



INVESTIGATING THE EFFECT OF COPPER IMPURITY AND HEATING ON THE SURFACE MORPHOLOGY, NANOSTRUCTURAL AND OPTICAL PROPERTIES OF CU DOPED COBALT OXIDE THIN FILMS

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KEYWORDS

Cobalt oxide, thin film, spray pyrolysis

ABSTRACT

Cobalt oxide thin films with different percentages of copper as doping material were deposited on glass substrates kept at 450°C by using spray pyrolysis method. Cu/Co mole ratios were selected as 0.0, 0.05, 0.1, and 0.15. For investigating the structure, morphology and optical properties of thin films, X-ray diffraction (XRD), scanning electronic microscope (SEM) and UV-vis spectra were used. Increasing dopant and heating caused to increase the crystal size. The optical band gap was increased according to the crystalline size enhancement.

INTRODUCTION

Cobalt oxide is one of the metal oxides that were extensively noticed because of its industrial application such as solar selective absorber [1], catalysts [2], sensors [3] and pigment for glasses and ceramics. Cobalt has three oxidation states, the cobaltous oxide (CoO), the cobaltic oxide (Co₂O₃) and the cobaltic oxide (Co₃O₄). Cobalt oxide thin film can be prepared by various methods such as electron beam evaporation [3], sol-gel [4] and spray pyrolysis technique [1,5]. In this work, spray pyrolysis method was applied to prepare copper doped cobalt oxide thin films with different percentage of copper.

EXPERIMENTAL

Aqueous solutions of cobalt chloride (CoCl₂.6H₂O) and copper chloride (CoCl₂.2H₂O) with different Cu/Co mole ratio = 0.0, 0.05, 0.1, 0.15 were deposited on glass substrate. Spray rate and carrier gas pressure were 6cc/min and 3atm, respectively. Glass substrate temperature was kept at 450°C during deposition and distance between the nozzle and substrate was 30 cm. Thin films were heated at 300°C for 3 hours in vacuum.

Structural information of samples was carried out by D8 advance Bruker X-ray diffractometer. (LEO 1450 VP system) scanning electron microscope was used to observe morphology of the films. The optical characterization of the samples was investigated by LABOMET-4057 UV-vis spectrophotometer.

RESULT AND DISCUSSION

Structural properties

XRD pattern of films before and after heating reveal formation of Co₃O₄ cubic phase in all samples and CuCoO₂ in samples that include Cu. Because of heating, major XRD peaks became sharper and improvement in the crystallinity can be observed. Also, by increasing dopant and heating, no other phase of Cobalt oxide was emerged. This shows that Co₃O₄ phase is stable. From the XRD peaks and by using Scherrer equation, the average grain size was calculated for different samples.

Table 1. Result of X-ray pattern for Cu-Co₃O₄ thin films and comparison between the nanocrystalline size calculated by Scherrer equation (a) before and (b) after heating.

Sample	mole ratio Cu/Co	(a)		
		2θ	β	D (nm)
S1	0	19.275	0.376	21
S2	0.05	18.85	0.324	25
S3	0.1	18.775	0.255	32
S4	0.15	18.85	0.281	29

Sample	mole ratio Cu/Co	(b)		
		2θ	β	D (nm)
S'1	0	18.8	0.372	22
S'2	0.05	19.15	0.371	22
S'3	0.1	18.725	0.213	38
S'4	0.15	18.75	0.219	37

Tables 1-a and 1-b show average grain size which are varied between 21-38 nm for different samples. They were increased after heating and also by increasing dopant.

Surface morphology

Fig. 1 shows SEM images of thin films. It exhibits the morphology and grain size of less than 100 nm. Furthermore, growth in the grain size by addition of copper and also by heating the films is also indicated.

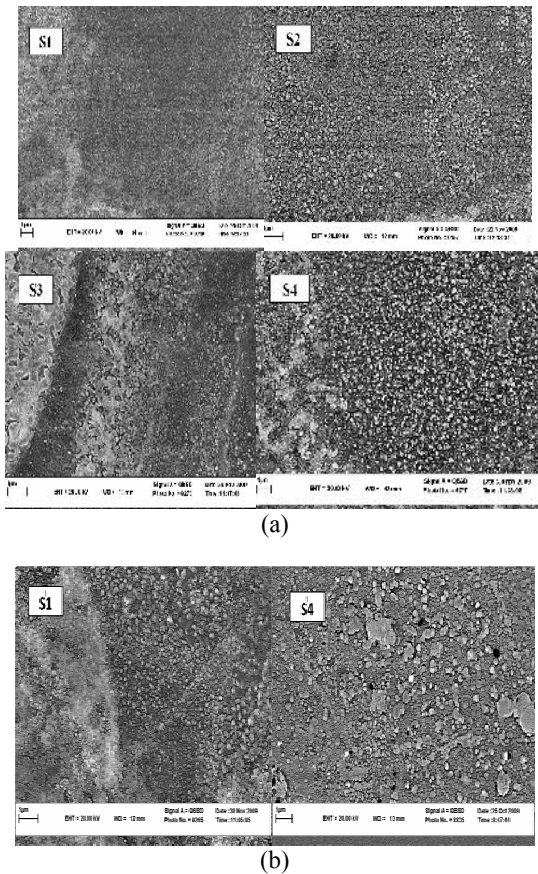


Fig.1. SEM images of Co doped Co₃O₄ with different Cu/Co mole ratios prepared by spray pyrolysis. (a) before heating, (b) after heating

Optical properties

Cobalt oxide has two band-gap values in the visible wavelength. The higher band gap value is related to the intrinsic transition and lower value is related to break the lattice symmetry and orbit-spin effect. The optical band gap for thin films was calculated using curves that were plotted by Tauc famous equation. The result of calculation for optical gap is presented in Table 2.

Band gap was increased by enhancing dopant. Also, heating caused to increase optical band gap except for sample No. 1.

Table 2. Optical band gap of thin films calculated from Tauc equation.

Sample No.	Eg1(eV)	Eg2(eV)
S1	1.43	2.01
S2	1.4	1.99
S3	1.36	1.97
S4	1.34	1.96

Sample No.	Eg1(eV)	Eg2(eV)
S'1	1.45	2.03
S'2	1.40	1.99
S'3	1.35	1.95
S'4	1.33	1.93

Conclusion

XRD pattern of films indicate formation of Co₃O₄ with cubic structure in all samples and CuCoO₂ in samples that include Cu. Increasing dopant and heating caused to increase crystalline size. Optical band gap was also increased by increasing both copper impurity and heating.

Acknowledgment

The authors are greatly acknowledge the financial support of the project by NIGC-Khorasan branch.

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