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Cobalt hexafluoroacetylacetonate polyether adducts for thin films of cobalt oxides

Antonino Gulino *, Ignazio Fragalà *

Dipartimento di Scienze Chimiche, Università di Catania and I.N.S.T.M. UdR of Catania, V.le A. Doria 6, 95125 Catania, Italy

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Abstract

The novel $[Co(C_5F_6HO_2)_2 \cdot 2H_2O \cdot CH_3(OCH_2CH_2)_2OCH_3]$ and $[Co(C_5F_6HO_2)_2 \cdot 2H_2O \cdot CH_3(OCH_2CH_2)_3OCH_3]$ low-melting adducts have been synthesized and characterized by elemental analysis, IR spectroscopy, mass spectra and TG–DTG thermal measurements. The former adduct is liquid at room temperature, whilst very mild heating of the latter results in a thermal stable liquid compound. Both adducts can easily be evaporated. Deposition experiments, in a low-pressure horizontal hot-wall reactor, on optical transparent SiO_2 substrates, using these precursors, result in CoO or Co_3O_4 films, depending on the deposition conditions. XRD measurements provide evidence that CoO and Co_3O_4 consist of cubic, highly oriented, (200) and (311) crystals, respectively. The mean crystallite sizes were evaluated from the XRD line broadening. Both optical spectra and resistivity measurements of Co_3O_4 films show that they are semi-conducting and their band-gap was determined from the optical induced transitions. The film cross section and the surface atomic composition were investigated by SEM and XPS analyses, respectively.

Keywords: Cobalt hexafluoroacetylacetonate; Cobalt oxide; MOCVD; Film; XRD; XPS; SEM; Semiconductor

1. Introduction

Materials based on cobalt oxides have been extensively investigated because of their potential applications in many technological fields [1].

The cobalt oxide system includes CoO, Co_3O_4, Co_2O_3 and CoO_2 [1–4]. CoO adopts the centrosymmetric rock-salt structure (cubic face centred system) in which pure O and Co (111) planes alternate along the (111) direction. Stoichiometric CoO has represented one of the two most important Mott insulators with a band-gap of 6 eV [2]. On the basis of resonance photoemission studies, it has recently been argued that CoO is a charge-transfer insulator instead of a band insulator [2]. Despite this behaviour, usually, CoO has a slight oxygen excess (CoO_{1+x}) thus representing a p-type semiconductor [3,4]. In addition, it shows an anti-ferromagnetic behaviour with a Neel temperature of 290 K [4].

Co_3O_4 shows the spinel structure based on a cubic close packing array of oxide ions where one-eighth of tetrahedral holes are occupied by Co(II) ions and one-half of octahedral holes are occupied by Co(III) ions. Moreover, it constitutes the most studied compound in view of application as an optical gas sensor [5], catalyst in oxidation reactions [1k,6] and electrochromic material [7,8]. Both the CoO and Co_3O_4 phases find application as high-temperature solar selective absorbers [9], magnetic materials [10] and as pigments for glasses and ceramics [4].

Many studies have been reported for preparation of bulk [1,6a,6c,9–11], thin films [1o–1q,4,5a,6b,7,9a, 9b,9d–9g,12,13], nanotubes [14], ordered nanoarrays [1i] and nanocubes [15] of Co oxides. In this regard, recently,

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* Corresponding author. Tel.: +39 095 7385067; fax: +39 095 580138.
E-mail addresses: agulino@dipchi.unict.it, agulino@mbox.unict.it (A. Gulino).

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we reported preliminary results on MOCVD of cobalt oxides using low-melting (53–57 °C) cobalt hexafluoroacetylacetonate adducts, as precursors [13a,13b].

In the present investigation, we report an extensive study concerning further novel $Co(hfac)_2$ adducts, one of them is liquid at room temperature and better suited for MOCVD of both CoO and Co_3O_4 thin films.

2. Experimental details

The $[Co(C_5F_6HO_2)_2 \cdot 2H_2O \cdot CH_3(OCH_2CH_2)_2OCH_3]$ and $[Co(C_5F_6HO_2)_2 \cdot 2H_2O \cdot CH_3(OCH_2CH_2)_3OCH_3]$ adducts, hereafter $[Co(hfac)_2 \cdot 2H_2O \cdot \text{diglyme}]$ and $[Co(hfac)_2 \cdot 2H_2O \cdot \text{triglyme}]$, ($C_5F_6HO_2$ = hexafluoroacetylacetonate = 1,1,1,5,5,5,-hexafluoro-2-4-pentanedionate = hfac, diglyme = bis(2-methoxyethyl) ether; triglyme = 2,5,8,11-tetraoxadodecane), were synthesized from stoichiometric quantities of $Co(OH)_2$, $C_5F_6H_2O_2$ (hereafter H-hfac), and the appropriate polyether. Aldrich grade reagents were used throughout all present syntheses.

Elemental analyses were performed using a Carlo Erba Elemental Analyzer EA 1108.

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

Electron impact mass spectra (EI-MS) were obtained using a 70 eV electron beam.

The thermal behaviour of the adducts was investigated by thermal and differential gravimetric analyses (TGA–DTG) under 1 at. of pre-purified nitrogen, using a 2 °C/min. heating rate. A Mettler Toledo TGA/SDTA 851 system was used. Six milligrams of samples was accurately weighed and examined in the 20–400 °C range.

MOCVD experiments were performed using an horizontal hot-wall reactor [13a,13b] under reduced pressure. Fused SiO_2 (amorphous quartz) was used as substrate after cleaning in an ultra-sonic bath with isopropyl alcohol. Optimized conditions require pure Ar (100 sccm) and O_2 (100 sccm for CoO and 400 sccm for Co_3O_4) as carrier and reaction gases, respectively. The source temperature was 100 °C for the $[Co(hfac)_2 \cdot 2H_2O \cdot \text{diglyme}]$ and 110 °C for $[Co(hfac)_2 \cdot 2H_2O \cdot \text{triglyme}]$. The substrate temperature (T_s) was maintained at 350 °C for CoO and 400 °C for Co_3O_4 thin films. The deposition time was 120 min. The total pressure, kept at 2 Torr (O_2 = 100 sccm) and 5 Torr (O_2 = 400 sccm), was measured using a MKS Baratron 122AAX system. Flow rates were controlled within ±2 sccm using MKS flow controllers and a MKS 147 Multi gas Controller.

X-ray diffraction (XRD) data of films were recorded with a Bruker D-5005 diffractometer (Cu Kα radiation, 30 mA and 40 kV).

X-ray photoelectron spectra (XPS) were made with a PHI 5600 Multi Technique System (base pressure of the main chamber 3×10^{-10} Torr). Resolution, correction for satellite contributions and background removal have been described elsewhere [16]. Depth profiles were obtained by alternating XPS core level measurements with Ar^+-ion sputter etching (4 kV, beam current 1.0 μA) every 30 s.

Scanning electron microscopy (SEM) analyses were performed with a LEO 1400 Microscope.

2.1. Synthesis of of $[Co(hfac)_2 \cdot 2H_2O \cdot \text{polyether}]$ complexes: general remarks

The title complexes were synthesized while stirring and refluxing at 40 °C for 2 h a CH_2Cl_2 suspension of stoichiometric quantities of $Co(OH)_2$, $C_5F_6H_2O_2$ (hereafter H-hfac), and the appropriate polyether. An excess of $Co(OH)_2$ was filtered off. Pale brown oils were obtained after evaporation of the CH_2Cl_2 solvent. Brown powders were obtained by dissolving the oils in 80 mL of hexane and leaving the solutions to concentrate. Similar synthetic procedures carried out with CoO instead of $Co(OH)_2$ gave much lower yield. This behaviour has previously been reported also for the synthesis of $Zn(hfac)_2$ adducts [17]. $Co(OH)_2$ was, therefore, freshly prepared by dropwise addition of a dilute NaOH solution to $[Co(NO_3)_2 \cdot 6H_2O]$ dissolved in H_2O. The hydroxide gel thus formed was filtered-off, washed with distilled water and dried overnight at room temperature.

2.2. Synthesis of $[Co(hfac)_2 \cdot 2H_2O \cdot \text{diglyme}]$

0.465 g (0.005 mol) of $Co(OH)_2$, 1.42 mL (0.01 mol) of H-hfac and 0.72 mL of diglyme (0.005 mol) were stirred and refluxed for 2 h with 40 mL of CH_2Cl_2: yield = 78%. Brown powders resulted by dissolving the oil in 80 mL of hexane and leaving the solutions to concentrate at 5 °C. Melting point: ~20 °C. Elemental *Anal.* Calc. for $CoC_{16}H_{20}F_{12}O_9$: C, 29.88; H, 3.13. Found: C, 30.85; H, 3.11%. MS (EI^+, 70 eV, *m*/*z* fragments; M = $[Co(hfac)_2 \cdot \text{diglyme}]$): 473 (54%) $(M - \text{diglyme})^+$, 404 (100%) $(M - \text{diglyme} - CF_3)^+$, 266 (39%) $(M - \text{diglyme} - \text{hfac})^+$, 216 (68%) $(M - \text{diglyme} - \text{hfac} - CF_3 + F)^+$. IR (KBr; ν/cm^{-1}): 3399 (m), 3157 (sh), 2985 (m), 2936 (m), 2883 (m), 1645 (s), 1620 (sh), 1558 (m), 1530 (s), 1489 (s), 1390 (w), 1353 (m), 1325 (vw), 1275 (s), 1219 (sh), 1202 (s), 1152 (s), 1099 (s), 1070 (sh), 1038 (sh), 948 (w), 924 (sh), 853 (w), 813 (m), 792 (m), 759 (vw), 743 (w), 730 (vw), 669 (s).

2.3. Synthesis of $[Co(hfac)_2 \cdot 2H_2O \cdot \text{triglyme}]$

0.465 g (0.005 mol) of $Co(OH)_2$, 1.42 mL (0.01 mol) of H-hfac and 0.9 mL of triglyme (0.005 mol) were stirred and refluxed for 2 h with 40 mL of CH_2Cl_2: