Multifunctional cadmium single source precursor for the selective deposition of CdO or CdS by a solution route†

Graziella Malandrino,*[a] Sebastiana T. Finocchiaro,[a] Patrizia Rossi,[b] Paolo Dapporto[b] and Ignazio L. Fragalà[a]

Received (in Cambridge, UK) 7th July 2005, Accepted 21st September 2005
First published as an Advance Article on the web 19th October 2005
DOI: 10.1039/b509623e

We report on the interesting properties of a novel single precursor, Cd(tta)$_2$·tmeda (Htta = 2-thenoyl-trifluoroacetone, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), ideally suited for the selective and reproducible fabrication of pure quality films of CdS or CdO through a simple solution process.

Cadmium-containing films have attracted continuously growing attention due to commercial applications in various strategic fields. In particular, cadmium sulfide (CdS)[1] thin films are used as a wide band-gap (2.42 eV) window layer in photovoltaic solar cells, providing one half of the p–n junction. Cadmium oxide (CdO)[2] is a transparent conductive oxide (TCO) material, and due to its high conductivity, high transmission and low band-gap, represents one of the most promising and appealing candidates for optoelectronic devices such as light emitting diodes, solar cells, flat panel displays, photovoltaics and anti-reflection coatings. Cadmium fluoride (CdF_2)[3] based thin films, doped and properly annealed, are important materials for optics and optoelectronics as light emitters and lasers due to their well pronounced semiconducting properties. Several techniques have been used to produce Cd-containing materials in thin film form, such as molecular beam epitaxy,[4,5] pulsed laser deposition,[6] MOCVD,[7–10] and chemical bath deposition.[11] Solution routes are very appealing in view of their ease, low cost and quick industrial scale-up. Nevertheless, cadmium alkyls, in some cases used as precursors,[12] are well known for being highly toxic and hazardous sources, not only because of their heavy metal content, but also because of their high volatility and pyrophoricity that requires cautious manipulation and precautions. In addition, the synthesis of CdS is even more complex since it also requires a sulfide source, usually thioacetamide or thiourea. All these issues fuel the stringent demand for the development of novel versatile and "safer" single source precursors.

In this communication, we report on the synthesis and characterisation of a novel multipurpose cadmium single source precursor for the deposition of Cd-containing films through solution processes. Thus, the novel Cd(tta)$_2$·tmeda (Htta = 2-thenoyl-trifluoroacetone, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) adduct (**1**) has been synthesized and both reproducibly and selectively applied to the preparation of nanostructured CdS and CdO films by an accurate tuning of processing parameters. The synthesis has been successfully attempted through a one pot reaction without any harmful handling of noxious and hazardous reagents. In particular, the vigorous shaking of a water solution containing $Cd(CH_3COO)_2$ and of a CH_2Cl_2 solution containing the Htta and tmeda (2 : 1) ligands causes the formation of the required precursor. The adduct is then extracted into the CH_2Cl_2 solution and isolated as yellow crystalline powder by evaporation of the solvent.‡

It has been characterised by ^{1}H, ^{13}C NMR, mass spectrometry, IR spectroscopy, elemental analysis and single crystal X-ray diffraction analysis. The single crystal X-ray diffraction§ showed (Fig. 1) that in the Cd(tta)$_2$·tmeda complex (**1**), the Cd^{2+} cation is hexacoordinated by the four oxygen atoms of the two tta anions and by the two nitrogen atoms of one tmeda ancillary ligand. The resulting coordination geometry is a distorted octahedron. Cd–O and Cd–N distances are in agreement with those found (Cambridge Structural Database (CSD) v. 5.25)[13] for cadmium acetylacetonate derivatives or complexes having a tmeda molecule as ligand. It is worth noting that the distances Cd1–O1 and Cd1–O2 are significantly longer than the Cd1–O3 and Cd1–O4 ones. The planes defined by the tta ligands, namely the planes defined by the atoms (O1, C1, C2, C3, O2) and (O3, C6, C7, C8, O4) form an angle of 59.7(3)°. The plane (N1, C19, C20,

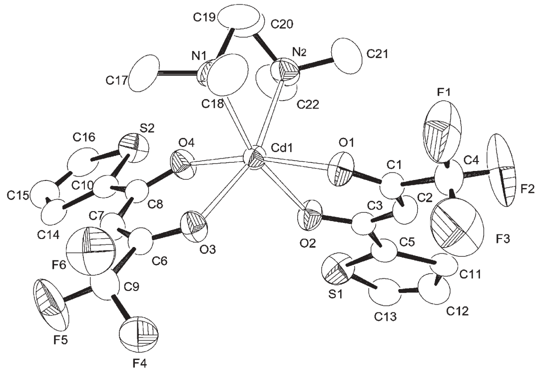

Fig. 1 ORTEP drawing of the mononuclear complex Cd(tta)$_2$·tmeda (**1**). Selected distances (Å) and angles (°): Cd1–O1 2.284(3), Cd1–O2 2.281(3), Cd(1)–O(3) 2.255(3), Cd(1)–O(4) 2.258(3), Cd(1)–N(1) 2.393(4), Cd(1)–N(2) 2.401(4), O(1)–Cd(1)–O(2) 79.6(1), O(1)–Cd(1)–O(3) 97.2(1), O(1)–Cd(1)–O(4) 167.8(1), O(1)–Cd(1)–N(1) 94.3(1), O(1)–Cd(1)–N(2) 98.0(1), O(2)–Cd(1)–O(3) 103.6(1), O(2)–Cd(1)–O(4) 89.0(1), O(2)–Cd(1)–N(1) 165.5(2), O(2)–Cd(1)–N(2) 90.4(2), O(3)–Cd(1)–O(4) 81.1(1), O(3)–Cd(1)–N(1) 90.2(2), O(3)–Cd(1)–N(2) 160.9(2), O(4)–Cd(1)–N(1) 97.9(1), O(4)–Cd(1)–N(2) 86.4(1), N(1)–Cd(1)–N(2) 77.4(2).

---

[a] *Dipartimento di Scienze Chimiche, Università di Catania and INSTM, UdR Catania, V.le Andrea Doria 6, I-95125, Catania, Italy. E-mail: gmalandrino@dipchi.unict.it*
[b] *Dipartimento di Energetica "S. Stecco", Università di Firenze, Via Santa Marta 3, I-50139, Firenze, Italy*

† Electronic supplementary information (ESI) available: Characterization details of the complex and EDX spectra of Cd-containing films. See DOI: 10.1039/b509623e

N2), containing the tmeda ligand, is almost orthogonal in respect to the two previously mentioned mean planes [87.2(3) and 88.0(3)° for (O1, C1, C2, C3, O2) and (O3, C6, C7, C8, O4), respectively].

The C–C distances found in the two tta anions, as well as the values retrieved for the dihedral angles O2–C3–C5–C11 and O4–C8–C10–C14 (−179.8(4) and 178.5(5)°, respectively), point to an extended conjugation in the ligand anions involving the thiophene moieties. As expected (both the nitrogen atoms coordinate the metal cation), the tmeda molecule shows a gauche conformation (N1–C19–C20–N2 = −60.7(8)°). The rather high thermal factors of some atoms of the thiophene rings could be indicative of a degree of disorder which cannot be modelled. Finally, no intermolecular contacts are present in the crystal lattice. A similar complex, $Co(tta)_2{\cdot}tmeda$,[14] was retrieved from the CSD. The main difference between the Cd(II) and Co(II) $M(tta)_2{\cdot}tmeda$ complexes is due to the disposition of the thiophene rings. In fact, if we consider the plane defined by the cadmium cation and the two CH atoms of the tta anions, the two thiophene rings lie on the same side with respect to it, giving rise to a *cis* conformation. On the other hand, in the cobalt complex they lie on opposite sides, giving rise to a *trans* conformation.

The thermal behaviour of the adduct, investigated through atmospheric pressure thermogravimetric (TG) analyses carried out under N_2, indicates a single step weight loss in the 200–360 °C temperature range, as confirmed by the first TG derivative (DTG), with a 22.40% residue remaining (Fig. 2). The chemical nature of this residue cannot be easily attributed since three different phases can form upon the precursor's thermal decomposition: cadmium fluoride, cadmium sulfide or cadmium oxide. In addition, even though the theoretical residue value for CdF_2 (22.41%) could point to a CdF_2 residue, the other phases, CdS and CdO, cannot be unequivocally ruled out considering their similar theoretical residue values of 21.53% and 19.14%, respectively. Nevertheless, the energy dispersive X-ray analyses (EDX) of the residue unequivocally points to it being CdF_2.

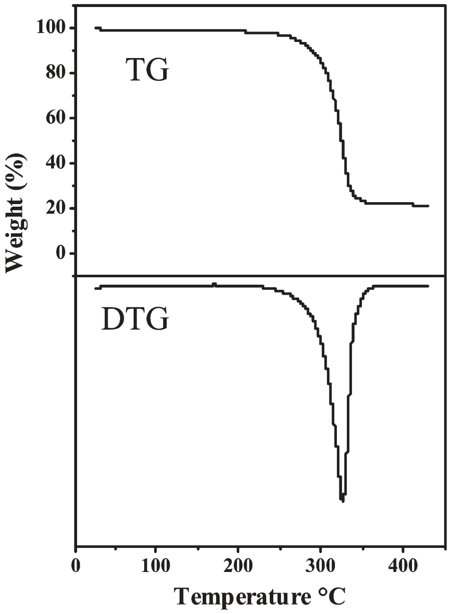

Fig. 2 TG–DTG curve of $Cd(tta)_2{\cdot}tmeda$ (**1**).

The $Cd(tta)_2{\cdot}tmeda$ precursor, due to its clean, single step thermal decomposition and solubility in organic solvents such as dichloromethane, has been successfully applied to the deposition of Cd-containing films on glass or Si substrates using solution processes through spin coating in air and post-thermal treatment. No decomposition of the complex occurs at this stage. A 0.3 M solution of $Cd(tta)_2{\cdot}tmeda$ precursor in CH_2Cl_2 has been used for all the deposition experiments.

Thermal treatments have been carried out at atmospheric pressure in the 300–700 °C temperature range under a controlled atmosphere. The reaction atmosphere has been tuned using nitrogen and oxygen to investigate the precursor decomposition under different processing environments. It is quite interesting that different films, namely CdO, CdS and CdF_2, have been reproducibly and selectively, in the case of CdO and CdS phases, obtained, depending on the processing conditions used to pyrolyse the adduct.

The nature of the obtained films has been investigated by X-ray diffraction (XRD) analysis in a grazing incidence mode. The CdO phase has been observed right across the investigated temperature range (300–700 °C) when the thermal treatments have been carried out under O_2. The XRD pattern (Fig. 3a) of a sample heated in oxygen (100 sccm) at 600 °C shows three peaks 33.02, 38.35 and 55.30°, corresponding respectively to 111, 200 and 220 reflections of the CdO cubic lattice. The sample is polycrystalline and randomly oriented, as indicated by the relative intensities of the XRD reflections, which agree fairly well with those reported for a

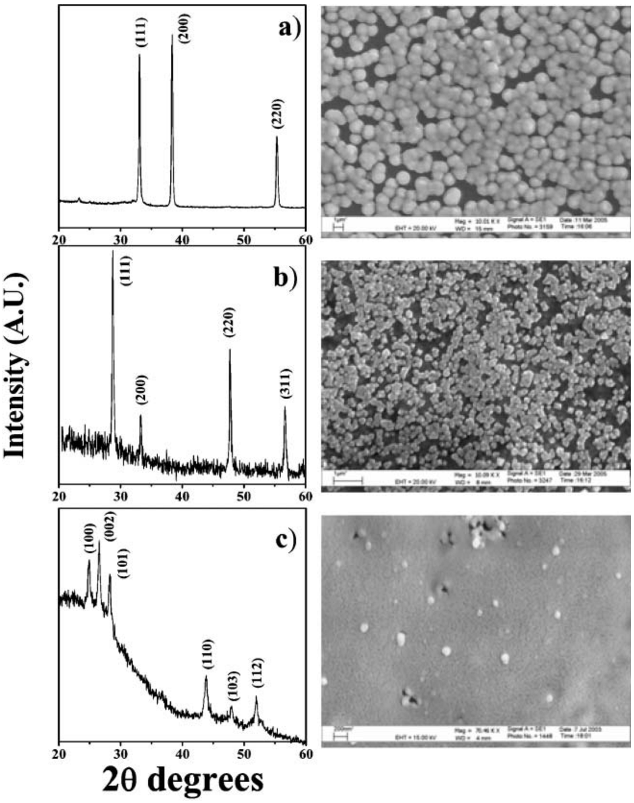

Fig. 3 XRD patterns and corresponding SEM images of films obtained under different processing conditions: (a) CdO obtained at 600 °C under O_2, (b) CdF_2 obtained at 350 °C under N_2 and (c) CdS obtained at 600 °C under N_2.

polycrystalline CdO powder (ICDD no. 05-0640; *Powder Diffraction File*, International Centre of Diffraction Data, Newton Square, PA).

Thermal treatments under nitrogen (100 sccm) result in two different phases, depending on the reaction temperature. In particular, the XRD pattern of films heated at 350–450 °C (Fig. 3b) show several peaks at 2θ = 28.75, 33.30, 47.75 and 56.70°, corresponding to the 111, 200, 220 and 311 reflections respectively of the CdF_2 cubic lattice, in accordance with the nature of the residue found in the TG analysis. Films are also polycrystalline and randomly oriented, in accordance with data reported in the ICDD database (ICDD no. 23-0864).

Thermal treatments under nitrogen at temperatures higher than 550 °C give rise to a different XRD pattern, with several peaks that point to the formation of a new Cd-containing phase, namely CdS. In fact, all the peaks (Fig. 3c) observed at 2θ = 24.85, 26.55, 28.20, 36.75, 43.85, 47.90, 51.90 and 52.80° can be associated with the reflections of the hexagonal CdS lattice (ICDD no. 41-1049). The presence of all the expected reflections also points to the polycrystalline nature of the CdS films. Actually, the low intensity of these peaks, together with the broad peak centered around 20°, indicate that the CdS films are of a poorly crystalline nature.

The change from CdF_2 to CdS is gradual, and at temperatures in the 450–550 °C range under N_2, both phases are present in the films.

The SEM images (Fig. 3) show completely different morphologies in accordance with the XRD data. Larger rounded grains and square shaped grains are observed for the CdO and CdF_2 films, respectively, while a nanostructured surface with grain dimensions less than 100 nm in diameter is observed for CdS films.

To better understand the decomposition mechanism under a N_2 atmosphere, the precursor decomposition process has been investigated through gas phase FT-IR (Fourier Transform-Infrared) analysis using nitrogen as the reaction gas. IR spectra show that precursor decomposition starts at 250 °C and is complete at 300 °C. This indicates that at the temperature of CdF_2 formation, the tta ligand is completely decomposed. This supposed decomposition mechanism does not give an immediate explanation of the CdS phase formation at higher temperatures since once the precursor has decomposed, no S should be available for further reaction unless a S residue remains in the film. The EDX analysis of CdF_2 films actually shows the presence of the S-Kα peak at 2.307 keV in addition to the F-Kα peak at 0.677 keV and the Cd-L peaks observed in the range 3.120–3.750 keV. The amount of S is about 15–20%.

Therefore, it is likely that at lower temperatures under N_2, the precursor decomposition yields the CdF_2 phase and some amorphous S and/or CdS that is not detectable using XRD. Upon increasing the temperature, the amorphous S reacts with CdF_2, yielding CdS and volatile species containing F. On the other hand, it is well known that CdS reacts with O_2 to yield CdO, the most stable of the two phases. Therefore, it is straightforward that CdO always forms independently of the processing temperature when reactions are carried out under O_2. The EDX data of CdO and CdS films show, in addition to the Cd peaks, the unique presence of O (Kα at 0.525 keV) and S (Kα at 2.307 keV), respectively. No peaks relative to other light elements have been detected, thus confirming for CdO and CdS their monophasic nature, assessed through XRD measurements, and the absence of any C contamination.

In summary, the novel adduct $Cd(tta)_2{\cdot}tmeda$ represents, to our knowledge, the first example of a multi-functional single source precursor which reproducibly and selectively yields CdO or CdS films, depending on the processing parameters. Its thermal properties point to its potential application as a single precursor for the synthesis of Cd-containing nanoparticles through a surfactant-based template approach,[15] and studies are currently in progress. In addition, the easy synthetic procedure and simple deposition process make the new cadmium adduct an attractive candidate, not only for laboratory solution processes, but also for large scale applications.

The authors thank the MIUR for the financial support. Dr. G. G. Condorelli is acknowledged for FT-IR measurements. CRIST (Centro Interdipartimentale di Cristallografia Strutturale), University of Florence is also gratefully acknowledged.

Notes and references

‡ Elemental analysis of **1**. Calc. for $C_{22}H_{24}CdF_6N_2O_4S_2$: C, 39.38; H, 3.61; N, 4.18; S, 9.56. Found: C, 39.15; H, 3.76; N, 4.25; S, 9.35%.

§ Crystallographic data for **1**: $C_{22}H_{24}CdF_6N_2O_4S_2$, M = 670.95, monoclinic, space group $P2_1/c$, a = 17.582(5), b = 8.335(2), c = 18.610(7) Å, β = 92.61(3)°, V = 2724.4(14) Å^3, T = 293 K, Z = 4, D_c = 1.636 g cm^{-3}, μ (Mo-Kα) = 1.026 mm^{-1}, 4804 reflections collected, 4640 unique (R_{int} = 0.0327). F^2 refinement, $R1$ = 0.0510 ($I > 2\sigma(I)$), $wR2$ = 0.1467 (all data). CCDC 277427. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b509623e

1 L. Weinhardt, Th. Gleim, O. Fuchs, C. Heske, E. Umbach, M. Bar, H.-J. Muffler, Ch.-H. Fischer, M. C. Lux-Steiner, Y. Zubavichus, T. P. Niesen and F. Karg, *Appl. Phys. Lett.*, 2003, **82**, 571–573.

2 *MRS Bull.* 2000, **25**, (8), ed. D. S. Ginley and C. Bright. Special issue on transparent conducting oxides.

3 S. A. Kazanskii, D. S. Rumyantsev and A. I. Ryskin, *Phys. Rev. B*, 2002, **65**, 165214–165225.

4 T. Kobori and K. Tsutsui, *Appl. Phys. Lett.*, 2001, **78**, 1406–1408.

5 A. B. M. A. Ashrafi, H. Kumano, I. Suemune, Y. W. Ok and T. Y. Seong, *J. Cryst. Growth*, 2002, **237–239**, 518–522.

6 M. Yan, M. Lane, C. R. Kannewurf and R. P. H. Chang, *Appl. Phys. Lett.*, 2001, **78**, 2342–2344.

7 A. W. Metz, J. R. Ireland, J. G. Zheng, R. P. S. M. Lobo, Y. Yang, J. Ni, C. L. Stern, V. P. Dravid, N. Bontemps, C. R. Kannewurf, K. R. Poeppelmeier and T. J. Marks, *J. Am. Chem. Soc.*, 2004, **126**, 8477–8492.

8 J. R. Babcock, A. W. Metz, N. L. Edleman, M. V. Metz, M. A. Lane, C. R. Kannewurf and T. J. Marks, *Chem. Vap. Deposition*, 2001, **7**, 239–241.

9 A. Gulino, P. Dapporto, P. Rossi and I. L. Fragalà, *Chem. Mater.*, 2002, **14**, 1441–1444.

10 D. Barreca, A. Gasperotto, C. Maragno and E. Tondello, *J. Electrochem. Soc.*, 2004, **151**, G428–G435.

11 Y. K. Hwang, S. Y. Woo, J. H. Lee, D. Y. Jung and Y. U. Kwon, *Chem. Mater.*, 2000, **12**, 2059–2063.

12 M. W. Jones, L. J. Rigby and D. Ryan, *Nature*, 1966, **212**, 5058–5060.

13 F. H. Allen, *Acta Crystallogr., Sect. B*, 2002, **B58**, 380–388.

14 L. C. Tzavellas, C. Tsiamis, C. A. Kavounis and C. J. Cardin, *Inorg. Chim. Acta*, 1997, **262**, 53–59.

15 M.-P. Pileni, *Nat. Mater.*, 2003, **2**, 145–150.