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SPIN COATED NANO STRUCTURED COBALT OXIDE THIN FILMS: SURFACE MORPHOLOGY

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ABSTRACT
Spin coating is currently the predominant technique used for the deposition of uniform thin films with thickness of the order of micrometer and nanometers. The film thickness and other properties depends on the nature of the resin viscosity, drying rate, percent solids, surface tension, etc. and the parameters chosen for the spin process. The main advantage of spin coating is film thickness can be easily changed by changing spin speed, or switching to a different viscosity. The present paper reports the synthesis and morphological studies of cobalt oxide thin films. Thin films of cobalt oxide were deposited by spin coating technique on glass substrate using cobalt acetate as precursor. The films were prepared with different number of layers of cobalt oxide viz, 1,2,3,4 and 5 - layers. The as-deposited samples are uniform and well adherent to the substrate. The thickness of the films is in the range of nanometer and it increases with number of layers. Structural and morphological studies have been carried out by means of XRD and SEM. The XRD reveals that as-deposited cobalt oxide films showed nano-crystalline in nature and cubic in structure. The intensity of peaks corresponding to plane [400] increases as coating of the film increases and maximum intensity peaks for the plane [111] were observed for all the samples. SEM micrographs shows that shape of nanograins are ground-nut type. An energy gap of 2.55 eV was calculated by the data obtained from optical absorption spectroscopy.

KEY WORDS: Nanocrystalline, SEM, Spin Coating, XRD.

INTRODUCTION
Metal oxides have very interesting properties that result in various important applications (Ricter, 2006). Transition metal oxides (TMO), a subgroup of metal oxides are those oxides in which cation has incompletely filled d or f shells (Halper M. S. et al., 2006). Among the various metal oxides, cobalt oxide has been expansively investigated because of their potential applications in many technological fields The crystalline Co_3O_4 film has been reported to be a good anodic coloration material for the supercapacitor application (Granqvsit. et al., 1995; Hee-Sang Shim et al 2008). There are several methods to grow thin films namely, vaccum evaporation, sputtering, molecular beam epitaxial, laser assisted vaccum evaporation (Monk et al., 1995).

Metal oxide chemical vapor deposition (MOCVD) is also one of the deposition techniques (Jogade et al., 2011; Sutrave et al., 2012). These processes are energy intensive and require high temperature. Hence researchers, studied wet chemical process from the economic considerations and some other advantages namely, simplicity and low temperature processing etc. spin coating , is widely applied amongst many wet chemical processes namely, chemical bath deposition(Monk et al., 1995), electrodeposition, spray pyrolysis, sol gel process, etc.(Sathaye et al., 2003)

EXPERIMENTAL
Substrate Cleaning
Before each deposition cleaning of substrate was carried in following sequence

- The substrates were scrubbed by using detergent. Washed with distilled.
- Kept in acetone for 2 hour.
- Washed with double distilled water and dried and kept in air tight container.
- This process was used to dislodge the dirt on the glass and also to ensure that the substrate surface were free from surface contamination and defects.

Preparation of precursor
A 2.456 gm of Cobalt Acetate was added into 100ml distilled water. The 2ml of isopropyl alcohol was added into the above solution. The color of the solution was light pink in color. The solution was heated on a hot plate for few minutes. After 24 hours the solution was clear with dark pink in color. The Figure.1 shows procedure for preparation of precursor.

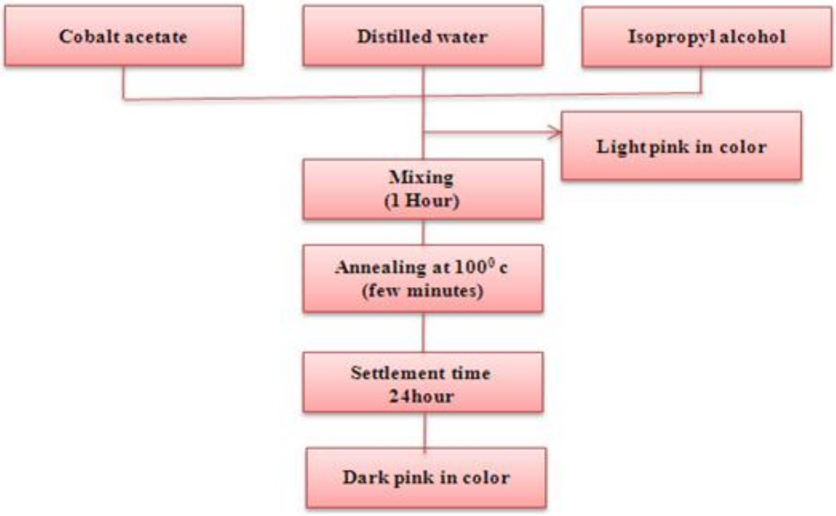

Figure 1. Flow diagram for the preparation of precursor

Preparation of the film using spin coating technique.

Key stages of spin coating: The physics of spin coating can be effectively modeled by dividing the whole process into four stages sketched in Figure. 2, which are deposition, spin-up, evaporation and repeat the prior stages for multiple layers of the film. To dry the film, the film was kept in furnace for 5 minutes and temperature of the furnace was set to 400^0 C.

Deposition*:* During this stage, solution is allowed to fall on rotating substrates from microsyrings and the substrate is accelerated to the desired speed. Spreading of the solution takes place due to centrifugal force and height is reduced to critical height. This is the stage of delivering an excess of the liquid to be coated to the surface of the substrate a portion of which is immediately covered.

Spin-up and stable fluid outflow: The second stage is when the substrate is accelerated up to its final, desired, rotation speed. This stage is usually characterized by aggressive fluid expulsion from the wafer surface by the rotational motion ultimately, the wafer reaches its desired speed and the fluid is thin enough that the viscous shear drag exactly balances the rotational accelerations. Depending on the surface tension, viscosity, rotation rate, *etc*., there may be a small bead of coating thickness difference around the rim of the final wafer. If the fluid thickness is initially uniform across the wafer then the fluid thickness profile at any following time will also be uniform.

Evaporation*:* When spin-off stage ends the film drying stage begins. During this stage centrifugal out flow stops and further shrinkage is due to solvent loss. This results in the formation of thin film on the substrate. The fourth stage is when the substrate is spinning at a constant rate and solvent evaporation dominates the coating thinning behavior.

Multilayer coating: To increase the number of layers of thin film, the first three stages can be repeated.

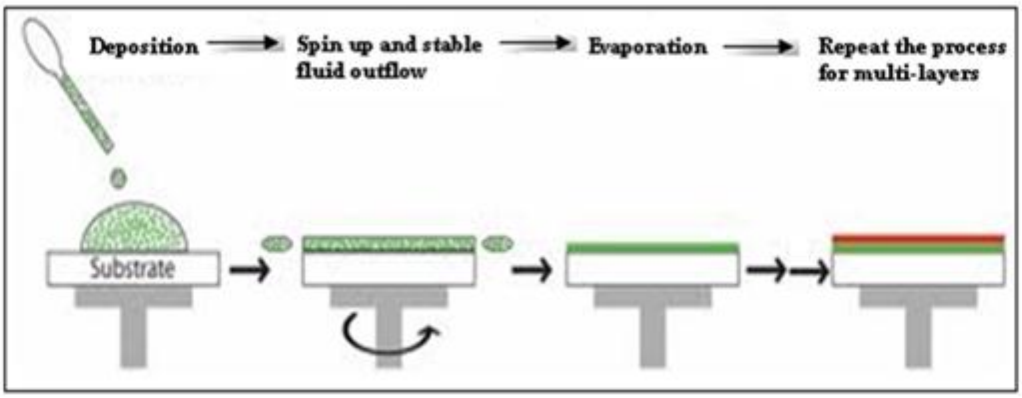

Figure 2. Spin coating procedure for deposition of thin films

Deposition conditions

The thin films of cobalt oxides are deposited with number of layers. The different deposition conditions and parameters are as shown in table 1.

Table 1. Deposition parameters and conditions

Sr. No	Parameters	Conditions
1	Precursor	Cobalt acetate
2	Substrate	Glass
3	Spin Time	300 sec
4	Spin Speed	3000 RPM
5	Temperature Of furnace	400^0C
6	Annealing Time	5 min

RESULT AND DISCUSSION

Thickness of the film

All the samples deposited on the glass substrate are well adherent and dark brown in color. The thicknesses of the samples were calculated by weight difference method. Following graph (Figure. 3) shows the variation of thickness with different layers. Thickness of the cobalt oxide film is maximum for the film with five coatings.

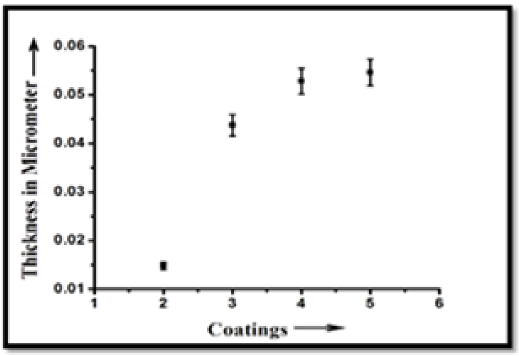

Figure 3. Variation of film thickness with number of coatings

Structural Analysis by XRD

The X-ray diffraction patterns were obtained for all these samples by using Bruker D8 advanced instrument with source CuKα1 with λ =1.5406 A^0. The angle-2θ is varied in the range between 10^0 to 80^0. The figure-4 shows the XRD patterns for cobalt oxide thin films. All the samples are nanocrystalline in nature with cubic in structure. The observed data of XRD is compared with standard JCPDS card (JCPDS, card number-76-1802) shown in table. 2. The intensity of peaks corresponding to plane [400] increases as coating of the film increases and maximum intensity peaks for the plane [111] were observed for all the samples.

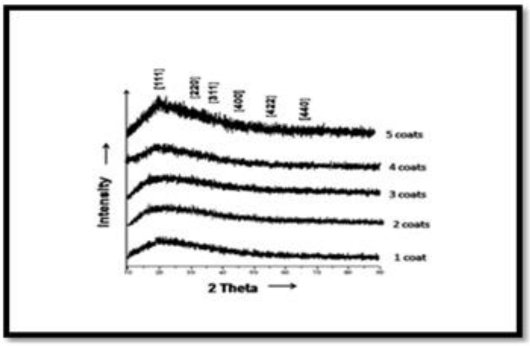

Figure 4. XRD of deposited thin films on glass substrate

Table 2. XRD analysis of cobalt oxide thin films for different layers

Sr.No	Standard JCPDS data For Co_3O_4 Card No 76-1802			Observed data for cobalt oxide thin films from XRD									
				Single coat		Two coats		Three coats		Four coats		Five coats	
	2θ	Plane	Int	2θ	Int	2θ	Int	2θ	Int	2θ	Int	2θ	Int
1	19.028	111	17.7	18.9	82.14	19.02	87.09	18.92	81.05	18.96	100	18.92	96.43
2	31.318	220	32	31.2	78.57	31.42	83.87	31.32	62.16	31.26	70	31.32	100
3	36.903	311	100	36.8	73.89	36.98	51.61	36.8	100	37.02	40	36.8	64.26
4	44.880	400	20.5	44.96	60.71	44.92	67.74	44.9	78.37	44.78	57.5	44.9	78.57
5	55.745	422	8.2	55.62	74.99	55.6	45.15	55.64	64.86	55.64	57.5	55.68	92.85
6	65.349	440	36.1	65.28	100	65.4	100	65.42	51.47	65.48	37.5	65.42	53.57

Morphological Analysis by S

As explained in the XRD pattern the SEM images of cobalt oxide shows nano grains diffused on glass substrate. The figure-5 shows SEM micrographs for cobalt oxide thin films for different layers. The SEM photographs show that after two layers new grains are formed. The SEM photographs of four and five layers reveals grains are little bit elongated appears like groundnut in shape and shows closely packed grains.

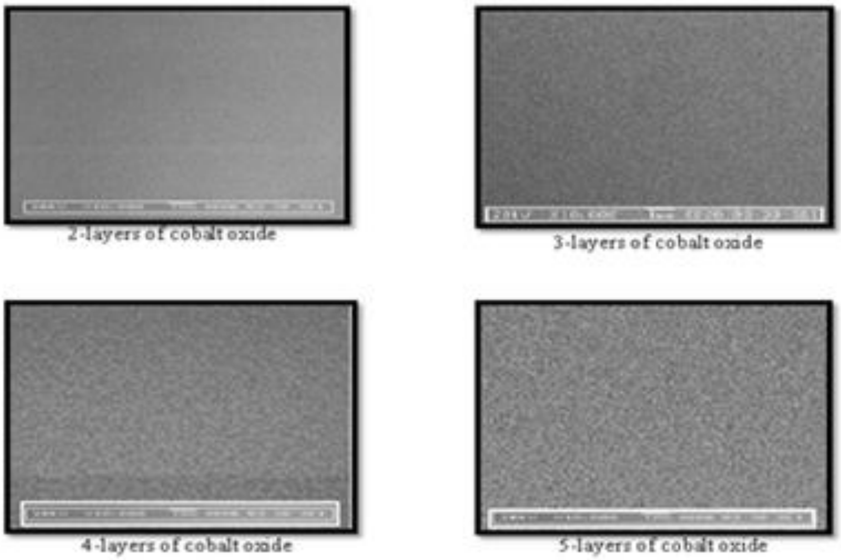

Figure 5. SEM analysis of cobalt oxide thin films deposited for different layers

As the coating layers are increased the gap between the two grains is filled up by new cobalt oxide grains and grains become closer to each other.

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 $(h\nu)$ which is shown in figure-6. The observed band gap is 2.55 eV.

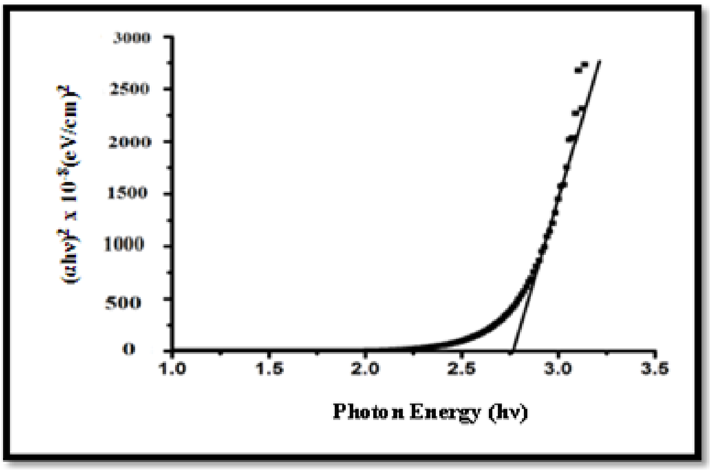

Figure 6. Optical absorption spectra

CONCLUSION

The spin coating technique is most suitable to deposit good quality thin films of cobalt oxide. The as-deposited samples are well adherent to the substrates and dark brown in color. Thickness of the film increases with number of layers. The XRD reveals samples are a nano-crystalline in nature with cubic in structure. The SEM images shows groundnut shaped and closely packed grains of cobalt oxide. As the coating layers are increased grains become closer to each other due to formation of new cobalt oxide grains**.** The average grain size is in the order of nanometer. From the graph the observed band gap of cobalt oxide film is 2.55 eV.

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