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RESEARCH ARTICLE

Optical Conduct of Nanostructure Co_3O_4 rich Highly Doping Co_3O_4: Zn Alloys

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Abstract

The spray pyrolysis technique (SPT) was used because it is simple, low cost and less equipment. Structural, morphological and optical properties of pure Co_3O_4 and doping 1% and 3% Zn: Co_3O_4 were anayzed by X- Ray diffraction (XRD), Atomic force Microscope (AFM) and UV-visible Spectroscopy. XRD indicate a polycrystalline structure with AFM images shows that the films was discontinuous surface with spherically grains increase from (70 to 84 nm) with increase doping from 1% to 3%. The energy gap Eg was decreased from 2.75 to 1.64 eV when doping increase.

Keywords: *Co_3O_4, Zn: Co_3O_4 thin films, XRD, AFM and optical characterizations.*

Introduction

Metal oxide semiconductor materials have attracted wide attention from researchers as sensitive materials for detecting toxic and harmful gas and also other applications [1, 2]. Cobalt oxide has gained much work in last year's according to their prospect application in many fields. Like solar selective, gas sensors, heterogeneous catalysts [3, 7], in lithium-ion batteries [8] and magnetic applications [9].Cobalt oxide presents various crystalline forms such as Co O, Co_2O_3 and Co_3O_4 [10].

Co_3O_4 thin films were deposited via different methods like, such as sputtering, ALD, CVD, sol-gel, PLD, CBD, and SPT [11, 18]. This work is subjected to prepare cobalt oxide and study their characteristics.

Experimental

Films were deposited onto glass substrates via SPT. Solution contain 0.1 M cobalt chloride. (Zn $(CH_3COO)_2 \cdot 2H_2O$) was added as a dopant agent of 1% and 3%. After many tests, they arrival at following optimal parameters: substrate temperature 400°C, space between spout and substrate was 29cm. Flux average 6 mL/min, spray rate was 10s followed by 2 min to avoid cooling. Carrier gas was Nitrogen. Structural parameters were obtained by XRD (Shimadzu, model: XRD-6000, Japan) using CuKα radiation (λ = 0.15406 nm). AFM (AA 3000 Scanning Probe Microscope) were utilized to study surface of the deposited films.

Results and Discussion

Figure 1 depicts XRD patterns of pure Co_3O_4 and doping in 1% and 3% Zn: Co3O4 thin films. All films were polycrystalline with orientation over (220) and (311) (JCPDS No. 41-1445). Crystallite sizes (D) of films were evaluated via Scherrer's formula equation 1 [19, 20].

$$D = \frac{k\lambda}{\beta cos\theta} \qquad ------1$$

Where β is full width at half- maximum (FWHM), λ is X-ray wavelength (1.5406Å) and θ is Bragg angle.

Dislocation density δ and strain Ɛ for preferential reflection (113) are calculated using the Eq. (2) and (3) [21].

$$\delta = 1/D^2 \qquad ------2$$

$$\varepsilon = \beta cos\theta/4 \qquad ------3$$

Table 1shows the D increased upon doping it is attributed to the change in concentration of doping.

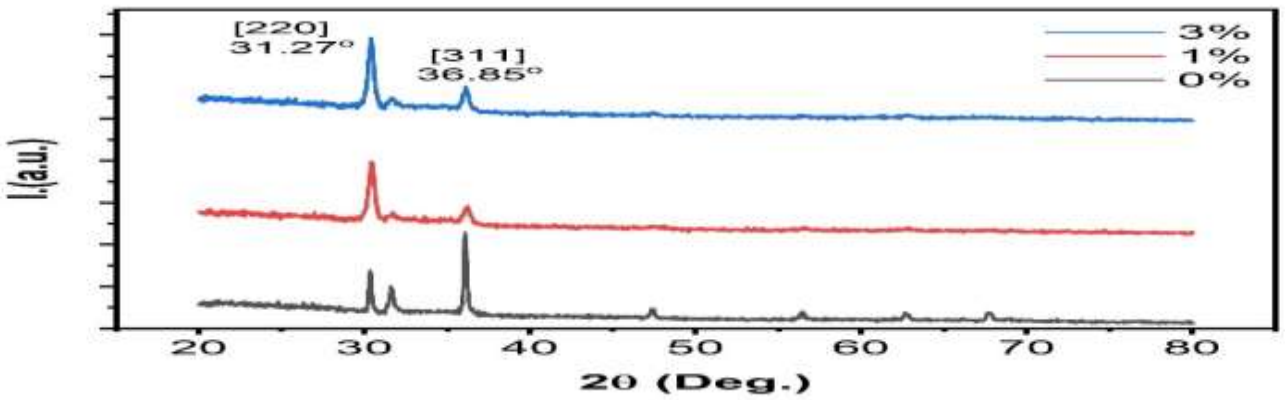

Fig.1: XRD patterns of prepared films

Table 1: Structural data of prepared films

Zn (%)	(hkl)	2Θ	a (Å)	B (Deg.)	D (nm)	ε x10^{-4}	(δ) 10^{e-4} (1/nm^2)
zero	(220)	31.27	8.083	0.207	7.97	9.01	6.29
1	(220)	31.27	8.083	0.4	17.25	17.427	23.50
3	(220)	31.27	8.083	0.41	19.64	18.29	25.91

Optical Analysis

The optical transmission spectra of Co_3O_4 various dopants in Zn: Co_3O_4 thin films are as shown in the fig 2. All films are highly transparent in visible region. Transmittance more than 80 % was observed for all films in visible region. This high transmittance may be due to the enhancement in the crystallinity.

Spectral absorption coefficient α can be calculated by using Eq. 4 as illustrated in Fig.3.

Energy gap of semiconductor materials can be deduced from transmission was determined by the equation 4 [22,23]. E_g values found to vary from (1.64–2.75) eV [24, 25]. It can notice that band gap value changes slightly with doping. Fig. 4 shows the $(\alpha hv)^2$ versus (hv).

$$\alpha hv = A(hv - E_g)^n \qquad -------- (4)$$

$$\alpha = \ln(1/Td) \qquad -------- (5)$$

Where a constant, hv is the photon energy and n is equal to 0.5 direct transitions.

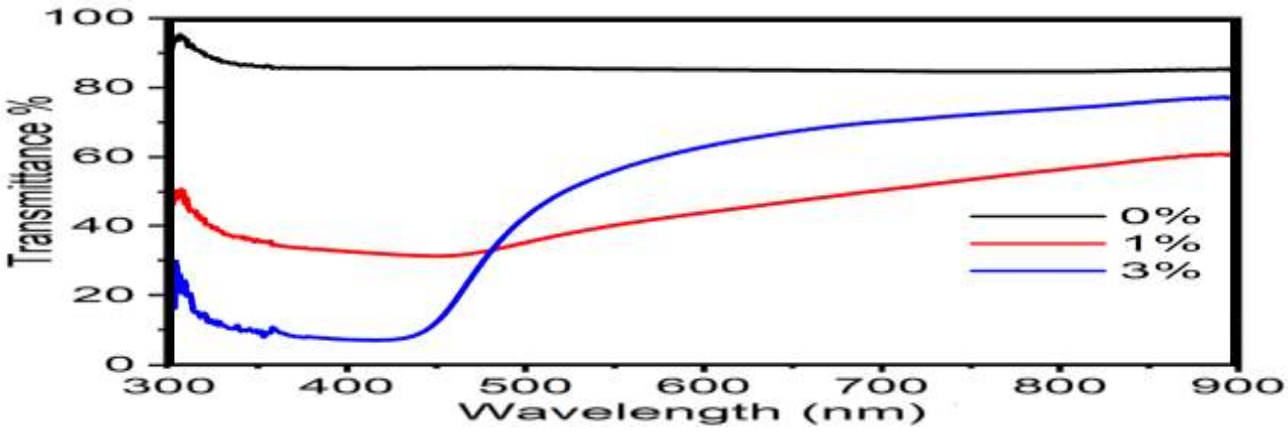

Figure 2: transmittance versus wavelength of prepared films

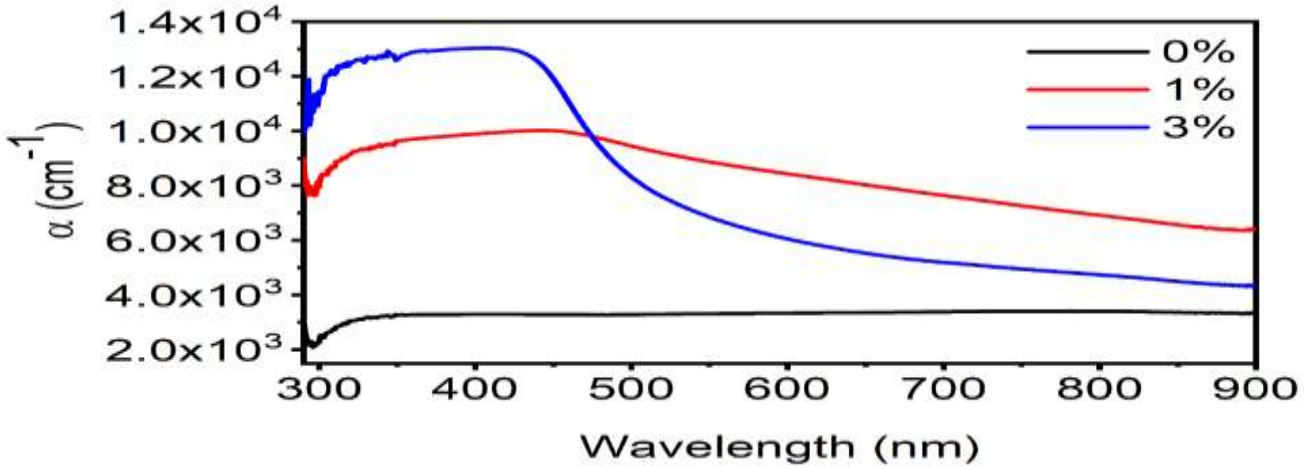

Fig.3: αagainst wavelength of prepared films

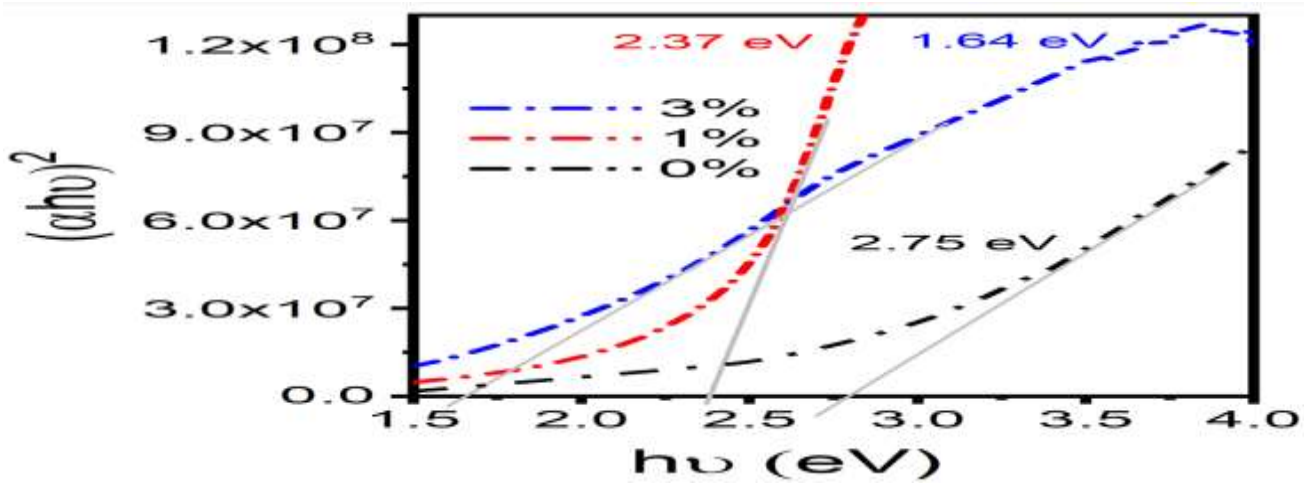

Fig.4: $(\alpha h\upsilon)^2$ versus (hv)

AFM Analysis

Figure 5 d, e and f shows three-dimensional AFM images. surface morphology of Co_3O_4 and Zn: Co_3O_4 films as noticed from the AFM micrographs assure that the spherical shape grains are uniformly distributed with average grain size of about (76) nm and the root-mean-square (rms) roughness of surface was about (2.37) nm. The Data in Table 3 indicate a high smooth surface.

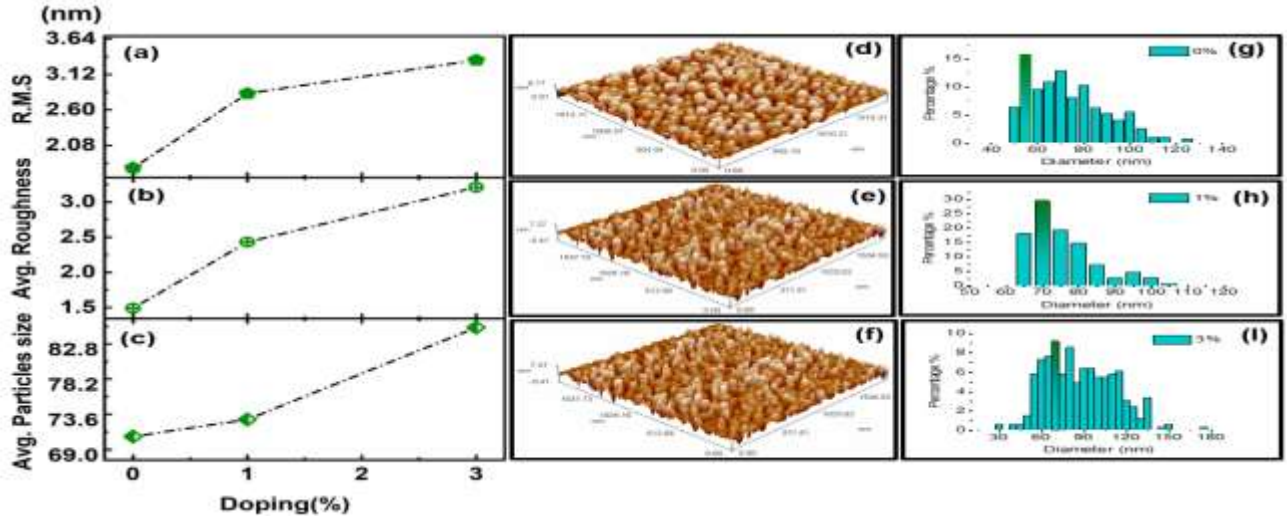

Fig.5: AFM parameters via doping (a, b, c), 3D image of the prepared films (d, e, f) and the granularly distributed of the prepared films (g, h, i)

Table 2: Surface morphology of prepared films

Zn doping (%)	Avg. Diameter (nm)	Average roughness (nm)	R. M. S. (nm)
0	70.71	1.49	1.75
1	72.93	2.43	2.84
3	84.94	3.21	3.33

Conclusions

XRD pattern confirmed that the thin film was polycrystalline. All samples show a preferential growth along the (220) crystal plane, for pure Co_3O_4 and doping rate 1% and 3% in Zinc and when increasing of Zn concentration the grain size was increased. The transparency and direct band gap were decreased when increasing of Zn concentration. AFM images show the average grain size of about (76) nm and root-mean-square (rms) roughness of surface is about (2.37) nm. Effect of crystallite size attributed to the change in concentration of Zn doping.

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