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MOCVD OF COBALT OXIDE USING CO-ACTYLACETONATE AS PRECURSOR: THIN FILM DEPOSITION AND STUDY OF PHYSICAL PROPERTIES

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Metal Organic Chemical Vapor Deposition (MOCVD) is the deposition method of choice for achieving conformal uniform (composition and thickness) continuous thin films over the micron geometry topology necessary for implementing advanced devices. Thin films of cobalt oxide were prepared by MOCVD technique on alumina substrate using a cobalt acetylacetonate as precursor. The thin films of cobalt oxide were deposited on alumina substrate by MOCVD at four different temperatures viz 490 °C, 515 °C, 535 °C, 565 °C. *The as deposited samples are uniform and well adherent to the substrate. Thickness of the cobalt oxide film is maximum at temperature* 535 °C. *The crystalline and phase composition of films were examined by X-ray diffraction. The XRD reveals the crystalline nature with cubic in structure for all the samples. The surface morphology of the films were studied by scanning electron microscopy. The SEM image shows well defined closely packed grains for all the samples. The hexagonal shape of grains are observed for sample at temperature* 515 °C. *Raman spectroscopy shows Fm3m,* 225 *space groups for cobalt oxide thin films deposited on alumina substrate.*

Keywords: *MOCVD, THIN FILM, XRD, SEM IMAGES, RAMAN SPECTRA.*

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1. INTRODUCTION

In response to the changing global landscape, energy has become a primary focus of the major world powers and scientific community. There has been great interest in developing and refining more efficient energy storage devices. One such device, the supercapacitor, has matured significantly over the last decade and emerged with the potential to facilitate major advances in energy storage. Supercapacitors, also known as ultracapacitors or electrochemical capacitors, utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances several orders of magnitude larger than conventional capacitors [1]. Electrodes for such supercapacitors are mainly made using conductive polymers or metal oxides. The metal oxide based supercapacitors have attracted increasingly more attention due to their high specific capacitance, long operation time and high output.

Metal oxides have many interesting properties that result in various important applications [2]. Transition metal oxides (TMO), a sub group of metal oxide are those oxides in which the cation has incompletely filled d or f shells [3, 4]. Tremendous efforts have been devoted in recent years to study these metal oxides as anomalous behavior observed in these materials.

Consequently it has become increasingly important to understand them in terms of their magnetic, electrical and optical properties. Some of the applications of the transition metal oxides (CaO, NiO, CuO) which have generated lots of interest among the research groups all over the world include superconductivity in electronics, electrocromism in smart windows and electrochemical properties in micro batteries and high density batteries [5].

Among the various metal oxides, cobalt oxides have been extensively investigated because of their potential applications in many technological fields, as well as those of cobalt nanoparticles films obtained by a number of techniques [6-9]. High quality magnetic films of cobalt oxide based alloys are currently used in magnetic heads and magnetic RAM. For example simple binary alloys produce high quality films for magnetic recording industry. On the other hand cobalt oxide based ceramics have attractive magnetic properties and their films and multilayer have been studied for decades and still motivate serious research and development efforts [10-13]. In this paper attempts are made to deposit the thin film of cobalt oxide using metal organic chemical vapor deposition technique (MOCVD). For this the precursor cobalt-actylacetonate is used.

2. BLOCK DESCRIPTION OF MOCVD SYSTEM

Block diagram of typical metal organic chemical vapor deposition system is shown in fig. 1 which consists of following sub units:

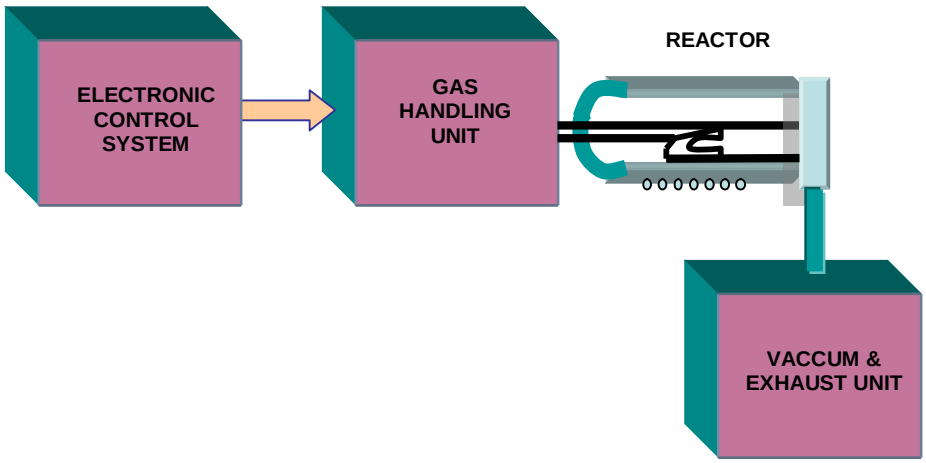

Fig. 1 *– Metal organic chemical vapor deposition system*

2.1 Gas handling unit

The gas handling system performs the functions like, mixing and metering of the gas that will enter into the reactor. Timing and composition of the gas entering the reactor will determine the epilayer structure. Leak-tight of the gas panel is essential, because the oxygen contamination will degrade the growing films' properties. Fast switch of valve system is very important for thin film and abrupt interface structure growth. Accurate control of flow rate, pressure and temperature can ensure the stable and repeat.

2.2 Reactor

A reactor is a chamber where the deposition process is carried on. The chamber is composed of reactor walls, a liner, gas injection units, and temperature control units.

2.3 Vacuum and exhaust unit

Pump and pressure controller is main part of this unit which will control the pressure growth. It is mainly used for low pressure growth. To handle large gas load the pump must be designed in proper manner.

2.4 Electronic control system

This system contains some electronic circuits, which controls various parameters like temperature, rate of flow of oxygen, argon gases, pressure in the reaction chamber etc.

3. THE GROWTH OF THIN FILM BY MOCVD

The vapor pressure is an important consideration in MOCVD, since it determines the concentration of source material in the reactor and the deposition rate. First the metal organic sources and hydrides inject to the reactor. The sources are mixed well inside the reactor and transfer to the deposition area. At the deposition area, high temperature result in the decomposition of sources and other gas-phase reaction, forming the film precursors which are useful for film growth and by-products. Then film precursor's transport to the growth surface, the film precursors absorb on the growth surface, the film precursors diffuse to the growth site. At the surface, film atoms incorporate into the growing film through surface reaction. The by-products of the surface reactions absorb from surface. The by-products transport to the main gas flow region away from the deposition area towards the reactor exit.

4. STEP BY STEP PROCESS IN DEPOSITION

4.1 Cleaning of substrates

The substrate used for depositions is alumina Al_2O_3. Prior to each deposition, the substrates, the substrate holders and the reaction chamber were scrubbed by using detergent, distilled water, trichloroethylene, acetone, ethyl alcohol and distilled water, respectively. The substrates were washed with 1:1 Hydrochloric acid and double distilled water. Then it is cleaned by ultrasonic cleaner for ten minutes. Again washed with double distilled water. 50 ml of acetone was boiled, and then with the vapors of acetone substrate were cleaned till entire acetone. After this 25 ml of trichloroethelene was boiled and substrate was cleaned in these vapors, and kept in air-tight container. 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 [4].

4.2 Preparation of precursor Co-acetylacetonate

The 2.4-pentanedione (acetylacetonate) 40 ml was added slowly to a solution of 16.0 gm of sodium hydroxide in 150 ml of water and kept at a temperature

bellow 40 °C The yellow solution was added drop wise to a solution of 47.6 gm of cobalt (II) chloride hydrate ($CoCl_2.6H_2O$) in 250 ml of water and stirred vigorously. The resulting orange precipitate was filtered in a large Buchner funnel and washed with about 500 ml of water until the washing was colorless The moist solid was then dissolved in hot mixture of 400 ml ethanol and 250 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 % ethanol and air dried [4]. The reactions are given bellow:

$$HC_5H_7O_2 + NaOH \longrightarrow NaC_5H_7O_2 + H_2O$$

$$2NaC_5H_7O_2 + CoCl_2 + 6H_2O \longrightarrow Co(C_5H_7O_2)_2 + 2NaCl + 6H_2O$$

4.3 Deposition conditions

The thin films of cobalt oxide were deposited on alumina substrate by MOCVD technique. The thin films of cobalt oxides are deposited at four different temperatures viz. 490 °C, 515 °C, 535 °C, 565 °C. The different deposition conditions and parameters are as shown in table 1.

Table 1 *– Deposition parameters and conditions*

Sr.No.	Parameters	Conditions
1	Precursor used for deposition	Cobalt acetylacetonate
2	Substrate used for deposition	Al_2O_3
3	Purging gas	Argon
4	Purging time	30 min
5	Reacting gas	Oxygen
6	Time of reaction	60 min
7	Base pressure	0.06 T
8	Purging gas pressure	0.21 T
9	Deposition pressure	10.00 T
10	Temperature of Vaporizer	185 °C
11	Line temperature	200 °C
12	Temperature of substrate	515 °C
13	Carrier gas (Argon) flow rate	9 %
14	Reacting gas (O_2) flow rate	5 %

5. PHYSICAL PROPERTIES OF THE SAMPLE

The thin films of cobalt oxides are deposited at four different temperatures viz. 490 °C, 515 °C, 535 °C, 565 °C. All the samples deposited on the alumina substrate are well adherent and grayish in color. The thicknesses of the samples were calculated by weight difference method. The table 2 shows the variation of thickness with temperature. Thickness of the cobalt oxide film is maximum at temperature 535 °C.

Table 2 – *Variations of thickness of cobalt oxide thin film at various temperatures*

Sr. No.	Temperature, °C	Thickness, mkm
1	490	0.04205
2	515	0.05600
3	535	0.11120
4	565	0.01905

6. STRUCTURAL ANALYSIS BY XRD

The X-ray diffraction patterns were obtained for all these samples by using Bruker D8 advanced instrument with source $CuK\alpha_1$ with $\lambda = 1.5406$. The angle-2θ is varied in the range between 10° to 90°. The fig. 2 shows number of peaks observed for various temperatures. All the samples are crystalline in nature with cubic in structure. The as deposited samples show dominating peaks these data are compared with the JCPDs-ICDD data no. 78 - 1970 and JCPDs-ICDD data no.78-0431 [14]. The cobalt oxide films obtained on alumina substrate shows more number of highly intensed peaks. The peak corresponding to a plane (311) of Co_3O_4 is most prominent which is observed for all the four samples and same is confirmed with JCPDS-ICDD data no. 78-1970 for Co_3O_4 [14] Few peaks corresponding to the CoO are also observed. The intensity patterns are more or less similar in all the cases. The peak corresponding to plane (222) shows less intensity as compared to other peaks and same is confirmed with JCPDS-ICDD data no. 78-0431 for CoO [14]. The table 3, shows comparison between intensity of no of peaks observed at different temperatures for angle-2θ with ASTM values. Similar results are obtained by D.Barreca et al. [15].

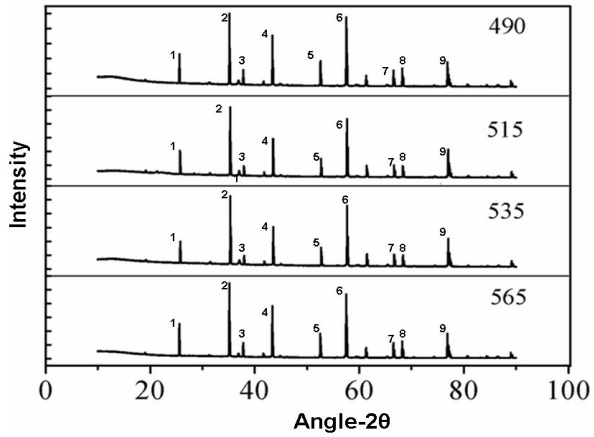

Fig. 2 – *XRD of cobalt oxide thin film deposited on alumina substrate*

Table 3 *– XRD Analysis of cobalt oxide thin films deposited at various temperatures*

Peak No.	Observed data		ASTM data		Plane
	Angle-2θ	Intensity	Angle-2θ	Intensity	
Temperature = 490 °C					
1	26.00	47.2	--	--	--
2	36.25	96.5	36.84	999	(311)
3	38.50	33.2	38.54	080	(222)
4	44.22	68.4	44.80	173	(400)
5	53.35	45.0	--	--	--
6	58.00	88.6	59.34	210	(511)
7	66.50	33.3	65.22	305	(440)
8	68.60	34.0	68.61	002	(531)
9	77.54	45.0	77.52	108	*(222)
Temperature = 515 °C					
1	25.75	45.5	--	--	--
2	36.60.	94.5	36.84	999	(311)
3	38.00	31.0	38.54	080	(222)
4	43.25	61.5	42.38	999	*(200)
5	53.00	43.3	--	--	--
6	58.10	77.2	59.34	210	(511)
7	67.30	37.5	68.61	002	(531)
8	68.50	31.5	68.61	002	(531)
9	77.50	52.0	77.52	108	*(222)
Temperature = 535 °C					
1	26.40	45.5	--	--	--
2	36.65	97.5	36.84	999	(311)
3	38.50	31.0	38.54	080	(222)
4	44.00	62.0	44.80	173	(400)
5	52.50	39.2	--	--	--
6	58.50	77.7	59.34	210	(511)
7	67.25	33.2	68.61	002	(531)
8	69.00	32.0	69.73	001	(442)
9	78.00	46.0	78.39	032	(622)
Temperature = 565 °C					
1	26.25	48.0	--	--	--
2	36.28	97.5	36.84	999	(311)
3	37.75	33.0	38.54	080	(222)
4	44.00	74.8	44.80	173	(400)
5	53.00	43.5	--	--	--
6	58.00	88.0	59.34	210	(511)
7	67.00	33.5	68.61	002	(531)
8	68.50	35.0	68.61	002	(531)
9	77.50	44.8	77.52	108	*(222)

7. MORPHOLOGICAL CHARACTERISTICS

The SEM images were obtained from ESEM Quonta 200 instrument. The SEM images obtained for cobalt oxide thin films on alumina substrate shows more packed grains with increase in size of grain. The hexagonal shape of grains are observed for sample at temperature 515 °C. Above this temperature the grain size found to be decreased. At temperature 565 °C the different shapes of grains are observed. The patterns are shown in fig. 3. The table 4 shows average grain size of deposited thin films observed from observed from SEM images. This is confirmed by Mordi et al. and Nygirnyi et al. [4, 16].

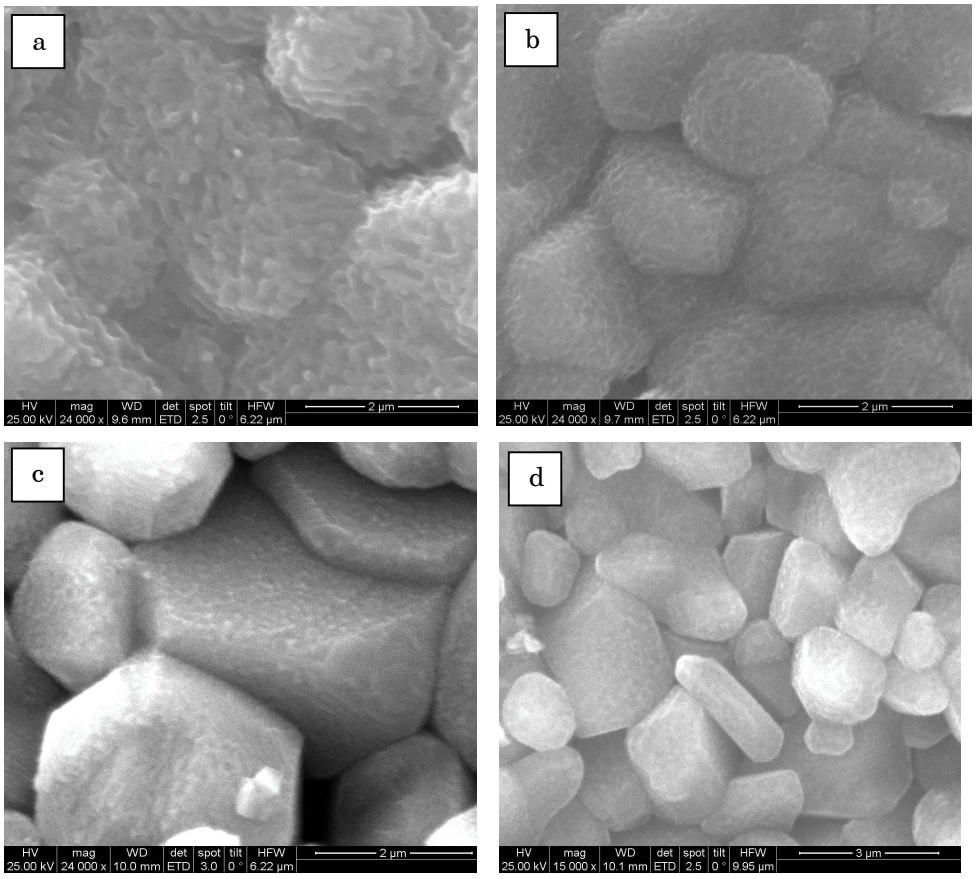

Fig. 3 *– SEM images of cobalt oxide thin film deposited on alumina substrate at* T = 490 °C *(a),* T = 515 °C *(b),* T = 535 °C *(c) and* T = 565 °C *(d)*

8. RAMAN SPECTRA ANALYSIS

The RAMAN Spectra for the cobalt oxide thin films are obtained with the help of "NSOM" instrument. The similar characteristic is observed for all the samples deposited on alumina substrate. Raman spectroscopy shows Fm3m, 225 space groups for cobalt oxide thin films deposited on alumina substrate. The Fig. 4 shows RAMAN Spectra for the cobalt oxide thin films deposited on alumina substrate.

Table 4 – *Average grain size observed from SEM images for various temperatures*

Sr.No.	Temperature, °C	Average grain size, mkm
1	490	2.82
2	515	2.35
3	535	3.26
4	565	2.55

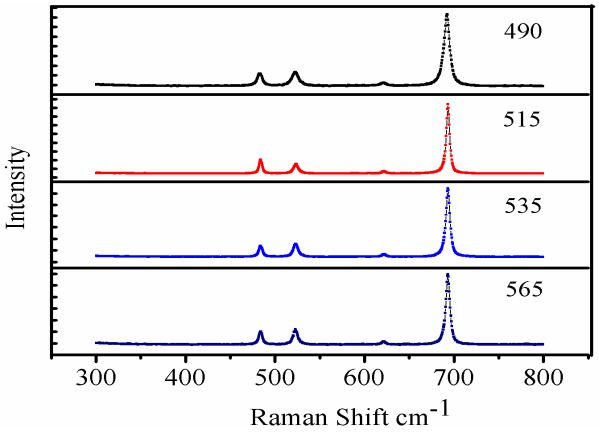

Fig. 4 – *Raman spectra of cobalt oxide thin film deposited on glass substrate*

9. CONCLUSION

The MOCVD technique is most suitable to deposit good quality thin films of cobalt oxide from a cobalt acetylacetonate precursor. The as-deposited samples are well adherent to the substrates. The samples are a crystalline in nature with cubic in structure. The SEM images shows well developed packed grains of cobalt oxide. Raman spectroscopy shows Fm3m, 225 space groups.

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