 400 °C and (iii) 450 °C (Inset: Tauc plot showing the estimated optical band gap of 2.38 ± 0.04 eV).



Fig. 4. Photoluminescence emission spectra of CdS thin films deposited at (i) 350 °C, (ii) 400 °C and (iii) 450 °C (λ_{exc} = 380 nm).



Fig. 5. Raman spectra of CdS thin films deposited by using complexes (1).



Fig. 6. Raman spectra of CdS thin films deposited by using complexes (2).



Fig. 7. Powder X-ray diffractograms of CdS films deposited on glass substrate using complex (1) at (a) 350 °C, (b) 400 °C and (c) 450 °C.



Fig. 8. Powder X-ray diffractograms of CdS films deposited using complex (2).

absorption peaks were not as distinct as those from complex (1) (ESI 1). The photoluminescence (PL) properties of the CdS thin films from complex (1) were also investigated by exciting the films at 380 nm excitation wavelength. A blue emission peak at 483 nm with FHWM of 9 nm is observed (Fig. 4). The broad red emission observed between 520 and 545 nm is due to electron-hole traps (surface defect emission from sulfur vacancies) [44]. It could also be related to microstructure imperfection and lattice defects of the CdS thin films [45], all leading to the red emission.

The Raman spectra of CdS thin films with 514.5 nm excitation wavelengths are shown in Figs. 5 and 6. The typical peaks of the longitudinal optical (LO) modes of CdS are evident from the Raman spectra. The fundamental frequencies at 297.5 and 599 cm⁻¹ correspond to the 1LO and 2LO of the bulk hexagonal CdS system [46,47], while the deposited CdS thin films have 1LO

and 2LO at 299 and 603 cm⁻¹ respectively. The shift in peak position of CdS thin films towards lower wavelength side was noted. Recently, it has been reported that phonon confinement, strain, defects and broadening associated with the size distribution were important factors which affect the Raman spectra [48]. Due to the phonon confinement and strain effect, we observed the shift in 1LO and 2LO peak positions of CdS nanoparticles with respect to the bulk CdS.

3.3. Physical properties of CdS thin films

The powder X-ray diffraction (p-XRD) patterns of the CdS thin films deposited at the three different temperatures are presented in Fig. 7 when complex (1) was used as a precursor. The three dominant peaks in diffraction patterns from films grown at 350, 400 and 450 °C can be assigned to the CdS (100), (002), (101) reflections of pure hexagonal phase and the values are matched to those in the ICDD values (card # 01-077-2306). The particle size were calculated using Scherrer equation reported elsewhere [49] and were found to be 57.37 nm (350 °C), 63.57 nm (400 °C) and 72.97 nm (450 °C) from the most prominent peak (101), relatively closer to the size determined by SEM. A similar diffraction pattern was observed when complex (2) was used, where the hexagonal phase of CdS was dominant (Fig. 8). Furthermore, the high intensity of (002) peak in p-XRD pattern of CdS thin films indicated that the particles were preferably elongated along the c-axis when complex (2) was used while complex (1) preferred the (101) plane.

Fig. 9 illustrates the scanning electron microscopy (SEM) micrographs of the surfaces of the CdS films deposited using complex (1) at different substrate temperatures, to achieve better uniformity. From the images, it can be seen that the coverage area was approximately 100% at the substrate temperature of 450 °C, while at lower temperature (350 and 400 °C) the coverage of the deposited films varied from 80–90%. Increasing the deposition temperature resulted in an increase in nucleation and deposition rates. The sizes of the thin films were in the ranges of 55–75 nm and 90–110 nm for CdS deposited at 350 and 450 °C temperatures, respectively.



Fig. 9. SEM images of CdS films deposited on glass substrate using complex (1) at deposition temperatures (a) 350 °C, (b) 400 °C and (c) 450 °C and (d) cross section (thickness) of the CdS films obtained at 450 °C.



Fig. 10. SEM images of CdS films deposited on glass substrate by AACVD using complex (2) at deposition temperatures (a) 350 °C, (b) 400 °C and (c) 450 °C and (d) EDX.



Fig. 11. 3D AFM height profiles of CdS thin films at (a) 350 °C and (b) 450 °C using complex (1) single source precursor.

The thickness of the sample obtained at 450 $^{\circ}$ C was estimated and found to be *ca*. 615 nm (Fig. 9d).

The SEM images of the cadmium sulfide (CdS) thin films deposited using complex (**2**) are showed in Fig. 10. There was a remarkable difference in grain sizes and their uniformity as the temperature was varied from 350 to 450 °C. The films deposited at 450 °C show smaller spherical particle aggregates (*ca.* 100 nm), while at 350 and 400 °C roughly cubic to spherical particles with uniform and regular patterns were observed. The particle sizes were larger in the 160–220 nm range. The EDX measurements (Fig. 10d) showed that the average percentage ratio of Cd:S is 1 for both cases.

AFM analysis from the films deposited using precursor (1) at different temperatures is shown in Fig. 11 and ESI 2. The film deposited at 350 °C consists of continuous film, composed of columnar and uniform nanosized grains, while the films deposited at 450 °C are slightly uniform, spherical crystallites with the typical root-mean-square roughness (Rq) of 17.65 and 23.36 nm at deposition temperatures 300 and 450 °C, respectively. The increase in surface roughness with increasing deposition temperature is

associated with an increase in grain size. Similarly well defined and densely packed isolated nanocrystallites were observed from films deposited at 350 °C when complex (**2**) was used (ESI 3.), while larger relatively non uniform crystalline grains were obtained at 450 °C with root-mean-square roughness (Rq) of 29.86 nm and 38.70 nm at deposition temperature 300 °C and 450 °C, respectively.

4. Conclusion

Piperidine and tetrahydroquinoline cadmium dithiocarbamato complexes have been synthesized and the single crystal X-ray structure of $[Cd(pip-dtc)_2]$ elucidated. Deposition of thin films by AACVD at various temperatures showed that the growth of CdS was influenced by deposition temperature. The morphologies of CdS films obtained showed that the thin films become increasingly dense with increase in temperature. The UV–Vis spectra of the films showed blue shift in absorption edge compared to bulk CdS. The fundamental frequency for CdS particles at 297.5 (1LO) and the first overtone at 599 cm⁻¹ (2LO) are observed from the Raman spectrum. The XRD, SEM/EDX and AFM analyses confirm the formation of hexagonal CdS thin films, with well-defined morphologies and precise elemental ratios. We plan to extend the use of these precursors for the deposition of others metal sulfides such as PbS. The synthetic parameters would also be varied in order to optimize the optical properties while controlling modifications of the crystal structure and morphology for potential applications.

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Appendix A. Supplementary material

CCDC 1008839 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac. uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10. 1016/j.ica.2015.05.024.

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