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Synthesis and characterization of cobalt precursors for the growth of magnetic thin films by the MOCVD method

N. D. PAPADOPOULOS[a], E. ILLEKOVA[b], H. S. KARAYANNI[c], E. HRISTOFOROU[a*]
[a]Laboratory of Physical Metallurgy, School of Mining and Metallurgical Engineering, National Technical University of Athens, 9, Iroon Polytechniou Street, 157 80 Zografou, Athens, Greece
[b]Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia
[c]Laboratory of Physical Chemistry, School of Chemical Engineering, National Technical University of Athens, 9 Iroon Polytechniou St., 157 80, Athens, Greece

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Two different organometallic precursors for Co metallization by MOCVD, namely cobalt acetylacetonate and the inclusion complex of β-cyclodextrin with cobalt iodide were synthesized in the laboratory and were characterized by means of X-Ray diffraction and differential thermal analysis. It was found that both samples were polycrystalline. The hydrated form of β-diketonates presents higher crystallinity than the anhydrous one and even higher when a few drops of NH_3 along with the NaOH solution was used. The inclusion complex exhibits a highly oriented character, in contrast with its parent β-cyclodextrin, with most crystal directions however remaining the same upon complexing. As it was observed by DTA, both samples partially volatized before 170 ^{O}C. Within the temperature range of 320-410 ^{O}C, oxidative decomposition of the hydrated cobalt acetylacetonate was strongly intensified. The dextrin inclusion complex may prove an innovative Co precursor for precise MOCVD applications at around 170 ^{O}C, where all easily movable crystalline waters and iodide ions have moved out. Beyond 170 ^{O}C the parent β-cyclodextrin shows remarkable thermal stability and upon complexing with cobalt acetylacetonate the latter's thermal stability can be improved significantly.

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1. Introduction

With the discovery of giant magnetoresistance (GMR) in magnetic multilayer structures, spin valves and granular alloys, the interest in the deposition of magnetic thin films of Co has increased significantly [2, 3]. Most of the published studies employed sputtering or evaporation techniques for Co deposition. Sputtering is typically preferred over evaporation due to the higher purity of sputter-deposited films, with the drawback however of the induced substrate damage caused by the highly energetic ions [2]. Recently, chemical vapor deposition (CVD) has emerged as a beneficiary alternative to previous processes [2, 9]. Its main advantages include, the ability to coat aggressive substrate topographies with excellent step coverage, tight control of film texture and grain size including the formation of metastable phases and epitaxial growth, and high purity without ion-induced substrate damage.

The majority of CVD Co activity has focused on fabrication of Co layers for magneto-optic applications, magnetic Co containing alloys or in situ doping with Co. A key component in the development of a viable Co CVD process is the identification of a suitable precursor source with the chemical characteristics required for growth of pure Co films at acceptable delivery and process temperature windows. However, there is only scarce literature on the synthesis and characterization of Co precursors, suitable for their use in CVD processes.

Since inorganic precursors usually demand high deposition temperatures, metal-organic or organometallic compounds are typically used, which decompose at relatively low temperatures [9]. Much of the chemistry of organometallic complexes as relevant to CVD process is dictated primarily by the ligand complement of the complex. However, the drawbacks are not few. Cobalt carbonyls typically employed in CVD systems present films with unacceptably rough surfaces containing up to 50 % atom carbon [10]. What is more, undesirable, but thermodynamically favourable precursor reaction pathways, which compete with Co deposition usually exist. Cobaltocene $Co(C_5H_5)_2$ and cyclopentadienylcobalt dicarbonyl $C_5H_5Co(CO)_2$ have been employed in APCVD systems with unacceptably rough surface morphology and low growth rates [2]. $HCo(CO)_4$ is unstable above –26 ^{O}C [3] and cobalt tricarbonyl nitrosyl $Co(CO)_3NO$, which has interesting physical properties, is not so easily prepared and upon synthesis usually employs the liberation of poisonous intermediate acids, such as the hydride of the corresponding potassium salt $HCo(CO)_4$ [14]. Furthermore, since the scaling down of the minimun feature size below 100 nm requires the implementation of innovative material and process solutions the trend in modern MOCVD systems is to have the ability of preparing the appropriate precursor in situ.

From this point of view, metal β-diketonates seem to be a promising alternative. The use of end-bond chelating donor ligands in CVD applications such as acetylacetonates has been extensive. Most of them are highly volatile and have been found to decompose at relatively low temperatures. They are stable in air and readily soluble in organic solvents. They can be relatively easily synthesized in the laboratory and many are used extensively as catalysts. Co(acac)$_2$ presents an interesting perspective, when compared to other organometallic sources, in the case of Co deposition. It produced Co films with less than 0.5% C and less than 0.2% O_2, at temperatures from 270 to 430 ^{O}C in a hot-wall reactor [12]. The optimum temperature was 280 to 310 ^{O}C, which was lower than 320 to 350 ^{O}C as was suggested by Jablonowski [11]. A patent also discusses the use of cobalt β-diketonate complexes [13].

Another major group of organic compounds, that can be useful in CVD metallization are the inclusion complexes of cyclodextrins or Schardinger dextrins. Cyclodextrins are cyclic oligosaccharides of three types: α-cyclodextrin, β-cyclodextrin and γ-cyclodextrin, which are composed of six, seven and eight glucopyranose units linked with α-(1,4) bonds, respectively [4, 7]. β-cyclodextrin is the most accessible, the lowest-priced and generally the most useful. The most notable feature of cyclodextrins is their ability to form solid inclusion complexes (host-guest complexes) with a very wide range of solid, liquid and gaseous compounds by molecular complexation. In these complexes a guest molecule is held within the cavity of the cyclodextrin host molecule. Complex formation is a dimensional fit between host cavity and guest molecule. The main driving force of the phenomenon is the release of enthalpy-rich water molecules from the cavity, which in turn are displaced by hydrophobic guest molecules present in the aqueous solution to attain an apolar-apolar association [4, 8]. Beneficial modifications of the physichochemical properties of the guest molecules can emerge upon complexing. Considering a suitable MOCVD precursor as the guest component, a number of certain characteristics concerning its storage and its delivery into the reactor chamber can be improved. These are: solubility enhancement of highly insoluble compounds, stabilization of labile compounds against the degradative effects of oxidation, visible or UV light and heat, control of volatility and sublimation, etc.

The aim of the present research work was the description of the synthetic procedure of two different organometallic compounds (cobalt acetylacetonate and the inclusion complex of cobalt iodide with β-cyclodextrin) and their characterization by means of X-ray diffraction and thermoanalytical study.

2. Experimental

2.1. Cobalt β-diketonate Co(acac)$_2$.

Cobalt acetyloacetonate was synthesized in the laboratory by slightly modifying the classic procedure of R.O Ragsdale [1]. All chemicals were purchased from Alfa. More specifically 6.6 ml (0.066 mol) of 2,4 – pentanedione (99% purity) was added slowly with stirring to a solution of 2 g (0.05 mol) of sodium hydroxide in 18.75 ml of distilled water. The following reaction occurs:

$$C_5H_8O_2 + NaOH \rightarrow C_5H_7O_2Na + H_2O \qquad (1)$$

Excess of acacH was used as it helped the reaction go to completion. The replacement of H^+ by the Na^+ ions was accompanied with a release of heat, which was exploited to homogenize the colloidal suspension that seemed to occur. The colloidal phase was enhanced by the reduction of the dispersion mean. On the other hand, its further increment beyond a certain limit led to reduced reaction effectiveness, evoked by the excessive dilution of the solution. Consequently, any white solid still remained in solution had to be dissolved with stirring at the temperature (about 40 ^{O}C) of the above exothermic reaction, before continuing.

The yellow solution was added dropwise to another solution of 5.95 g (0.025 mol) of cobalt (II) chloride hexahydrate (99.9% purity) in 45 ml of distilled water. The following reaction took place:

$$2C_5H_7O_2Na + CoCl_2{\cdot}6H_2O \rightarrow Co(C_5H_7O_2)_2{\cdot}2H_2O + \\ + 2NaCl + 4H_2O \qquad (2)$$

The resulting orange precipitate was filtered by suction in a Buchner funnel and washed with 80-100 ml of distilled water. Then it was dissolved in a hot mixture (around 60 ^{O}C) of 50 ml of 95% ethanol and 32 ml of chloroform. Vigorous stirring was employed, since lengthy boiling azeotropically dehydrates the compound. The resulting dark red solution was allowed to cool very slowly to room temperature in a Dewar flask, containing water at the same temperature (60 ^{O}C). After about 4 hours it was immersed in an ice bath and remained there for 24 hours. Long (4-5cm), fine, orange needles were grown and were collected with suction filtration, washed with 50 ml of cold 95% ethanol, air-dried and stored in a dark bottle. The yield was 5.0 g, 68%.

In the presence of base, 2,4 pentanedione readily loses a proton to form the acetylacetonate anion. Hydrogen atoms on α-carbon atoms that are adjacent to carbonyl groups are relatively acidic. The basic solution needed to remove the proton from the acacH is provided either by a strong base, such as sodium hydroxide or by weaker bases, such as ammonia and urea. The NH_4^+ ions derived from the hydrolysis of the afore-mentioned bases avert the formation of precipitated traces of $Co(OH)_2$, which could be found in strong alkaline solutions, because intermediate readily soluble complexes are formed. The presence of $Co(OH)_2$ adversely affects the completion of reaction (2), even if its formation possibility depends strongly on the pH value of the starting solution.

For this reason three more experiments were conducted with the alkalinity mean being: a) NH_3 solution, b) $(NH_2)_2CO$ solution and c) $NaOH/NH_3$ solution with $[NaOH]<10^{-2}$ M, respectively. Regarding the $Co(NH_2)_2$ solution hydrolysis takes place in two stages and the resulting colloidal solution was only slightly alkaline (pH=7.5). Large dilutions were not investigated for reasons of economy. In the case of NH_3 solution and at pH values of about 9.5, traces of dark green precipitants were formed together with $Co(acac)_2$. These were attributed to the known formation of the $Co(NH_3)_6^{4+}$ complex. This occurrence seemed to inhibit the ratio of $CoCl_2$ conversion into the aimed organometallic compound and was enhanced in large concentrations of NH^{4+} ions. Finally, the $NaOH/NH_3$ solution was investigated under different relative concentration ratios. The best results seemed to arise again by the use of excess NaOH solution (2.5 M) along with 6.25 ml of 25% NH_3 solution.

The final product was in hydrated form. Its dehydration was accomplished by heating at reduced pressures. More specifically the diaquo compound was placed in a modified Abderhalden drying apparatus (Aldrich) with phosphorus oxide and calcium hydroxide as the desiscants. After about 8 hours at 70 ^{O}C and at a pressure of 0.5 psi (a rotary pump was used) dehydration seemed to have completed. The compound was weighed (4.4 g) and the loss (0.6 g) agreed with the theoretical (about 12%).

2.2 Inclusion complex of β-cyclodextrin with cobalt iodide

Anhydrous cobalt iodide, β-cyclodextrin and iodine were purchased from Fluka. 1 g of β-CD was dissolved in 80 ml of distilled water at room temperature with stirring until the solution became almost saturated [5]. Then 0.36 g of cobalt iodide and 0.44 g of solid iodine were added simultaneously to the solution. This was then heated to 60-65 ^{O}C for 20 min and was gravity filtered into an empty beaker. It was transferred quickly into a Dewar flask with an end cap containing water at the same temperature. After 12 hours it was immersed in an ice bath and remained there for another 24 hours. Fine, brown needles of complex Co β-CDs were grown and were collected by gravity filtration in a Buchner funnel. Finally, they were dried in air.

The mineralogical phases and the mean grain size of the produced films were determined by X-ray diffraction (XRD) using a Siemens D5000 diffractometer with nickel-filtered $CuK\alpha_1$ radiation (1.5405 A), 40 kV and 30 mA. Thermoanalytical study of the precursors was carried out by the high temperature PerkinElmer DTA 7, which was calibrated by Al and Au standards. Alumina crucibles with alumina lids were used and the heating rate was 10 ^{o}K/min. Typically 10-15mg portion of the test samples was used and Al-Ni-Sm-Pd alloy was the thermally inert reference material. DTA curves were recorded on heating up to 700 ^{O}C in dynamic atmosphere of either argon (30 ml/min) or air. All samples were cooled down to 25 ^{O}C at the same rate (10 ^{o}K/min) and then a second run up to 700 ^{O}C was employed, after a holding period of 60 min (10 min in the case of the dextrin inclusion complex) at 25 ^{O}C. The measurements are valuable from about 30 up to 600 ^{O}C.

3. Results and discussion

3.1 X-Ray diffraction.

XRD analysis of the solid precursors confirmed that these were polycrystalline with large grain size. In the case of cobalt diketonates (Fig. 1) the diffraction data was obtained with a 0.030 step width over a 2θ range from 5^0 to 60^0 (5^0 to 55^0 in the case of dextrins). The crystallinity of different hydrated samples by the use of only NaOH solution seemed to improve proportionally with the cooling time. By the use of the $NaOH/NH_3$ alkaline solution the crystallinity of the solid improved further (Fig. 2).

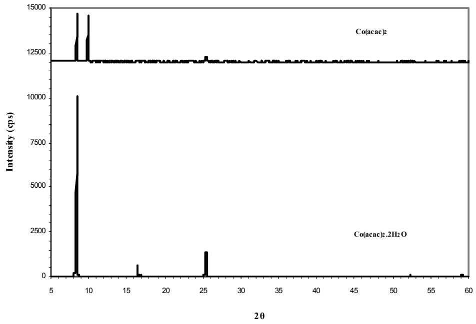

Fig. 1 XRD analysis of hydrated and anhydrous form of Co-β diketonate.

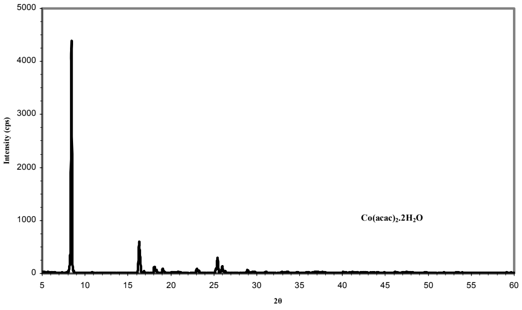

Fig. 2. XRD analysis of Co-β diketonate, by the use of $NaOH/NH_3$ alkaline solution.

The anhydrous form of cobalt acetylacetonate exhibited significantly lower crystallinity, (which is obviously due to the loss of crystalline waters), even if the hydrated form was thermally treated during the dehydration stage. This however, may prove advantageous in MOCVD processes, since lower decomposition temperatures and higher precursor volatility can be expected.

Concerning the dextrin inclusion complex two major peaks are seen, as opposed to only one of the parent β-cyclodextrin (Fig. 3). In contrast to the latter, the inclusion complex is highly oriented. Most of the characteristic peaks of the parent dextrin however, can be also observed at the diffraction data of the formed complex. This should be expected, since the β-cyclodextrin's cavity is of the order of a few A and its molecular weight exceeds 1100 [4, 5, 7].

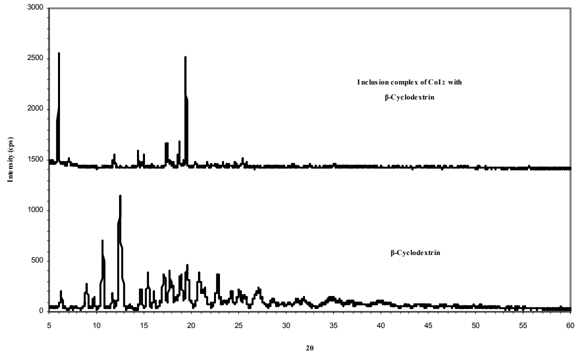

Fig. 3. XRD analysis of β-cyclodextrin and its inclusion complex with cobalt iodide.

The mean grain size was determined from the full width at half maximum of the main peak using the classical Debye-Scherrer formula. The calculated value for all β-diketonate samples was about 90 nm and about 75 nm for the β-cyclodextrin inclusion complex.

3.2 Differential thermal analysis

In the case of cobalt acetylacetonate partial volatilasation seems to occur in the temperature range of 50 to 130 ^{O}C (Fig. 4). The volatility – if low – of certain metal β-diketonates can be improved, because the β-diketonate ligand is bi-dentate when bonded through the oxygen ligands, although this is not always the case and generally prefers to chelate rather than bridge.

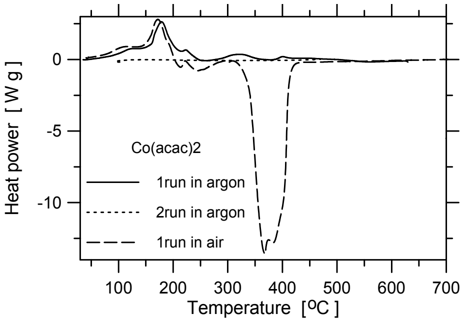

Fig. 4. Differential Thermal Analysis of $Co(acac)_2$.

At about 170 ^{O}C, the precursor starts to melt. Decomposition occurs shortly after and the rest of $Co(acac)_2$ burns out leaving free Co, H_2O and amorphous C [6]. The next thermal decomposition occurs in two stages within the temperature range 320 to 410 ^{O}C. Especially by heating in air oxidative decomposition becomes violently intensified as evident by the strong exothermic peaks at 360 and 380 ^{O}C. Instead of Co, Co_3O_4 in addition with CO_2 are expected to have been formed.

The hydrated form of cobalt acetylacetonate melted easier than the anhydrous one. Furthermore, a small portion of crystalline waters seems to remain still tightly bound to the rest of the parent Co β-diketonate (at about 330 ^{O}C) and thus distinctly separates the two exothermic peaks, probably due to partial precursor reformation (fig. 5). By further increment of temperature, decomposition completes releasing even higher amount of energy than at the first stage.

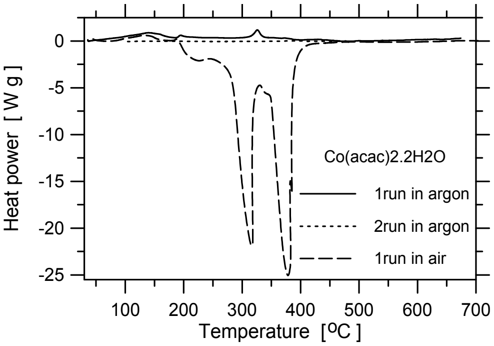

Fig. 5. Differential Thermal Analysis of $Co(acac)_2{\cdot}2H_2O$.

In inert gases volatilisation and subsequent melting seem to delay for about 10 ^{O}C, due to the absence of O_2, thus increasing the solid precursor's thermal stability.

The DTA trace of the dextrin inclusion complex shows two endothermic peaks with onset temperatures of 120 and 170 ^{O}C (fig. 6). At this temperature the easily movable waters as well I^- ions, which form long polyiodide chains in a Z-like structure have moved out leaving free Co^{++} ions [5]. Then, if in air, dextrine starts to melt and oxidatively decomposes before it burns out completely at around 420 ^{O}C.

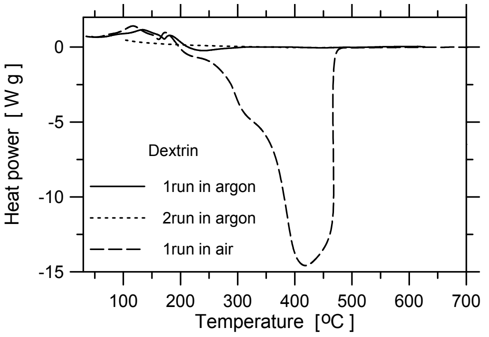

Fig. 6. Differential Thermal Analysis of β-cyclodextrin inclusion complex with CoI_2.

Surprisingly however, no signs of other phase transformations were depicted when the DTA trace was recorded in a dynamic argon atmosphere. The parent β-cyclodextrin, which probably is the only compound remaining beyond 170 ^{O}C, shows remarkable thermal stability. As a result, in a typical MOCVD process it could be removed as a volatile by-product, even at relatively low deposition temperatures.

Concerning a MOCVD experiment conducted in air by the use of the aforementioned dextrin inclusion complex there is an obvious need for further investigation regarding the thermal transformations that take place at temperatures above 200 ^{O}C [15]. The by products should be removed easily out of the reactor chamber as volatile compounds and not contaminate the deposited film with amorphous carbon. Volatility investigation of the solid precursor at relatively low temperatures worths exploring, too [16, 17].

4. Conclusions

Cobalt acetylacetonates can be well used as a Co precursor for MOCVD, especially in the anhydrous form. Synthesis of the precursor must take place preferably at strong alkaline solutions, since high pH values favor the replacement of H^+ ions in acacH. The addition of small quantities of NH_3 and at pH values of less than 12 totally inhibits the precipitation of $Co(OH)_2$ traces, with the drawback however of lower $Co(acac)_2$ yield.

The inclusion complex of β-cyclodextrin with CoI_2 may prove an innovative Co precursor for precise MOCVD applications, since most of its crystalline waters are easily movable and I^- ions, which form long polyiodide chains, move out by sublimation of the complex, leaving Co^{++} ions free for Co metallization.

The thermal instability of β-diketonates and their narrow thermal process windows may improve by combination of $Co(acac)_2$ with β-cyclodextrins, the former acting as the guest molecules in the dextrin's cavity.

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[*] Corresponding author: eh@metal.ntua.gr