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STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF COBALT OXIDE THIN FILMS DEPOSITED BY MOCVD TECHNIQUE

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ABSTRACT
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 glass substrate using a cobalt acetylacetonate as precursor. The films were deposited on glass substrate at four different temperatures viz 490^0C, 515^0C, 535^0C, 565^0C. All the deposited samples are crystalline in nature with cubic in structure. The crystalline nano structure is evidenced by X-Ray diffraction (XRD). The SEM images shows well defined closely packed grains for all the samples. Raman spectroscopy has been carried out and it shows Fm3m, 225 space groups for the films. An energy gap of 2.55 eV was calculated by the data obtained from optical absorption spectroscopy.

KEY WORDS: THIN FILM, COBALT OXIDE, XRD, SEM, RAMAN SPECTRA.

INTRODUCTION

Metal oxides have many interesting properties that result in various important applications (Ricter, 2006). Transition metal oxides, a subgroup of metal oxides, are those oxides in which the cation has incompletely filled d or f shells. Tremendous efforts have been devoted in recent years to studying these metal oxides as anomalous behaviors observed in these materials. Consequently, it has increasingly important to understand them in terms of their magnetic, electrical and optical properties (Mordi *et al.,* 2009).

Some of the applications of the transition metal oxides which have generated lots of interest among research groups all over the world include superconductivity in electronics, electromism in smart windows and electrochemical properties in micro batteries and high density batteries (Lampart and Granquist, 1990). Materials based on cobalt oxides have attracted a great interest in view of their potential applications in scientific and technological fields (Jimenez *et al.,* 1995; Hamada *et al.,* 1997; Tanaka *et al.,*, 1996; Mane *et al.,* 2002). They also received attention for the production of solid state sensors heterogeneous catalysts and as an intercalation compounds for energy storage. One of the most important applications is the preparation of electrochromic devices (ECDs) (Granquist, 1995). Such a broad perspective of utilization has increased the importance of synthesis procedure. Among the various synthesis techniques, MOCVD offers many advantages since it offers an accurate tailoring of the system composition, microstructure and morphology by a suitable choice of the precursor compound and deposition conditions (Maruyama and Nakai, 1991).

EXPERIMENTAL

1.1 Growth of Thin Films

Metal organic sources and hydrides inject to the reactor. The sources are mixed inside the reactor and transfer to the deposition area. At the deposition area, high temperature result in the decomposition of sources and other gas, forming the film precursors which are useful for film growth. The film precursors transport to the growth surface, and absorb, 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.

1.2. Deposition of Cobalt Oxide Thin Films

1.2.1 Preperation of Precursor

The 2, 4-pentanedione 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 400C The yellow solution was added drop wise to a solution of 47.6 gm of cobalt (II) chloride hydrate (CoCl2.6H2O) 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 (Jogade *et al.,* 2011).

1.2.2 Cleaning of Substrates

The substrate was washed with 1:1 Hydrochloric acid and double distilled water. Then it was cleaned by ultrasonic cleaner for ten minutes and again washed with double distilled water. 50 ml of acetone was boiled, then with the vapors of acetone substrate were cleaned till entire acetone. After this 25 ml of trichloroethelene was boiled and substrate were cleaned in these vapors, and kept in air-tight container.

1.2.3 Deposition Conditions

The thin film of cobalt oxide was deposited on quartz glass substrate by MOCVD technique. The various deposition conditions and parameters are as follows

Table1. Deposition conditions and Parameters.

No	Parameters	Conditions
1	Precursor for deposition	Cobalt acetylacetonate
2	Substrate for deposition	Glass
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	185^0C
11	Line temperature	200^0C
12	Temperature of substrate	515^0C
13	Carrier gas flow rate	9 %
14	Reacting gas flow rate	5 %

2. RESULT AND DISCUSSION

2.1. XRD Analysis

The x-ray diffraction patterns were obtained for all these samples by using Bruker D8 Advanced instrument with source CuKα1 with λ =1.5406. The 2θ angle is varied from 100 to 90^0. All the samples are crystalline in nature with cubic in structure. The as deposited samples show dominating peaks and these data are compared with the JCPDs-ICDD data no. 78-1970 (JCPDS, 1970). The crystal structure is cubic. The patterns are shown in figure. The information obtained is that the intensity of the peak corresponding to [111] plane and [220] plane is decreasing as the temperature is increased and finally disappears at temperature 535^0C.

Again it starts developing at 565 ^{0}C temp. The pattern shows dominating peak at 2θ angle 38.54^0 corresponding to plane [222] for all the samples. Similar results are obtained by D.Barreca et al. (2001).

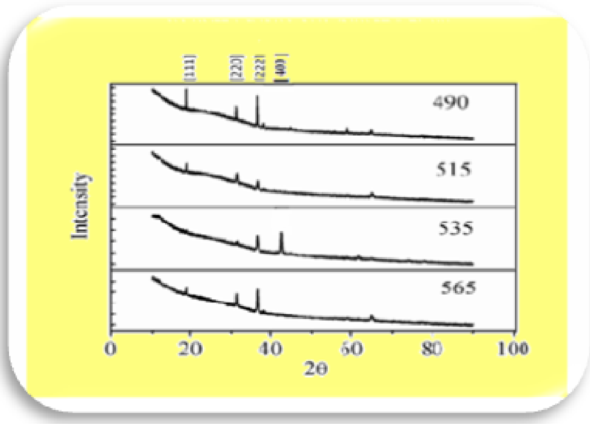

Figure 1. XRD of Cobalt Oxide Thin Film deposited on glass substrate.

2.2 SEM Analysis

Images were obtained from "ESEM Quonta 200" instrument. The photographs of the cobalt oxide films deposited on glass substrate is shown in figure-2. The micrographs shows that the films are composed of course, continuous, uniformly distributed crystalline grains. Which is confirmed by Mordi *et.al.(*2009) and Nygirnyi *et.al.* (2002).

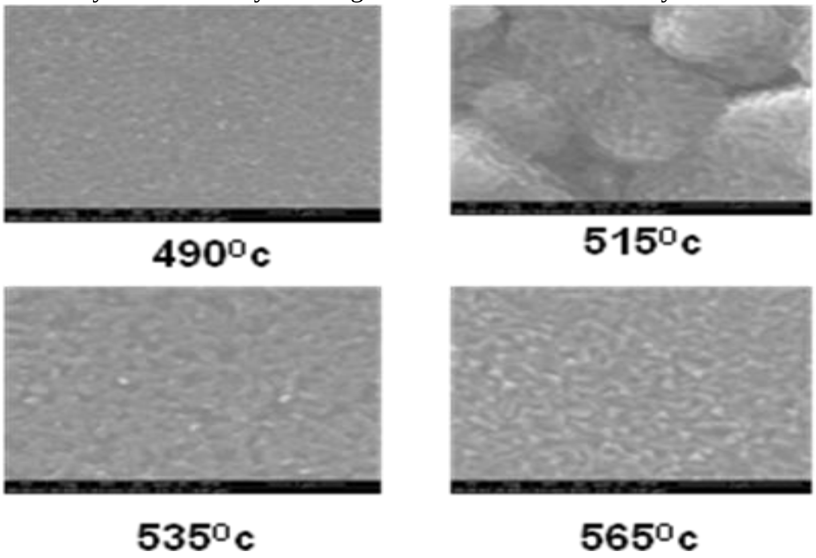

Figure 2. SEM images of Cobalt Oxide thin film deposited on glass substrate at various temperatures.

2.3 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 glass substrate. Raman spectroscopy shows Fm3m, 225 space groups for cobalt oxide thin films deposited on glass substrate.

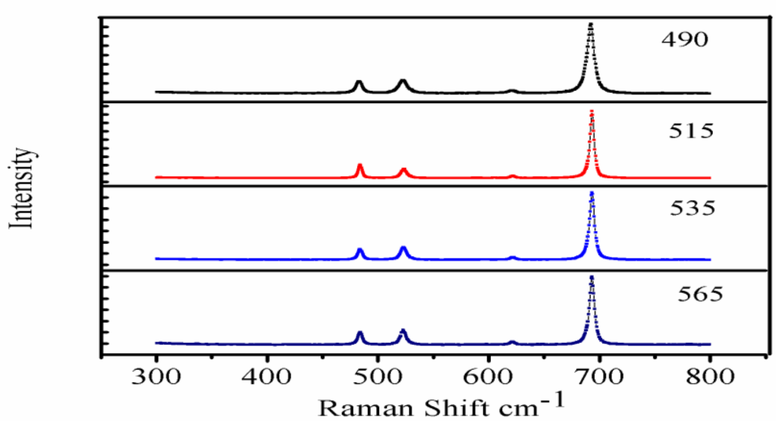

Figure 3. Raman Spectra of Cobalt Oxide Thin Films

2.4 Optical Analysis

The optical studies were performed in the range of 400-2600 nm, a double beam photospectrometer "Hitachi-330" Japan was used for this purpose. The optical band gap was determined from these studies. The optical band gap was determined by plotting the graph of $(\alpha h\nu)^2$ versus (hν) which is shown in figure-4 The observed band gap is 2.55 eV.

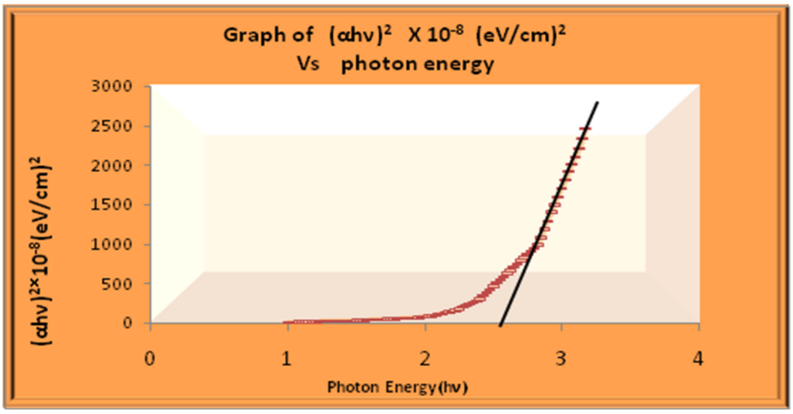

Figure 4. Optical absorption spectra.

CONCLUSION

The thin films of cobalt oxide were successfully deposited from cobalt acetylacetonate precursor by MOCVD technique. The as deposited samples are well adherent to the substrates. The samples are 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. Observed band gap of cobalt oxide film is 2.55 eV.

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