Metal Organic Chemical Vapour Deposited Thin Films of Cobalt Oxide Prepared via Cobalt Acetylacetonate

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The single solid source precursor, cobalt (II) acetylacetonate was prepared and characterized by infrared spectroscopy. Thin films of cobalt oxide were deposited on soda lime glass substrates through the pyrolysis (metal organic chemical vapour deposition (MOCVD)) of single solid source precursor, cobalt acetylacetonate, Co[Cl(H2O)2]2 at a temperature of 420 °C. The compositional characterization carried out by rutherford backscattering spectroscopy and X-ray diffraction (XRD), showed that the films have a stoichiometry of CoO3 and an average thickness of 227 ± 0.2 nm. A direct energy gap of 2.15 ± 0.01 eV was calculated by the data obtained by optical absorption spectroscopy. The morphology of the films obtained by scanning electron microscopy, showed that the grains were continuous and uniformly distributed at various magnifications, while the average grain size was less than 1 micron for the deposited thin films of cobalt oxide.

KEY WORDS: Precursor; Thin film; Oxide; Metal organic chemical vapour deposition (MOCVD); Rutherford backscattering spectroscopy (RBS)

1. Introduction

Metal oxides have many interesting properties that result in various important applications[1]. Transition metal oxides (TMO), a subgroup of metal oxides, are those oxides in which the cation has incompletely filled d or f shells[2]. Tremendous efforts have been devoted in recent years to studying these metal oxides as anomalous behaviours observed in these materials. Consequently, it has become increasingly important to understand them in terms of their magnetic, electrical and colour (and optical) properties.

Some of the applications of the transition metal oxides (CoO, NiO, CuO) which have generated lots of interest among research groups all over the world include superconductivity in electronics, electrochromism in smart windows and electrochemical properties in micro batteries and high density batteries[3].

Metal organic compounds which are generally used as precursors for the preparation of metal oxides are either commercially available or can be prepared easily in the laboratory. There are four types of such metal organic compounds frequently used: metal acetylacetonates, metal alkoxides, alkylmetals, and metal carboxylates. Some of these compounds do not require the use of oxygen while alkylmetals need oxidizing agents for the deposition of the metal oxides. Of all the metal organic compounds, acetylacetonates are the easiest to prepare, requiring no special atmosphere or environment. They are easily prepared from commercially available reagents[4]. Metal β-diketonates serve as non-toxic (hence environmentally friendly), volatile and inexpensive precursors for chemical vapour deposition (CVD) of metals and metallic oxide thin films[5]. Some common precursors, used for the deposition of metal oxides require reduced pressures[6] because of their low volatility. Occasionally, atmospheric vapour deposition becomes feasible when the precursor is sufficiently volatile. Such is the case reported for ZnO using Zn(acac)2[7]. The use of a single solid source precursor has reduced the number of parameters determining the stoichiometric ratio of the elements in the film. The ratio is therefore controlled by the design variables, such as the deposition temperature and the flow rate of the carrier gas.

Cobalt oxide, a prototype material model, has been studied over the decades, because of its scientific and technological importance in understanding defect chemistry, electrochemical transport properties of semiconducting oxides[8] and also for understanding the strong electron-electron correlation in solids[9]. Cobalt oxides are commonly used in glass industry for colouration and in chemical processes as catalytic activator in oxidation reactions[10]. Cobalt oxide occurs in two common forms, viz: as CoO and Co3O4, both having cubic lattice structure. Co3O4, a spinell with Co2+ and Co3+ ions being simultaneously present but at different lattice sites in the crystal[10], constitutes the most studied oxide. Co3O4 is useful as an optical gas sensor[11] and electrochromic device[12]. Both oxides (CoO and Co3O4) are normally non-stoichiometric with excess of oxygen. Another form of cobalt oxide which is also available is Co2O3.

Various studies have been reported for the preparation of bulk and thin films of cobalt oxide on different substrates. These include sintering technique, evaporation technique, radio frequency (RF) sputtering technique[13], thermal oxidation[14,15] of cobalt in dry oxygen at high temperature and metalorganic chemical vapour deposition (MOCVD) technique[16–19]. Many properties of cobalt oxide

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such as stoichiometry and electronic defect[20], optical characterization[16,21] have also been carried out and reported.

In this paper, we report the preparation of cobalt acetylacetonate (precursor) and cobalt oxide thin film from single solid source precursor using metallorganic chemical vapor deposition (MOCVD) technique. The characterization techniques include: IR spectroscopy, UV-visible spectroscopy, rutherford backscattering spectroscopy (RBS) and scanning electron microscopy (SEM).

2. Experimental

2.1 Preparation and characterization of the precursor

The precursor, cobalt acetylacetonate, was prepared via the modification of the method earlier reported[22]. The procedure of the preparation is as follows: 2, 4-pentanedione (acetylacetonate) (40.0 ml) was added slowly to a solution of 16.0 g of sodium hydroxide in 150.0 ml of water and kept at a temperature below 40°C. The yellow solution was added drop wise to a solution of 47.6 g of cobalt (II) chloride hydrate (CoCl$_2$
$.6H_2O$) in 250.0 ml of water and stirred vigorously. The resulting orange precipitate was filtered in a large Buchner funnel and washed with about 500.0 ml of water until the washing was colourless. The moist solid was then dissolved in a hot mixture of 400.0 ml of ethanol and 250.0 ml of chloroform. The red solution was allowed to cool slowly to room temperature, and then further cooled in ice. The orange needles were suction filtered and washed with cold 95% ethand and air-dried. The reaction is given as:

$$\text{HC}_3\text{H}_7\text{O}_2 + \text{NaOH} \rightarrow \text{NaC}_6\text{H}_7\text{O}_2 + \text{H}_2\text{O}$$

$$2\text{NaC}_6\text{H}_7\text{O}_2 + \text{CoCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow$$

$$\text{Co(C}_5\text{H}_7\text{O}_2)_2 + 2\text{NaCl} + 6\text{H}_2\text{O}$$

The transmission spectrum of the cobalt acetylacetonate precursor was measured in KBr at normal incidence by using an M 500 infrared spectrophotometer over the range of 4000–500 cm$^{-1}$.

2.2 Preparation of the thin film

Prior to each deposition, the substrates, the stainless steel blocks (substrate holders) and the reaction chamber were scrubbed by using detergent, distilled water, trichloroethylene, acetone, ethyl alcohol and distilled water, respectively. This process was used to dislodge the dirt on the glass, and ensure that hydrocarbon and grease were removed from the substrate and also to ensure that the substrate surfaces were free from surface contamination and defects.

The thin film of cobalt oxide was prepared by using the pyrolytic method of metallorganic chemical vapour deposition which had been reported previously[23].

The set-up for the deposition is shown in Fig. 1. The fine powder of the precursor was poured into an unheated receptacle and nitrogen gas (passed through calcium chloride pellets as drying agent) was blown through the precursor at a rate of 2.5 dm$^3$/min. The nitrogen-borne precursor was transported into the working chamber kept at 420°C by using an electrically heated furnace. On getting to the hot zone, the precursor first sublimed before it thermally decomposes, resulting in the coating of the substrates. The process was left on for 1 h at the deposition temperature of 420°C. The whole process was carried out in a fume hood, to minimize some of the handling problems associated with such compound.

2.3 Characterization of cobalt oxide thin film

The compositional analysis of the thin film was carried out by rutherford backscattering spectroscopy (RBS). The RBS facility is a 2 MeV Tandetron accelerator of general geometry having a 170° backscattering angle, with a silicon detector solid angle of 6.7 mstr and a He+ beam current of 10 nA. The absorbance measurement was carried out to study the optical behaviour of the cobalt oxide thin film in the range of 400–1100 nm by using a Pye-Unicam 300 series Helios Alpha Version 2.05 UV-Visible spectrophotometer. All measurements were made with a blank soda lime glass substrate in the reference beam.

The X-ray diffraction pattern of the cobalt oxide thin films was obtained by using a MD10 mini diffractometer for an exposure time of 1200 s and radiation of CuKα.

3. Results and Discussion

3.1 Infrared spectrophotometric analysis of the precursor

Figure 2 shows the infrared spectrum obtained for cobalt acetylacetonate in KBr. A close examination of the spectra showed that the precursor exhibits the basic absorption frequency bands between 4000 and 500 cm$^{-1}$. The prominent bands observed in the spectrum include: C-H vibration at 2927; Carbonyl stretching (C=O) frequencies near 1567 and 1630, C=C stretching between 1150 and 1250 cm$^{-1}$, and M-O band at below 1000 cm$^{-1}$. These peaks matched well with those of the cobalt acetylacetonate spectrum reported earlier by Lawson[24]. Cobalt (II) acetylacetonate is a tetramer in which each Co atom is six-coordinate as given by Cotton et al.[25].
3.2 Compositional studies of the cobalt oxide thin films

The compositional analysis was carried out using Rutherford backscattering spectroscopy (RBS). The RBS spectrum of the thin film is shown in Fig. 3(a–c). Figure 3(a) shows RBS spectrum (dark spectrum), obtained from the back of the substrate while Fig. 3(b) clearly excludes the substrate from the surface, giving a good fit. Figure 3(c) gives an average thickness of 227±0.2 nm for the thin films. RBS gave the stoichiometric ratio of the prepared cobalt oxide thin film as Co:O=2:3 (Co$_2$O$_3$), which is cobalt (III) oxide. This shows that the decomposition of cobalt (II) acetylacetonate in nitrogen gas medium produced cobalt (III) oxide (Co$_2$O$_3$). However, Mane[26] reported that the stoichiometric ratios of the films obtained through the pyrolysis of cobalt (II) acetylacetonate in two different oxidant gases O$_2$ and N$_2$O were Co$_3$O$_4$ and a mixture of Co$_3$O$_4$ and CoO, respectively. Whereas, Drasovean et al.[27] obtained Co$_3$O$_4$ thin films from methanoic solution of cobalt acetate, using dipping sol-gel process. This shows that the films were obtained through different degrees of oxidation. Co$_3$O$_4$ is a stable intermediate oxide between CoO and Co$_2$O$_3$. CoO has a cubic lattice with Co$^{2+}$ ion at the cation sites, while Co$_2$O$_3$ has a cubic lattice structure with Co$^{3+}$ at the cation sites.

3.3 UV-Visible spectrophotometric analysis

Figure 4 shows the absorbance spectra for a representative of as-deposited cobalt oxide thin film in the region of wavelength 400–1100 nm. The spectrum shows that this property (absorption) of the film is affected by the irradiation frequency. The cobalt oxide thin film system showed varying degree of absorption throughout the region of wavelength, exhibiting distinct optical edge and excitation from the uppermost occupied level to the next higher lying empty band. Apart from the absorption edge, a moderate absorption occurs between 601 and 734 nm, a peak at 751 nm and a hump at 772 nm. There are also broad peaks above 826 nm observed in the spectrum and this can be ascribed to charge carrier absorption.

The semiconductor optical absorption results from several processes that can be divided into two groups. The first is associated with its chemical nature and irradiation wavelength used. The main process here, include: excitonic and plasmonic, which concern the fundamental absorption. The other group is correlated to the quantity and motion of species in the material, which is mainly extrinsic absorption. However, the latter group can be ignored since one is dealing with polycrystalline samples.

The absorption coefficient, $\alpha$, of the film was obtained from the expression:

$$\alpha = \frac{1}{d} \log_{10} \frac{1}{T}$$

where $d$=thickness of the film, $T=10^{-A}$=transmittance and $A$=absorbance. The theory of interband absorption$^{[28]}$ showed that the fundamental edge, the absorption coefficient should vary according to the
Fig. 5 A plot of $(\alpha h\nu)^2 \times 10^{16}$ against energy for cobalt oxide thin film

Fig. 6 SEM micrograph of the cobalt oxide thin film at different magnifications

Fig. 7 XRD spectrum of cobalt oxide thin film

expression:

$$\alpha = A(h\nu - E_g)^n$$

(2)

where $h=$Planck’s constant, $\nu=$frequency, $E_g=$energy gap and $n=$integer, a number which characterizes the transition process as either direct allowed ($n=1/2$) or direct forbidden transition ($n=3/2$).

From the optical absorption data gathered in Eq. (1), a linear region is evident from the plot of $(\alpha h\nu)^2$ against energy $(h\nu)$ for direct allowed transition ($n=1/2$) and $E_g$ is estimated to be 2.15 eV by extrapolation of a straight line regime of the plot to $(\alpha h\nu)^2=0$ for the cobalt oxide thin film shown in Fig. 5. Many reports exist for cobalt oxides, such as CoO and $\text{Co}_2\text{O}_3$ but the literature is deficient of the information on $\text{Co}_2\text{O}_3$ thin films, particularly on its energy bandgap. Drasovean et al.[27] reported 2.09–2.10 eV and 1.25–1.30 eV for direct and indirect bandgaps respectively for $\text{Co}_3\text{O}_4$ thin films. However, bandgap values of 2.2–2.8 and 1.4–1.8 eV have also been reported for CoO and $\text{Co}_3\text{O}_4$, respectively[29]. The value obtained in this work is close to others previously reported for the direct transition in CoO and $\text{Co}_3\text{O}_4$ thin films[27,29,30].

3.4 Morphological Characterization of the thin films

Figure 6(a–c) shows the SEM micrograph (morphology and microstructure at various magnifications) of the cobalt oxide thin film.

The micrographs show that the films are composed of coarse, continuous, uniformly distributed crystalline grains. This is confirmed by Nagirnyi et al.[31] on the electrolytic deposition of cobalt (III) oxide. The average grain size is less than 1 µm.

3.5 X-ray diffraction

The X-Ray diffraction pattern of the cobalt oxide ($\text{Co}_2\text{O}_3$), is shown in Fig. 7. The intense peaks occur at diffraction angles, $2\theta=22.7^\circ$, 23.53°, 28.84° 29.99°, 33.90°, 47.43°, 54.51°, 63.51°. There seems to be an ambiguity as to the actual compound. The obtained diffraction pattern indicated three possible compounds CoO, $\text{Co}_2\text{O}_3$ (Card Number 02-1079), and $\text{Co}_3\text{O}_4$ (Card Number 09-0418)[32]. This ambiguity however was finally resolved through the RBS. From the RBS spectrum $\text{Co}_2\text{O}_3$ is indicated and from the precursor $\text{Co}_2\text{O}_3$ is likely the compound obtained. A broad band was observed between angle, $2\theta=10^\circ$ and $30^\circ$. This behaviour is indicative that the film might be amorphous[32].

4. Conclusions

(1) We have prepared and characterized a single solid source precursor of cobalt acetylacetonate.

(2) We have also shown that it is possible to deposit thin films of cobalt oxide ($\text{Co}_2\text{O}_3$) through the pyrolysis of the single solid source precursor, cobalt (II) acetylacetonate, by using our simple setup.

(3) Cobalt oxide thin films which have stoichiometric composition of $\text{Co}_2\text{O}_3$ have been prepared by MOCVD technique using a single solid source precursor.

(4) The characterization shows the cobalt oxide film has a direct energy gap of 2.15±0.01 eV and an average thickness of 227±0.02 nm.
The morphology of the film showed the grains were continuous and uniformly distributed at various magnifications, while the average grain size was less than 1 μm for the deposited thin film of cobalt oxide.

Both RBS and X-Ray Diffraction (XRD), showed that the films have a stoichiometry of Co$_2$O$_3$.

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