

## Structural Characterization and Optical Properties of cobalt oxide Thin Films

\*Zohra Nazir Kayani<sup>1)</sup>, Saliha Arshad<sup>1)</sup>, Saira Riaz<sup>2)</sup>, Rehana Zia<sup>1)</sup> and Shahzad Naseem<sup>2)</sup>

<sup>1)</sup> Lahore College for Women University, Lahore-54000, Pakistan

<sup>2)</sup> Centre of Excellence in Solid state Physics, University of the Punjab, Lahore-54900 Pakistan

<sup>\*1)</sup> [E-mail:zohrakayani@yahoo.com](mailto:zohrakayani@yahoo.com)

### Abstract

A Sol-gel dip coating route has been employed to synthesize cobalt oxide thin films on glass substrates. The obtained films are characterized by X-ray diffraction (XRD), UV-VIS spectrophotometer, vibrating sample magnetometer (VSM), Scanning Electron Microscope and Fourier Transform Infra Red (FTIR) spectroscopy. The films are identified as  $\text{Co}_3\text{O}_4$  by FTIR. XRD further confirmed  $\text{Co}_3\text{O}_4$  phase. Upon increasing withdrawal speed of substrate, the transmission and band gap decreases due to increase in film thickness. Thin films show room temperature ferromagnetism and magnetic properties enhance by increasing thickness of thin films. SEM shows porous surface of films.

### 1. INTRODUCTION

Cobalt oxide is a metal oxide material with various industrial applications such as thin film catalysis, electro-chemical capacitor (Barrera 2001), and gas and humidity sensors (Ando 1997). Cobalt oxide is also used in solar cell and memory devices (Avila 2004, Voges 1998).

This paper reports efforts which are taken to study new method of fabrication of nano-crystalline  $\text{Co}_3\text{O}_4$  thin films by simple and cheap sol-gel dip coating method and to observe the influence which different withdrawal speeds of substrate have on the structural, optical and magnet properties of cobalt oxides thin films.

### 2. EXPERIMENTAL

#### 2.1. FILM PREPARATION

The Sol preparation was carried out by using Co (II) nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), water, acetic acid and  $\text{NH}_4\text{OH}$ . Sol thus obtained was stirred for 4 hours at room temperature. Sol was aged for 24 hours before deposition of thin films.

Cobalt oxide thin films were deposited on glass substrates utilising the sol-gel dip coating technique. Before fabrication process, the substrates were thoroughly cleaned.

The deposition process was repeated by changing withdrawal speed 100 and 200 mm/s. Then thin films were dried at room temperature. Cobalt oxide thin films were calcined at 700 °C for 4 hours.

## 2.2. CHARACTERIZATION TECHNIQUES

### 2.2.1 FTIR

Figure 1 shows the FTIR spectrum of cobalt oxide in the 2000–400  $\text{cm}^{-1}$  by FTIR Model M 2000 Midac USA. FTIR analyses revealed the presence of 4 main bands. The absorption bands located at 489.8, 702, 829.2 and 983.5  $\text{cm}^{-1}$  are characteristic of the optical vibration modes of  $\text{Co}_3\text{O}_4$  (Nkeng 1996, Ahmed 2005). On the basis of FT-IR spectrum, formation of  $\text{Co}_3\text{O}_4$  thin films by sol-gel dip coating is confirmed.

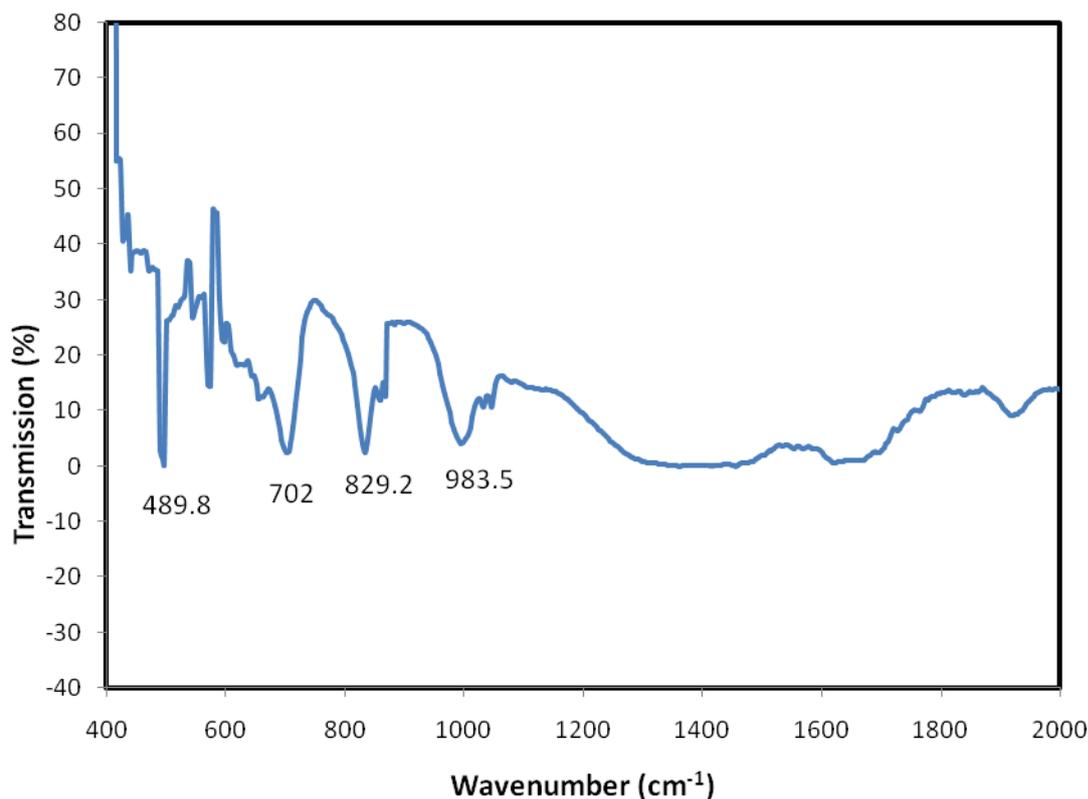


Fig. 1 FTIR spectrum of  $\text{Co}_3\text{O}_4$

### 2.2.2 X-RAY DIFFRACTION

Structural analysis of thin films of cobalt oxide deposited at withdrawal speed 100 and 200 mm/s were carried out by X-ray diffractometer Bruker XRD model D8 Discover (Germany). It showed amorphous nature of thin films at 100 mm/s but at 200 mm/s

withdrawal speed film has crystalline nature with a peak at  $36.95^\circ$  (Fig. 2). This peak is characteristic of  $\text{Co}_3\text{O}_4$  phase.

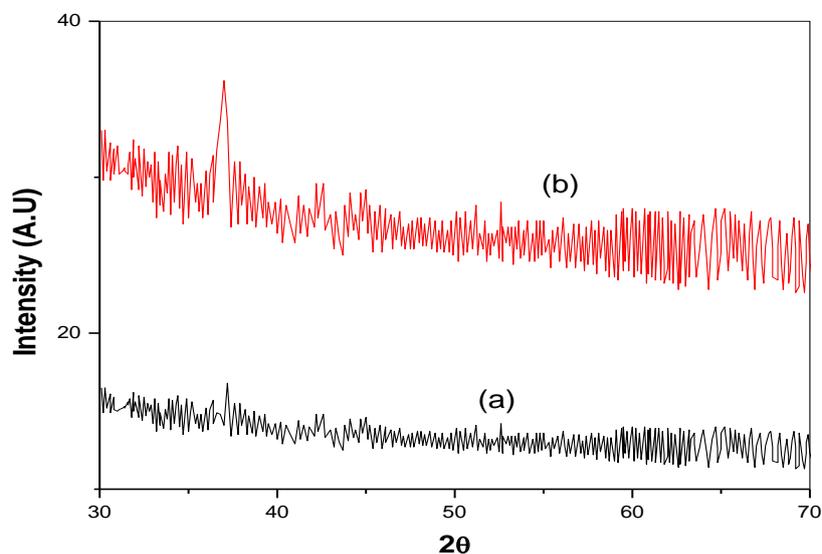


Fig. 2 XRD of thin films of cobalt oxide deposited at withdrawal  
Speed (a) 100 and (b) 200 mm/s

### 2.2.3 OPTICAL RESULTS

The transmission curves in the UV-VIS region of the spectrum by Hitachi U 2800 for cobalt oxide thin films deposited at 100 and 200 mm/s withdrawal speeds are shown in Figure 3. It shows that transmission decreased with increase in withdrawal speed.

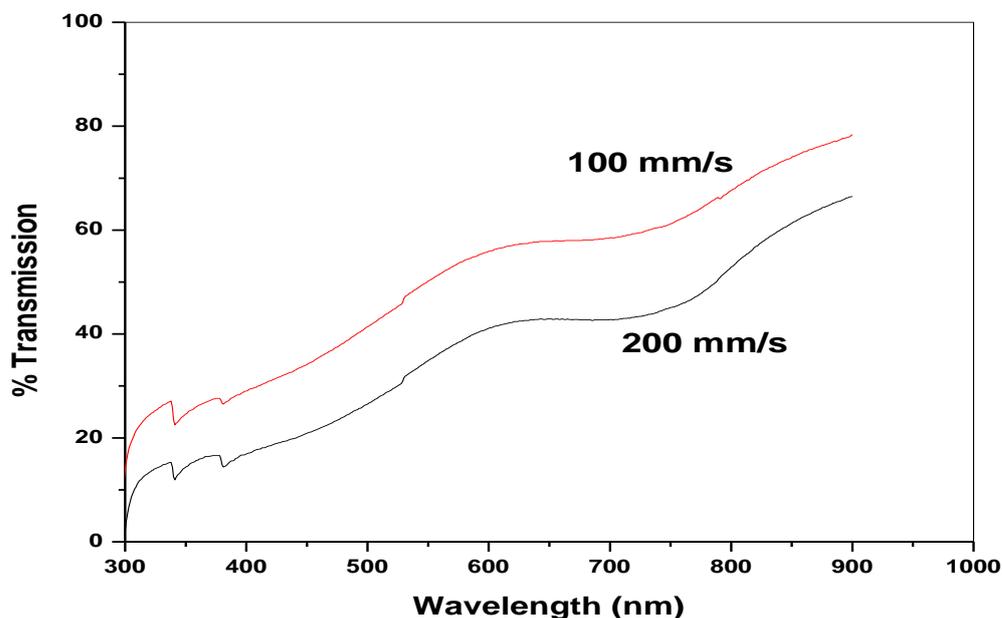


Fig. 3 Transmission spectrum of thin films of Co<sub>3</sub>O<sub>4</sub> deposited at 100 and 200 mm/s withdrawal speed of substrate.

Direct band gaps have been deduced from the plots of  $(\alpha h\nu)^2$  Vs  $h\nu$  as shown in Figure 4. These direct optical band gaps are 2.30 eV for thin film deposited at 100 mm/s while this value is 2.18 eV for 200 mm/s withdrawal speed of substrate. This value of band gap is in agreement with other researcher band gap values (Drasovean 2006, Kadam 2001).

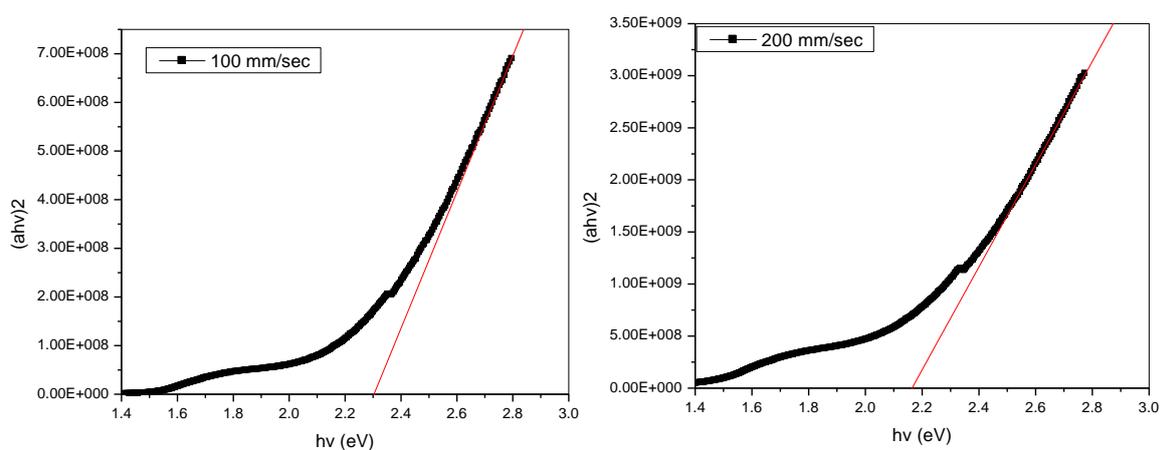


Fig. 4 Plots of  $(\alpha h\nu)^2$  against  $h\nu$  of Co<sub>3</sub>O<sub>4</sub> thin films prepared at withdrawal speed 100 and 200 mm/s.

## 2.2.4 MAGNETIC PROPERTIES

Magnetic hysteresis loops shown in Figure 5 were registered by using Lake Shore Vibrating sample magnetometer (VSM). From the hysteresis loop shown in figure 5, saturation magnetization ( $M_s$ ) was 1.492 and 2.475  $\text{emu}/\text{cm}^3$  while coercivity was found to be 93.3 Oe and 9 Oe for thin films deposited at 100 and 200 mm/s withdrawal speed of substrate. It shows that with the increase in withdrawal speed coercivity of thin films decreases while saturation magnetization increases.

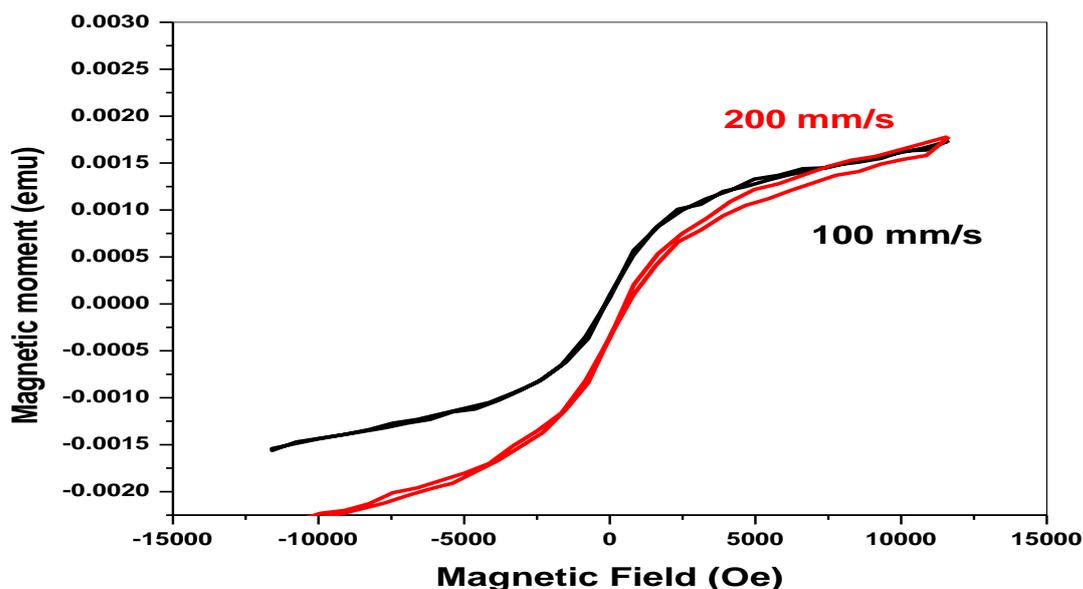


Fig.5 Hysteresis loops for thin films of  $\text{Co}_3\text{O}_4$  deposited at withdrawal speed 100 and 200 mm/s.

## 2.2.5 SURFACE MORPHOLOGY

Fig. 6 shows surface morphology of the cobalt oxide films deposited at withdrawal speed of 100 and 200 mm/s studied by using scanning electron microscopy (SEM) (S-3400N, Hitachi). The thin film deposited at 100 mm/s shows relatively denser surface morphology comprising of smaller grains (Fig. 6a) while the cobalt oxide samples deposited at the withdrawal speed 200 mm/s represent surface with larger grains (Fig.6b). The cobalt oxide thin films surface is well covered free of any cracks. This type of surface morphology increase surface area.

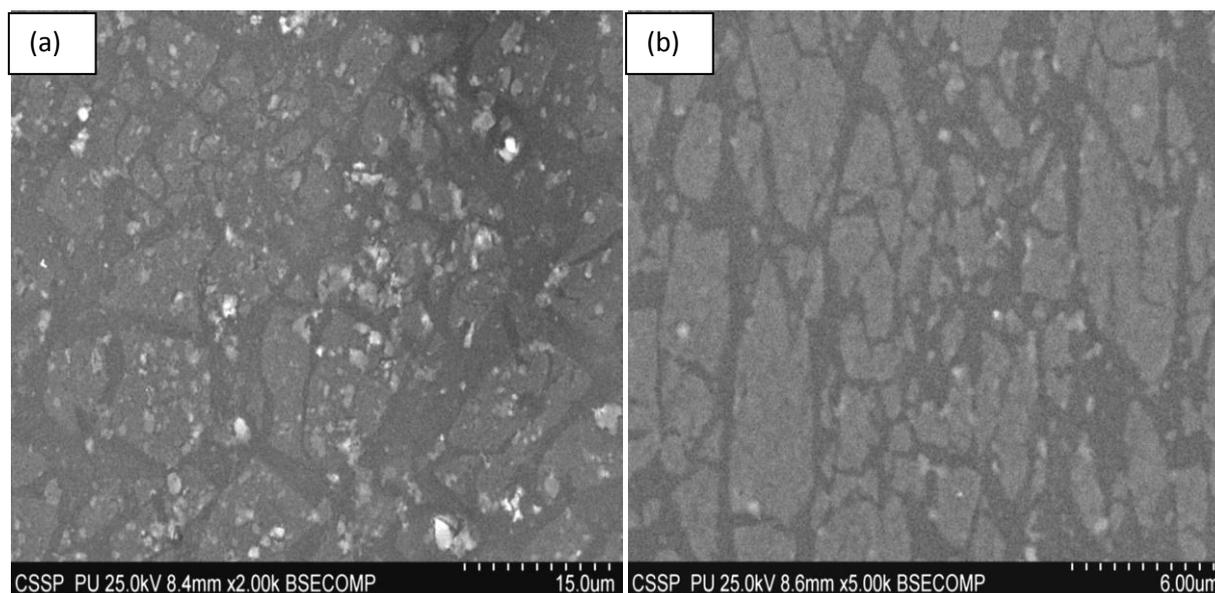


Fig. 6 Surface morphology of thin films of cobalt oxide deposited at withdrawal Speed (a) 100 and (b) 200 mm/s

### 3. CONCLUSIONS

Cobalt oxide thin films were prepared using a Sol-gel dip-coating method. The presence of  $\text{Co}_3\text{O}_4$  phase was predicted by FTIR studies and confirmed by XRD results. Thin films have direct band gaps which decreases with increase in withdrawal speed of substrate. With increase of withdrawal, magnetic properties of thin films are enhanced with decrease in coercivity and increase in saturation magnetization. SEM images showed that surface is well covered with large grains with no cracks.

### REFERENCES

- Ahmed, R. S. and Kofinas, P. (2005), "Magnetic properties and morphology of block copolymer-cobalt oxide nano-composites," *J. Magn. Mag. Mater.*, Vol. **288**, 219-223.
- Ando, M. Kobayashi, T. Haruta, M. (1997), "Combined effects of small gold particles on the optical gas sensing by transition metal oxide films," *catal. Today*, Vol. **36**, 135- 141.
- Ando, M. Kobayashi, T. Iijima, M. Haruta, M. (1997), "Optical recognition of CO and H<sub>2</sub> by use of gas sensitive Au- $\text{Co}_3\text{O}_4$  composite films," *J. Mater. Chem.* Vol, **7**, 1779-1783.
- Avila, A. Barrera, E. Huerta, L. and Muhl, S. (2004), "Cobalt oxide films for solar selective surfaces, obtained by spray pyrolysis," *Sol. Energy Mater. Sol. Cells*, Vol. **82(2)**, 269-278.
- Barrera, D. Massignan, C. Daolio, S. Fabrizio, M. Piccirillo, C. Armelao, L. and Tondello, E. (2001), "Composition and Microstructure of Cobalt Oxide Thin Films Obtained from

a Novel Cobalt(II) Precursor by Chemical Vapor Deposition," *Chem. Mater.*, Vol. **13 (2)**, 588-593.

Drasovean, R. Monteiro, R. Fortunato, E. and Musat, V. (2006), "Optical properties of cobalt oxide films by a dipping sol-gel process," *J. Non-Cryst. Solids*, Vol. **352**, 1479-1485.

Kadam, D. L. Patil, S. P. (2001), "Thickness-dependent properties of sprayed cobalt oxide thin films," *Mater. Chem. Phys.*, Vol. **68**, 225-232.

Nkeng, P. Koenig, F. J. Gautier, L. J. Chartier, P. and Poillerat, G. (1996), "Enhancement of surface areas of  $\text{Co}_3\text{O}_4$  and  $\text{NiCo}_2\text{O}_4$  electrocatalysts prepared by spray pyrolysis," *J. Electroanal. Chem.*, Vol. **402 (1-2)**, 81-89.

Voges, de Gronckel, F. H. Schreiber, R. C. and Grünberg, P. (1998), "Spin valves with  $\text{CoO}$  as an exchange bias layer," *J. Magn. Magn. Mater.* Vol. **190(3)**, 183-186.