Synthesis and Characterization of Thin Films of Cadmium Oxide

Antonino Gulino,*[,†] Francesco Castelli,[†] Paolo Dapporto,[‡] Patrizia Rossi,[‡] and Ignazio Fragalà*[,†]

Dipartimento di Scienze Chimiche, Università di Catania, Via le Andrea Doria 6,
95125 Catania, Italy, and Dipartimento di Energetica, Università di Firenze,
Via Santa Marta 3, 50139 Firenze, Italy

Received July 17, 2001. Revised Manuscript Received November 13, 2001

The $Cd(C_5F_6HO_2)_2{\cdot}2H_2O$ complex was investigated by X-ray crystallography, mass spectroscopy, ^1H NMR spectroscopy, TG−DTG thermal measurements, and infrared transmittance spectroscopy. X-ray single-crystal data show that the cadmium ion is chelated by the oxygens of the hfa anion ligand and bound to the oxygens of two cis-disposed water molecules. Deposition experiments, in a low-pressure horizontal hot-wall reactor, on optically transparent SiO_2 substrates using the above complex result in CdO films. XRD measurements provide evidence that these complexes consist of highly oriented cubic crystals. UV−vis spectra show that the transmittance of as-deposited films in the visible region is about 70%. The surface structure of the CdO films was investigated by XPS. Resistivity measurements of the CdO films suggest TCO properties.

Introduction

CdO adopts the centrosymmetric rocksalt structure (face-centered-cubic system). It exhibits interesting electronic and optical properties that have been thoroughly studied from a scientific perspective and for technological applications.[1] In fact, it shows a narrow direct gap of 2.27 eV between the O 2p-based valence band and the Cd 5s-based conduction band minimum.[2] Many of the properties of CdO originate from its nonstoichiometric composition, which, in turn, strongly depends on the synthetic procedure adopted.[2,3]

Many techniques have been employed for the preparation of thin films of CdO,[1,3−10] including one example[8] of metal organic chemical vapor deposition (MOCVD), a technique that might involve metal β-diketonates as precursors. In this context, only $Cd(CH_3)_2$ has been employed as a precursor thus far.[8] In 1966, the synthesis, elemental analysis, melting point (129−131 °C), sublimation temperature interval (125−130 °C), and IR characterization[11a] were reported for the cadmium hexafluoroacetylacetonate dihydrate complex (hexafluoroacetylacetonate = 1,1,1,5,5,5,-hexafluoro-2,4-pentanedionate), $Cd(C_5F_6HO_2)_2{\cdot}2H_2O$, hereafter denoted $Cd(hfa)_2{\cdot}2H_2O$.[11a] Therefore, it should be considered to represent a well-suited volatile cadmium precursor for the MOCVD deposition of CdO films.

From this perspective, there is sufficient motivation to further characterize the above compound and perform deposition experiments of CdO.

Experimental Details

Cadmium-containing compounds are exceedingly toxic; therefore, care was taken during all sample manipulations.

The $Cd(hfa)_2{\cdot}2H_2O$ was synthesized as already reported.[11a] Good single crystals for X-ray analysis were obtained from a 1:10 diethyl ether/carbon tetrachloride $[(C_2H_5)_2O/CCl_4]$ solution.

The FT-IR transmittance spectrum of the complex in Nujol mull is identical to that previously reported.[11a] Nevertheless, at variance with the literature datum,[11a] a sharp melting point in the 129−131 °C temperature range was not observed. By contrast, many changes were observed up to 265 °C, the temperature at which the liquid phase becomes predominant.

The elemental analyses, performed using a Carlo Erba EA 1108 elemental analyzer, gave results close to the theoretical values.

Fast atom bombardment mass spectra (FAB-MS) were obtained using a Kratos MS 50 spectrometer with 3-nitrobenzyl alcohol ($O_2NC_6H_4CH_2OH$ = 3NBA) as the matrix and cesium as the bombarding atoms (35 kV). FAB-MS (3NBA) *m/z* fragments, M = $Cd(hfa)_2{\cdot}2H_2O$: 474 $(M - 2H_2O - hfa + 3NBA)^+$, 628 $(MH - 2H_2O - hfa + 2(3NBA))^+$.

---

* Authors to whom correspondence should be addresses. E-mail: lfragala@dipchi.unict.it and agulino@dipchi.unict.it.

[†] Università di Catania.

[‡] Università di Firenze.

(1) Ginley, D. S., Bright, C., Eds. *MRS Bull.* **2000**, 25.

(2) Dou, Y.; Egdell, R. G.; Walker, T.; Law, D. S. L.; Beamson, G. *Surf. Sci.* **1998**, *398*, 241.

(3) Gulino, A.; Fragala, I. *J. Mater. Chem.* **1999**, *9*, 2837.

(4) Ferro, R.; Rodrìguez, J. A. *Thin Solid Films* **1999**, *347*, 295.

(5) Xiaochun, W.; Rongyao, W.; Bingsuo, Z.; Li, W.; Shaomei, L.; Jiren, X. *J. Mater. Res.* **1998**, *13*, 604.

(6) Gurumurugan K.; Mangalaraj, D.; Narayandass, Sa. K.; Nakanishi, Y.; Hatanaka, Y. *Appl. Surf. Sci.* **1997**, *113/114*, 422.

(7) Meinhold, R. H. *J. Phys. Chem. Solids* **1987**, *48*, 927.

(8) (a) Coutts, T. J.; Young, D. L.; Li, X.; Mulligan, W. P.; Wu, X. *J. Vac. Sci. Technol. A: Vac. Surf. Films* **2000**, *18*, 2646. (b) Recently, we had a private communication from Prof. T. J. Marks, Northwestern University, Evanston, IL, 2001, concerning the MOCVD of CdO from a novel $Cd(hfa)_2$(TMEDA) precursor.

(9) Alétru, C.; Greaves, G. N.; Sankar, G. *J. Phys. Chem. B* **1999**, *103*, 4147.

(10) Dragon R.; Wacke, S.; Gòrecki, T. *J. Appl. Electrochem.* **1995**, *25*, 699.

(11) (a) Chattoraj, S. c.; Cupka, A. G.; Sievers, R. E. *J. Inorg. Nucl. Chem.* **1966**, *28*, 1937. (b) Fernelius, W. C.; Bryant, B. E. *Inorg. Synth.* **1957**, *5*, 107.

10.1021/cm011175q CCC: $22.00

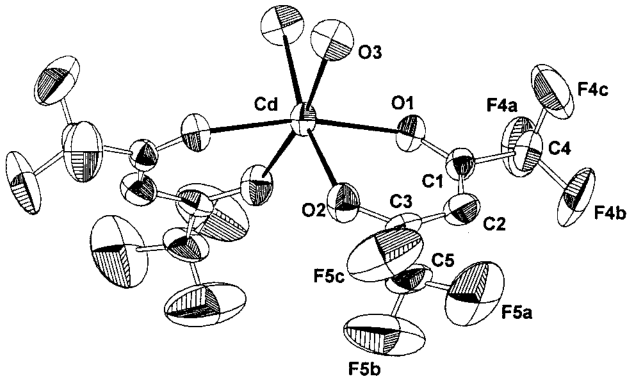


Figure 1. ORTEP drawing of $Cd(hfa)_2{\cdot}2H_2O$.

^1H NMR spectra ($CDCl_3$) were recorded using a Varian 500-MHz spectrometer and gave the following signals: δ 6.03 (s, 2H), 1.264 (s 4H).

The thermal behavior was investigated by thermal and differential gravimetric analysis (TGA and DTG, respectively) under 1 atm of prepurified nitrogen, using a 1 °C/min heating rate. A Mettler TA 4000 system equipped with a TG 50 thermobalance and a TC 11 processor was used.[12] Samples (5−6 g) were accurately weighed and examined in the 10−400 °C range.

Infrared transmittance spectra were recorded using a Jasco FT/IR-430 spectrometer. The instrumental resolution was 2 cm^{-1}.

For the crystal structure determination, cell parameters and intensity data for $Cd(hfa)_2{\cdot}2H_2O$ were obtained on a Siemens P4 diffractometer using graphite monocromatized Cu Kα radiation ($\lambda = 1.541\ 84$ Å). Cell parameters were determined by least-squares fitting of 25 centered reflections. Intensity data were corrected for Lorentz and polarization effects, and an absorption correction was applied once the structure was solved by using the Walker and Stuart method.[13] The structure was solved using the SIR-97[14] program and subsequently refined by the full-matrix least squares program SHELX-97.[15] $Cd(hfa)_2{\cdot}2H_2O$ crystallizes in the monoclinic space group $C2/c$, $Z = 4$, with cell dimensions $a = 22.084(3)$, $b = 8.256(1)$, $c = 9.959(2)$ Å, and $\beta = 96.27(1)°$. The structure was refined to a final R factor of 0.0824 based on 1415 independent reflections (133 refined parameters). A view of the complex is given in Figure 1. The hydrogen atom of the ligand hfa was introduced in the calculated position and its coordinates were refined in agreement with those of the linked atom. The hydrogen atoms of the water molecules were not found in difference syntheses. All of the nonhydrogen atoms were refined anisotropically. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from ref 16. Geometrical calculations were performed by PARST97.[17] The molecular plot was produced by the ORTEP program.[18] Crystal and structure refinement data are reported in Table 1.

X-ray diffraction (XRD) data for the deposited films were recorded on a Bruker D-5005 diffractometer operating in a $\theta-\theta$ geometry (Cu Kα radiation at 30 mA and 40 kV).

XPS measurements were made with a PHI 5600 Multi Technique System (base pressure in the main chamber of 3×10^{-10} Torr). Resolution, correction for satellite contributions, and background removal have been described elsewhere.[19]

Table 1. Crystal Data and Structure Refinement for $Cd(hfa)_2{\cdot}2H_2O$

empirical formula	$C_{10}H_6CdF_{12}O_6$
formula weight	562.55
λ (Å)	1.5418
crystal system, space group	monoclinic, $C2/c$
unit cell dimensions (Å, °)	$a = 22.084(3)$
	$b = 8.256(1)$, $\beta = 96.27(1)$
	$c = 9.959(2)$
volume (Å^3)	1804.9(5)
Z	4
d (calc) (g/cm^3)	2.070
μ (mm^{-1})	11.126
F(000)	1080
crystal size (mm)	0.4 × 0.45 × 0.5
2θ range for data collection (°)	8−130
reflections collected/unique	1869/1415
data/restraints/parameters	1415/0/133
final R indices [$I > 2\sigma(I)$]	R1 = 0.0824, wR2 = 0.2222
R indices (all data)	R1 = 0.0824, wR2 = 0.2228
largest diff. peak and hole (e Å^{-3})	1.994 and −2.378

Table 2. Selected Bond Lengths (Å) and Angles (°) for $Cd(hfa)_2{\cdot}2H_2O^a$

Cd(1)−O(1)	2.233(6)
Cd(1)−O(3)	2.253(6)
Cd(1)−O(2)	2.293(6)
O(1)′−Cd(1)−O(1)	166.6(3)
O(1)−Cd(1)−O(3)′	93.4(2)
O(1)−Cd(1)−O(3)	96.5(2)
O(3)′−Cd(1)−O(3)	84.2(3)
O(1)′−Cd(1)−O(2)	91.2(2)
O(1)−Cd(1)−O(2)	80.2(2)
O(3)′−Cd(1)−O(2)	168.9(2)
O(3)−Cd(1)−O(2)	87.5(2)
O(2)−Cd(1)−O(2)′	101.6(3)

[a] Prime (′) indicates $-x, y, 1.5 - z$.

Table 3. Intermolecular Interactions (Å)

O1···O3[a]	2.869(8)
O2···O3[b]	2.911(9)

[a] $x, 1 - y, z + 0.5$. [b] $-x, 1 - y, 1 - z$.

MOCVD experiments were performed using a horizontal hot-wall reactor[12] under reduced pressure with the present, as-synthesized $Cd(hfa)_2{\cdot}2H_2O$. Optically transparent SiO_2 was used as the substrate after being cleaned in an ultrasonic bath with isopropyl alcohol. Pure Ar and O_2 saturated with H_2O vapor were used as the carrier and reaction gases, respectively. The total pressure, kept in the 2−5 Torr range, was measured using a MKS Baratron 122AAX system. Flow rates were controlled to within ±2 sccm using MKS flow controllers and a MKS 147 multigas controller.

Results and Discussion

The asymmetric unit of $Cd(hfa)_2{\cdot}2H_2O$ contains one-half of the cadmium complex. A 2-fold symmetry axis, passing through the metal cation, relates the two halves. The cadmium ion is bound to the oxygen atoms of the hfa fragments and to the oxygens of two water molecules. The six donors are located at the vertexes of a distorted octahedron (see Table 2). The oxygen atoms of the two H_2O molecules are cis-disposed, with the O3−Cd1−O3′ angle being 84.2(3)°. Table 3 shows the oxygen intermolecular interactions. As expected on the basis of the π resonance involving bonds C1−C2 and C2−C3, the C1−C2 and C2−C3 distances are shorter [1.42(1) and 1.39(1) Å, respectively] than the C1−C4 and C3−

---

(12) Gulino, A.; Castelli, F.; Dapporto, P.; Rossi, P.; Fragalà, I. *Chem. Mater.* **2000**, *2*, 548.

(13) Walker, N.; Stuart D. D. *Acta Crystallogr. A* **1983**, *39*, 158.

(14) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(15) Sheldrick, G. M. *SHELXL-97*; University of Göttingen, Göttingen, Germany, 1997.

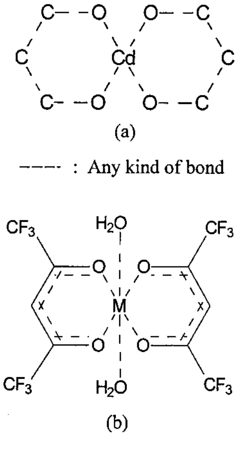
(16) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

(17) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

(18) Johnson, C. K. *ORTEP*; Report ORNL 3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

(19) Gulino, A.; La Delfa, S.; Fragalà, I.; Egdell, R. G. *Chem. Mater.* **1996**, *8*, 1287.

Scheme 1. Searched Fragment in the CSD



C5 distances [1.51(1) and 1.525(9) Å, respectively]. As already found for hfa ligands in complexes similar to $Cd(hfa)_2{\cdot}2H_2O$, the fluorine atoms show a rather large anisotropic temperature factor.[12]

An analysis of the solid-state structures collected in the Cambridge Structural Database[20] (CSD) gave the following results: (i) The $Cd{\cdots}O_{hfa}$ distances found in our compound (see Scheme 1a for the retrieved fragment) are in agreement with those found for Cd complexes having similar ligands[21] [for example, cadmium acetylacetonate[21a] and its 2,2′-bipyridine,1,10-phenanthroline and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine adducts[21b] and bis(1,3-bis-(2-hydroxyphenyl)-1,3-propanedione)bispyridinecadmium(II)[21e]], whose $Cd{\cdots}O$ distances are in the range 2.207−2.337 Å, with a mean value 2.270 Å. (ii) The $Cd{\cdots}O_{water}$ distance found for our compound falls in the range found for structures retrieved on CSD (2.188−2.841 Å, with a mean value of 2.236 Å), such as potassium tris(acetylacetonato)-cadmate(II) monohydrate.[21d] (iii) In a CSD search performed on analogous complexes (with two hfa ligands and two water molecules) having transition metals (see fragment b in Scheme 1) as cations, 10 complexes were retrieved, and among them, four have the two water molecules cis-disposed[22a−d] and can be considered isomorphous with $Cd(hfa)_2{\cdot}2H_2O$.

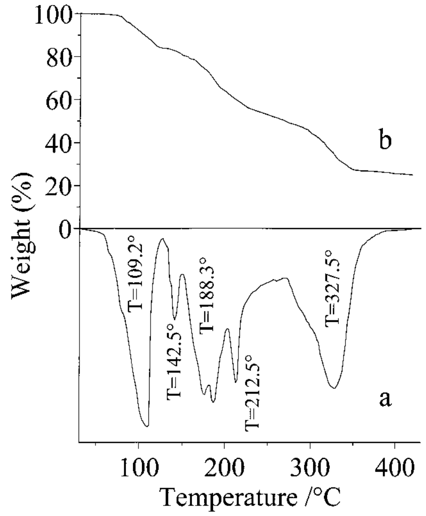


Figure 2. (a) DTG and (b) TG of $Cd(hfa)_2{\cdot}2H_2O$.

Table 4. DTG Analysis

peak	peak temperature (°C)	mass loss (%)
1	109.2	16.6
2	142.5	2.9
3	188.3	18.0
4	212.5	13.3
5	327.5	24.2

The crystals of this series of compounds contain only the $M(hfa)_2{\cdot}2H_2O$ (M = transition metal) complex, whereas the remaining six[12,22a,d,e−g] (which have the two water molecules trans-disposed) also contain other solvent or ligand molecules in the crystal structure, as in the case of $Zn(hfa)_2{\cdot}2H_2O$,[22a] $Co(hfa)_2{\cdot}4H_2O{\cdot}(tmp)$,[22d] and $Mn(hfa)_2{\cdot}2H_2O{\cdot}1.5(tmp)$[22d] (where tmp = tetramethylpyrazine). It is interesting to notice that, in the complexes with cis-disposed water molecules, the same kind of hydrogen-bonded chains have been found as the coordinated H_2O molecules are hydrogen-bonded with oxygen atoms of the neighboring hfa ligands. Every H_2O molecule forms H bonds interacting with two oxygen atoms of two different hfa ligands coordinated to the same metal cation.

The FAB-MS spectrum of $Cd(hfa)_2{\cdot}2H_2O$ does not show the molecular ion peak. The observed peaks always show the characteristic isotope pattern of Cd and are due to the losses of H_2O and of the hfa fragments. The most intense peak at 474 *m*/*z* (100%) corresponds to the $(M - 2H_2O - hfa + 3NBA)^+$ fragment. At higher mass, the most significant peak is at 628 $[MH - 2H_2O - hfa + 2(3NBA)]^+$.

The ^1H NMR spectrum of $Cd(hfa)_2{\cdot}2H_2O$ always shows a singlet at $\delta = 6.03$, integration of which accounts for two protons of the two hfa ring ligands.[12] Moreover, the resonance at $\delta = 1.264$ (four protons) is associated with the two coordinated H_2O molecules.[12]

TGA and DTG analyses of $Cd(hfa)_2{\cdot}2H_2O$ show rather complex behavior. At least five mass loss processes (Figure 2 and Table 4) are evident in the 40−400 °C temperature range. In this regard, it has been already reported that, by heating a similar cadmium complex, $NH_4Cd(hfa)_3{\cdot}H_2O$, in a vacuum, the sublimate $Cd(hfa)_2{\cdot}NH_3{\cdot}H_2O$ was obtained rather than the starting compound or $Cd(hfa)_2$ or its simple hydrate.[11] In addition, it has been recently demonstrated that the sublimation of the $Zn(hfa)_2{\cdot}2H_2O{\cdot}$polyether parent complex is accompanied by H_2O removal.[12] Nevertheless, water recoordination occurs as soon as the product is brought into contact with air.[12]

---

(20) Allen, F. H.; Kennard, O. Cambridge Structural Database. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1131.

(21) (a) Maslen, E. N.; Greaney, T. M.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 400. (b) Bustos, L.; Green, J. H.; Hencher, J. L.; Khan, M. A.; Tuck, D. G. *Can. J. Chem.* **1983**, *61*, 2141. (c) McSharry, W. O.; Cefola, M.; White, J. G. *Inorg. Chim. Acta* **1980**, *38*, 160. (d) Greaney, T. M.; Raston, C. L.; White, A. H.; Maslen, E. N. *J. Chem. Soc., Dalton Trans.* **1975**, 876. (e) Casabo, J.; Colomer, J.; Llobet, A.; Teixidor, F.; Molins, E.; Miravitlles, C. *Polyhedron* **1989**, *8*, 2743.

(22) (a) Adams, R. P.; Allen, H. C. Junior; Rychlewska, U.; Hodgson, D. J. *Inorg. Chim. Acta* **1986**, *119*, 67. (b) Romero, R. R.; Cervantes-Lee, F.; Porter, L. C. *Acta Crystallogr. C: Cryst. Struct. Commun.* **1992**, *48*, 993. (c) Troyanov, S. I.; Gorbenko, O. Yu.; Bosak, A. A. *Polyhedron* **1999**, *18*, 3505. (d) Adams, H.; Bailey, N. A.; Fenton, D. E.; Khalil, R. A. *Inorg. Chim. Acta* **1993**, *209*, 55. (e) Luneau, D.; Rey, P.; Laugier, J.; Belorizky, E.; Cogne, A. *Inorg. Chem.* **1992**, *31*, 3578. (f) Dickman, M. H. *Acta Crystallogr. C: Cryst. Struct. Commun.* **1997**, *53*, 402. (g) Burdukov, A. B.; Ovcharenko, V. I.; Sagdeev, R. Z.; Pervukhina, N. V.; Ikorskii, V. N.; Kirilyuk, I. A.; Grigor'ev, I. A. *Polyhedron* **1996**, *15*, 4211.

Table 5. MOCVD Conditions

substrate temperature	320−400 °C
total pressure	3−5 Torr
O_2 gas flow rate	100−400 sccm
Ar gas flow rate	70−100 sccm
source sublimation temperature	110−200 °C
deposition time	120 min

Therefore, the various mass losses observed during the thermal characterization have been compared against sublimation, potential decomposition, and oligomerization pathways, with due allowance being made for the surprisingly complicated result. In particular, we suppose that the first mass loss peak at 109.2 °C (Table 4) observed for the $Cd(hfa)_2{\cdot}2H_2O$ hydrogen-bonded chain system can be interpreted in terms of the loss of smaller chains of $Cd(hfa)_2$ hydrated fragments. The second peak at 142.5 °C is likely to be due to the loss of the remaining water (from a total of 6.38% water in the compound). The peak envelope between 188.3 and 212.5 °C, corresponding to the sublimation temperatures of a large group of similar complexes,[23] could be due to the sublimation of anhydrous $Cd(hfa)_2$. This latter system might be similar to the $Cd(acac)_2$, which shows a rather complicated structure[21a] and allows, in its turn, for other complicated thermal behavior to be forecasted. At higher temperatures, decomposition processes are operative. In fact, the remaining nonvolatile brown material (25% of the the starting material) was CdO, as confirmed by XRD analysis.

The literature datum that the IR spectrum of the sublimed $Cd(hfa)_2{\cdot}2H_2O$ (~130 °C) agrees well with that of the unsublimed compound[11a] is consistent with our results and in tune with the thermal behaviors of both $NH_4Cd(hfa)_3{\cdot}H_2O$ and $Zn(hfa)_2{\cdot}2H_2O{\cdot}$diglyme.[11,12]

Prototypical MOCVD experiments were carried out using the crystallized $Cd(hfa)_2{\cdot}2H_2O$ complex. The substrate temperature was maintained in the 320−400 °C range, and the deposition time was 120 min (Table 5). Preliminary experiments carried out at a source temperature of 110 °C (the temperature of the first DTG peak) resulted in almost no deposition of CdO. Depositions at a higher sublimation temperature (190 °C), related to the third DTG peak, were attempted. Under these conditions, evaporation rates of 6.05 mg/min, suitable for MOCVD experiments, were found.

XRD measurements (Figure 3) of as-deposited films provide evidence of cubic CdO crystallites. Only the (200) reflection was observed, whereas the (111) remained hardly evident. This finding suggests highly oriented CdO.[24] This result was found to be highly reproducible using the deposition parameters reported in Table 5. The mean crystallite size evaluated from the XRD line broadening[19,25] (substrate temperature = 320 °C) is equal to 50 nm. Energy-dispersive X-ray (EDX) results confirm the absence of carbon and fluorine contamination in the films.

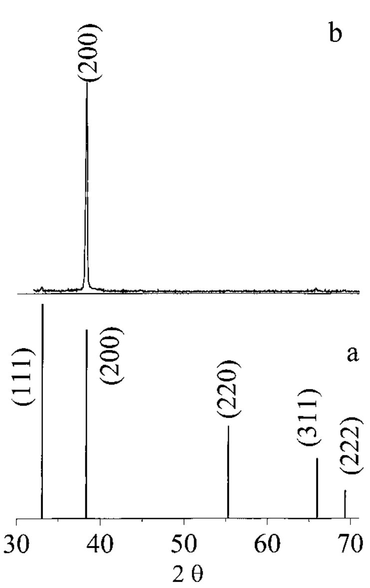


Figure 3. X-ray diffraction patterns over a $30° < 2\theta < 70°$ angular range: (a) powder diffraction standards of cubic CdO; (b) as-deposited SiO_2-supported CdO film.

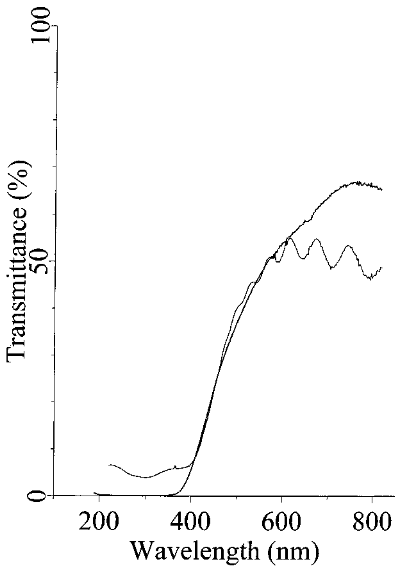


Figure 4. UV−visible transmission spectra for representative CdO thin films on SiO_2 substrate. The solid line refers to films obtained using low O_2 flow rates (100 sccm); the dotted line refers to films obtained using high O_2 flow rates (400 sccm).

The deposited films are transparent and their UV−visible spectra (Figure 4) find counterparts in previously reported data.[8,26−31] In particular, the transmittance has a minimum at $\lambda = 396$ nm (the absorption edge) and reaches a 55% value in the visible range for films deposited using a 100 sccm gas flow rate of O_2. Similar transmittance values have been reported for CdO films deposited by activated reactive evaporation.[30] The film thickness d was evaluated from UV−visible data using

---

(23) Mehrotra, R. C.; Bohra, R.; Gaur D. P. *Metal β-Diketonates and Allied Derivatives*; Academic Press: London, 1978.

(24) *Powder Diffraction Files*; Joint Committee on Powder Diffraction Standards, American Society for Testing and Material: Philadelphia, PA, 1971; #5-0640.

(25) Jiang, H. G.; Rühle, M.; Lavernia, E. J. *J. Mater. Res.* **1999**, *14*, 549.

(26) Benramdane, N.; Murad, W. A.; Misho, R. H.; Ziane, M.; Kebbab, Z. *Mater. Chem. Phys.* **1997**, *48*, 119.

(27) Wu, X.; Coutts, T. J.; Mulligan, W. P. *J. Vac. Sci Technol. A* **1997**, *15*, 1057.

(28) Narushima, S.; Hosono, H.; Jisun, J.; Yoko, T.; Shimakawa, K. *J. Non-Cryst. Solids* **2000**, *274*, 313.

(29) Ortega, M.; Santana, G.; Morales-Acevedo, A. *Solid-State Electron.* **2000**, *44*, 1765.

(30) Reddy, K. T. R.; Sravani, C.; Miles, R. W. *J. Cryst. Growth* **1998**, *184/185*, 1031.

(31) Miyata, N.; Miyake, K.; Fukushima, T. *J. Electrochem. Soc.: Solid-State Sci. Technol.* **1980**, *127*, 918.

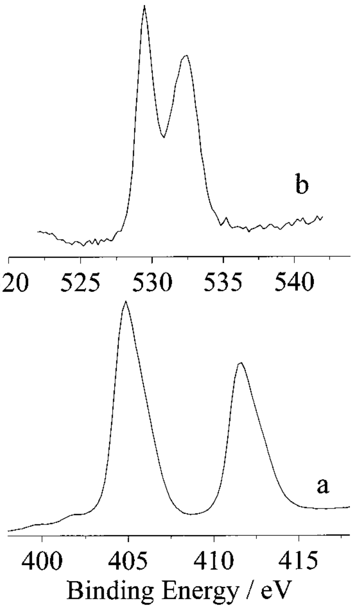


Figure 5. Al Kα excited XPS of a representative CdO thin film measured in the (a) Cd 3d and (b) O 1s energy regions. Structures due to satellite radiation have been subtracted from the spectra.

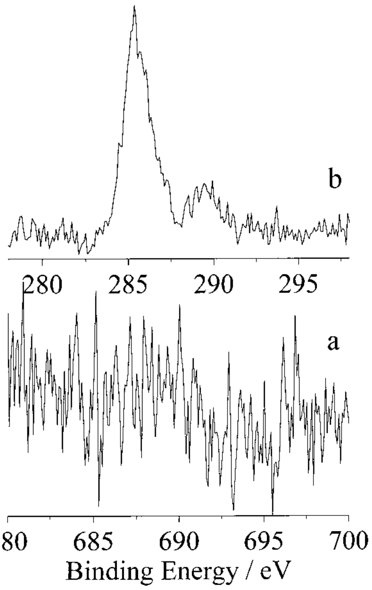


Figure 6. Al Kα excited XPS of a representative CdO thin film measured in the (a) F 1s and (b) C 1s energy regions. Structures due to satellite radiation have been subtracted from the spectra.

the classical equation[32]

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \qquad (1)$$

where n_1 and n_2 are the refractive indices at two adjacent maxima or minima at wavelengths λ_1 and λ_2. Assuming $n_1 = n_2 = 2.49$ for cubic CdO[33] films, the calculated d value is 1450 nm for a 120-min experiment (source temperature = 190 °C). Therefore, the resulting growth rate of the CdO films corresponds to 12 Å/min. Films obtained using higher O_2 gas flow rates (400 sccm) show lower growth rates (340 nm for a 120-min experiment), higher transmittance (up to 70%), and an absorption edge at $\lambda = 365$ nm. Similar transmittance and growth rate behaviors with respect to the oxygen partial pressure during deposition have already been reported for CdO films deposited by dc magnetron reactive sputtering.[34] In this case, the transmittance behavior was interpreted on the basis of the nonstoichiometry of the CdO films obtained at low oxygen partial pressure.[34]

Figure 5 shows the Al Kα XPS spectrum of a representative as-deposited CdO film, obtained using an O_2 gas flow rate of 400 sccm, in the Cd 3d and O 1s binding energy (BE) regions. The Cd 3d features consist of the main $3d_{5/2}$ and $3d_{3/2}$ spin–orbit components at 404.8 and 411.6 eV, respectively.[2] Two O 1s peaks (Figure 5) are evident at 529.4 and 532.4 eV. These features are identical to those already reported for related CdO systems and are due to the presence of hydroxide species on the surface, which are ubiquitous in air-exposed CdO materials.[35−39] In particular, it has been reported that atomically clean CdO surfaces that are exposed for a few minutes in air give the characteristic double XPS O 1s peak.[38] In addition, the XPS spectra (Figure 6) show small features due to some carbon surface contaminant (3 atom %), which is almost ubiquitous in similarly MOCVD fabricated materials.[12] In contrast, almost no fluorine signal was detected.

Resistivity values of the as-deposited CdO films were measured. The resulting values are in the range between 4×10^{-3} and 7×10^{-4} Ω cm and indicate conducting films. In particular, higher resistivity values were observed for films deposited using higher oxygen flow rates. In this compound, the electronic conduction is promoted by the presence of cadmium interstitials or oxygen vacancies, which act as n-type defects and produce donor states in the bulk band gap. Therefore, synthesis under more oxidizing condition yields less defective, thus less conducting, compounds. Similar resistivity values have already been reported for other CdO- and CdO-based films.[27,30,31,34]

Conclusions

X-ray single-crystal data for $Cd(hfa)_2 \cdot 2H_2O$ show that the cadmium ion is bound to the oxygen atoms of the two hfa fragments and to the oxygens of two cis-disposed water molecules. The six donors are located at the vertexes of a distorted octahedron. The coordinated H_2O molecules are hydrogen-bonded to the oxygen atoms of the neighboring hfa ligands. Deposition experiments in a low-pressure horizontal hot-wall reactor on fused SiO_2 substrates result in CdO thin films. XRD spectra of the as-deposited films provide evidence of cubic CdO crystallites. Only the (200) reflection was observed, thus

---

(32) Swanepoel, R. *J. Phys. E: Sci. Instrum*. **1983**, *16*, 1214.

(33) *Handbook of Chemistry and Physics*, 65th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1985.

(34) Subramanyam, T. K.; Uthanna, S.; Srinivasulu Naidu B. *Mater. Lett.* **1998**, *35*, 214.

(35) Niles, D. W.; Waters, D.; Rose, D. *Appl. Surf. Sci.* **1998**, *136*, 221.

(36) Nefedov, V. I.; Firsov, M. N.; Shaplygin, I. S. *J. Electron Spectrosc. Relat. Phenom*. **1982**, *26*, 65.

(37) Gaarenstroom, S. W.; Winograd, N. *J. Chem. Phys.* **1977**, *67*, 3500.

(38) Hammond, J. S.; Gaarenstroom, S. W.; Winograd, N. *Anal. Chem.* **1975**, *47*, 2193.

(39) Nefedov, V. I.; Gati, D.; Dzhurinskii, B. F. *Russ. J. Inorg. Chem.* **1975**, *20*, 2307.

indicating highly oriented CdO thin films. Optical spectra show that the transmittance of the films is around 70% in the visible range. The resulting resistivity ($\sim 10^{-4}\ \Omega$ cm) of the as-deposited films points to TCO properties. This behavior suggests that $Cd(hfa)_2{\cdot}2H_2O$ is a good precursor for MOCVD deposition of CdO films.

Acknowledgment. Drs. E. Amato and G. Malandrino are gratefully acknowledged for the NMR and EDX measurements, respectively. MIUR and CNR are also acknowledged for financial support.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for $Cd(hfa)_2{\cdot}2H_2O$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM011175Q