Structural, Morphological and Optical Properties of Co_3O_4 Thin Film

Dr. Sabah Habeeb Sabeh
Applied Sceince Deparment,Uneversity of Technology/Baghdad.
Email:sabahhabeeb@yahoo.com
Rahab Jabbar Abd Al-Hassan
Applied Sceince Deparment,Uneversity of Technology/Baghdad.

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ABSTRACT
The sol-gel technique was used because it is simple, economic and less equipment. The films deposited by dip coating method on glass substrate. The effect of pH value and annealing temperatures on structural, morphological and optical properties of Co_3O_4 were studied by X-Ray diffraction (XRD), Scanning Electron Microscope (SEM) and UV-visible Spectroscopy (UV-VIS). XRD measurements show that all the films are nanocrystallized in the cubic spinel structure and the films quality improved with increase the pH value and annealing temperatures. SEM images shows that the films was discontinuous surface with spherically grains increase from (65 to 83 nm) with increase the pH from 10.5 to 11.5. the annealing temperature improved the surface morphology. The optical band gap Eg was decrease from 2.7 to 2.4 eV when the pH alter from 9.5 to 11.5 while decrease from 2.5 to 2 eV with increase the annealing temperature from 300 to 600 °C .

INTRODUCTION
The Semiconductor metal oxide (SMO) nanostructures have attracted increasing interest in many fields including chemistry, physics, and material science.[1] they are promising material for many applications because of inexpensive, simple manufacture technique, small size, durability and low detection limits (< ppm for gas sensor application).[2] Sol-gel process describes the formation of solid material mainly inorganic non-metallic materials from solution. Compared to other thin film deposition processes sol gel have advantages of (economic, high purity, high optical quality, small thickness, easy coating of large surface and less equipment).[3] Cobalt oxide has a cubic lattice with stable normal spinal structure of AB_2O_4 type with black color. Where Co^{+2} ions occupy the tetrahedral 8a sites and Co^{+3} ions occupy the octahedral 16d sites and O^{-2} ions occupy the 32e sites. The interatomic distances of $d(Co^{+2}\text{–}O)$ is equal to 1.93 °A and for $d\ (Co^{+3}\text{–}O)$ equal to 1.92 °A. It is normally non-stoichiometric with an excess of oxygen which causes the p-type semiconducting with optical band gap (1.48 – 2.19 eV). Cobalt oxide is an antiferromagnetic oxide. Co_3O_4 is promising material in gas-sensing, solar energy absorption, catalysts, ceramic and glass pigments and magnetic material.[4,5,6]

Experimental Procedure
Synthesis
The cobalt oxide films were prepared over microscope glass substrate used sol-gel technique dip coating method. The substrate was cleaned in a soap solution, distilled and deionized water, alcohol then place in an alter sonic for 30 min and heating in an oven at 100 °C for 20 min. The solution prepared by adding (1 M) (NaOH) solution to (0.2 M) cobalt chloride solution stirring with magnetic stirrer for one hour to allow the reaction to complete then

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

whished the obtain powder with distilled and deionized water to remove the NaCl and any impurity. The powder dispersed with 75 ml distilled water and 25 glycerol (the glycerol added to improve the adherent the films with substrate) and heating at 100 °C for one hour with stirring films was deposited with dipping system at constant speed (0.4 cm/s) with deposition time (60 s). The pH value was changed by Ammonia solution from (9.5 to 11.5) the films was annealed at 200 °C for 30 min. The films annealed at various annealing temperatures (300 to 600 °C) used furnace type Nabertherm GmbH – Germany.

Characterization Studies

The structural properties of prepared cobalt oxide films was investigated by X-ray diffraction using Philips PW 1050 X-ray diffractmeter of λ= 1.5 A° from Cu-kα.The morphological characteristics of the thin films were examined by scanning electron microscope type (INSPECT S50(FEI)-Netherlands). In order to determine the band gap energy of the films, optical transmission study was carried using UV/VIS-1650 PC Shimadzu ultraviolet spectrophotometer - Japan.

Result and Discussion

Structural Studies

The X-Ray diffraction patterns recorded for the dip coated Co_3O_4 thin films on to glass substrates at various solution pH and at various annealing temperature are shown in Figures (1) and (2). The XRD studies revealed that the dip coated Co_3O_4 films exhibited cubic structure with polycrystalline in nature. This agree with data of JCPDS of Co_3O_4 in card No.42-1467. The average crystalline size (D) of the polycrystalline material can be calculated from the X-ray spectrum by means of Full Width at Half Maximum (FWHM) method (Scherrer relation).[7]

$$\frac{\quad}{\quad} \qquad \ldots (1)$$

Where β is Full Width at Half Maximum of the XRD peak appearing at the diffraction angle θ and employing over a range of (20–80) at the room temperature.

The micro strain produced through growth of thin films can be calculated from the follows formula. [7]

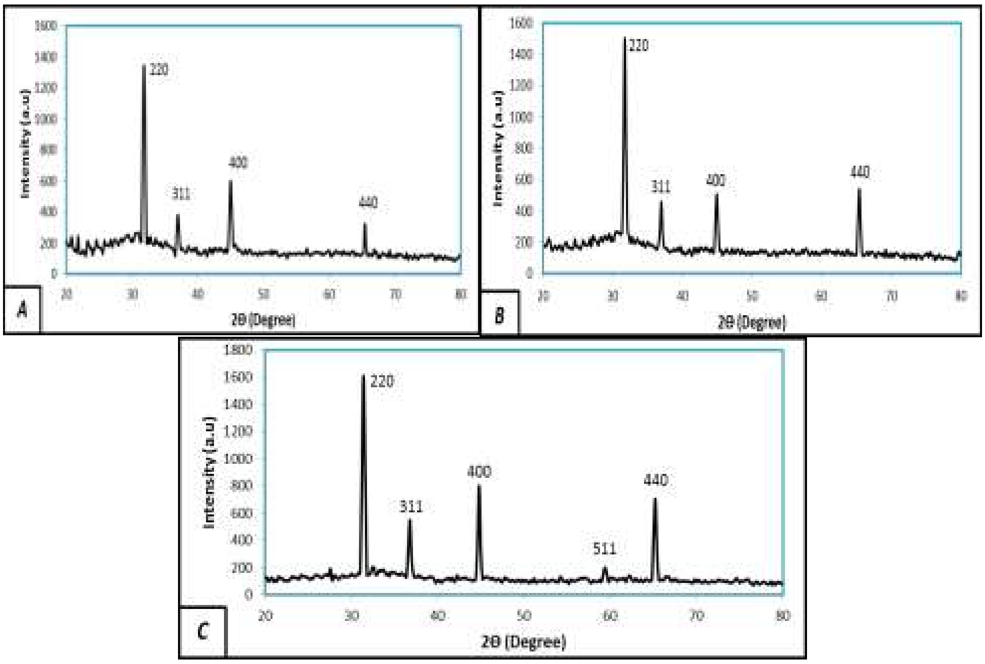
$$\varepsilon \quad \frac{|a \qquad XRD|}{\quad} * 100\,\% \qquad \ldots (2)$$

a is the lattice constant .

The dislocation density was calculated from the following relation [8]

$$d = 15\,\varepsilon / a\,D \qquad \ldots(3)$$

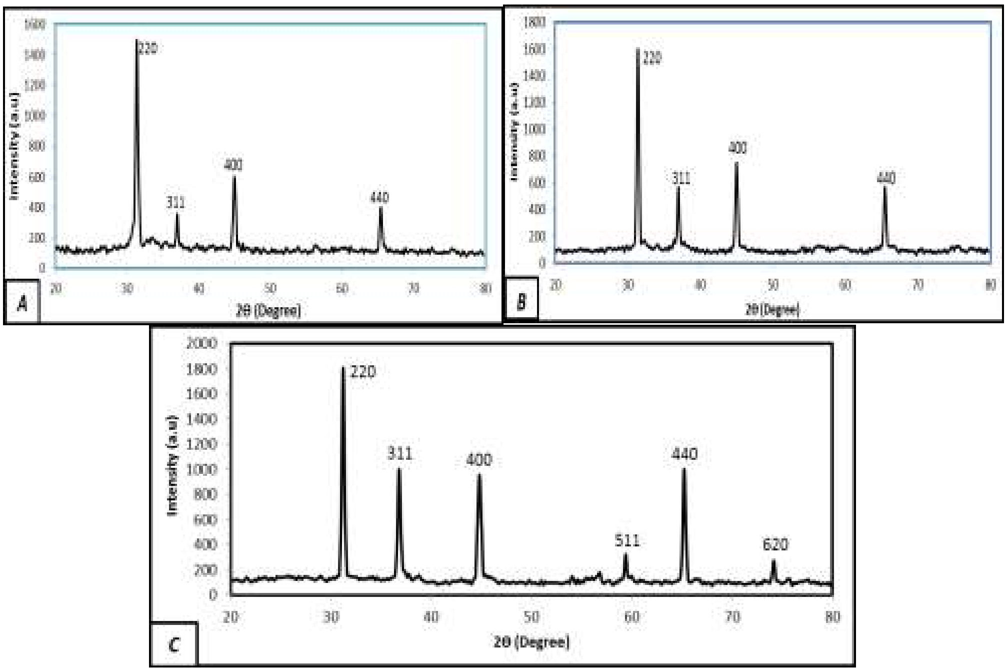
The X-Ray results indicated that the films crystallinity increases with increase the pH value and annealing and (220) plane is the is preferentially oriented for cobalt oxide thin films and it is the more crystalline peaks. Other peaks was observed corresponding to planes (311), (400),(440),(511) and (620). It is clear from the figures that the peaks sharpness and intensity increases with increase both the pH value and annealing temperatures this due to high annealing temperature providing energy to crystallites gaining enough energy to orient in proper equilibrium sites, resulting in the improvement of crystallinity and degree of orientation of the films. This agrees with other published works.[9,10] Table (1 and 2) shows the X-Ray diffraction result of the Co_3O_4 thin films.



Figure(1) The XRD of Co_3O_4 thin film at various pH values (A) pH=9.5, (B) pH = 10.5, (C) pH = 11.5

Table (1) The X-Ray result of Co_3O_4 thin films at various pH values

pH values	Crystalline size (nm)	Lattice constant (A°)	d (A°)	Microstrain	Dislocation density $x10^{14}$ line/m^2
9.5	16.5	7.9485	2.8102	0.01626	18.5
10.5	15.8	7.9503	2.8108	0.01604	19.5
11.5	20.1	8.0626	2.8374	0.00673	7.1



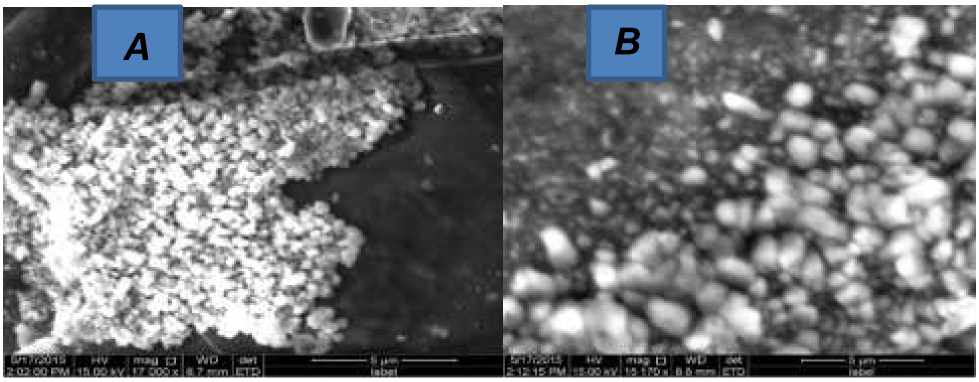
Figure(2) The XRD of Co_3O_4 thin film at different Annealing Temperatures (A) Ta=300 °C, (B) Ta = 400 °C, (C) Ta = 600 °C

Table (2) The X-Ray results of Co_3O_4 thin films at different Annealing Temperatures

Annealing Temperatures °C	Crystalline size (nm)	Lattice constant (A°)	d (A°)	Microstrain	Dislocation density x10^{14} line/m^2
300	16.2	7.9485	2.8102	0.007751	10.31
400	18.5	7.9503	2.8108	0.006965	8.57
600	27.2	8.0626	2.8374	0.000431	0.361

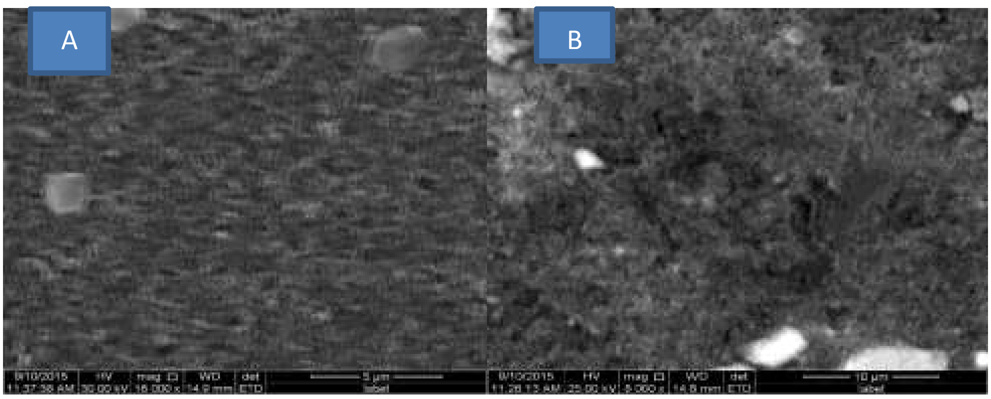
The Morphological

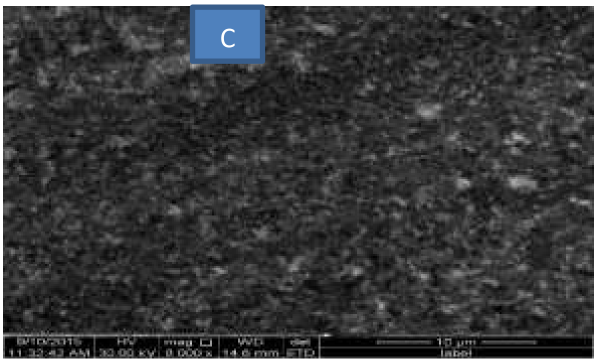
Figures (3) shows the SEM micrographs of Co_3O_4 thin films prepared by sol–gel dip coating technique at various pH value (10.5 and 11.5). SEM image of Co_3O_4 thin film has exhibited with discontinuous surface distribution of spherically shaped grains. At pH 10.5 found the grain size (65 nm) the growth continues the grain size increase to (83 nm) at pH 11.5. The surface morphology improved slightly by increase the pH value.



Figure(3) SEM of the Co_3O_4 thin film at various pH values (A) pH=10.5, (B) pH= 11.5

The figure (4) shows the SEM images of Co_3O_4 thin films prepared by sol–gel dip coating technique at different annealing temperatures (300, 400 and 600). The films relatively have similar surface morphology but there is a slight increase in the grain size of the films with increase the annealing temperature. The films surface is smooth and composed of contacted grains with good covered films without voids and cracks and some overgrowth of the grain can see of the films. The surface morphology of this structure provides an increase in surface area, which it suitable for super capacitor and gas sensing applications.[11]





Figure(4) SEM of the Co_3O_4 thin film at different annealing temperatures (A) Ta=300 °C, (B)Ta= 400 °, (C) Ta =600 °C

Optical Studies

The optical transmittance variations with wavelength for Co_3O_4 thin film coated at different deposition parameters were obtained. The optical band gap of the films was evaluated from the transmittance spectra employing Tauc's method. The absorption coefficient (α) is calculated using the equation[12]

$$\alpha = 1/d \ \ln \ 1/T \qquad \ldots(4)$$

Where T is transmittance and d is film thickness. The absorption coefficient (α) and the incident photon energy (hυ) is related by the following equation[13]

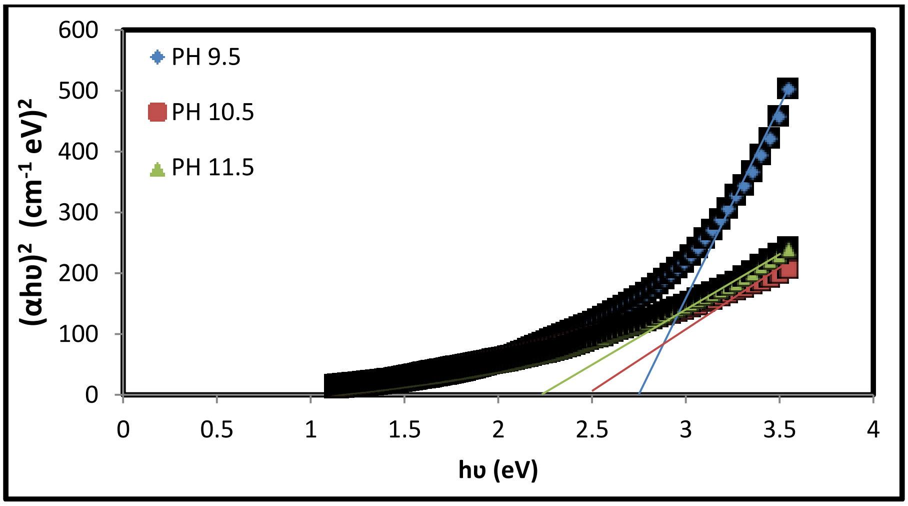
$$(\alpha h\upsilon)^2 = A\,(h\upsilon - Eg) \qquad \ldots(5)$$

Where

A and Eg are constant and optical band gap, respectively. The Eg value can be determined by extrapolation of the linear portion of the curve to the hυ axis.

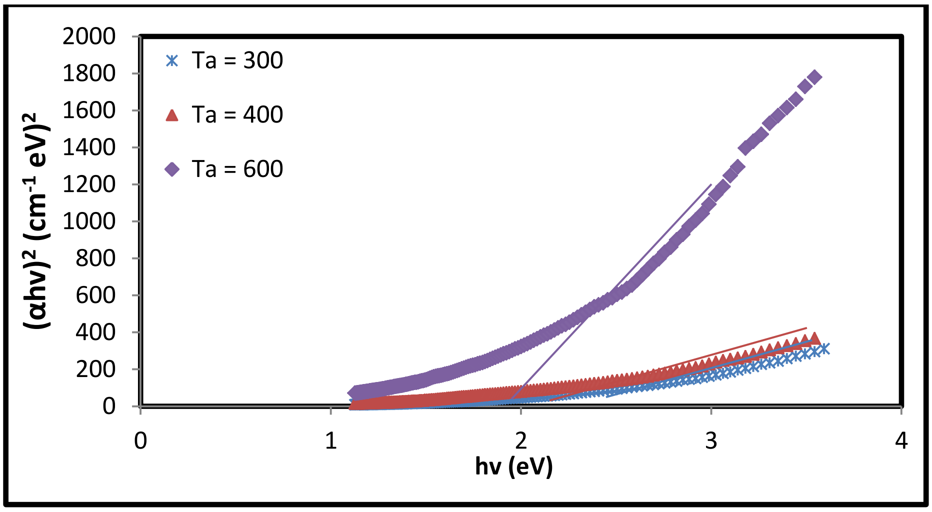
The results shows that all the films have high absorption (weak transmission not more 50 %). The films have high absorption coefficient more than 10^5 cm^{-1}.

The figure (5) shows the variation the optical band gap of Co_3O_4 thin films at various pH values. The energy band gap was decrease with increase the pH value from (2.75 to 2.42 eV). This is due to the formation of very small crystallites in the nano-range contributing significantly to size quantization effects [14]



Figure(5) The effect of the pH value on the energy band gap of Co_3O_4 thin film

Figure (6) shows the variation the optical band gap of Co_3O_4 thin films at different annealing temperatures. The energy band gap was decrease with increase the annealing temperatures . this is due to increase in crystalline size and reduction of defect sites and this agree with X-Ray diffraction results this an agreement with V. Patil et al.[15] The decrease in optical band gap is observed for annealed semiconductors film Hayder M. A. et al [16] found the decrease in optical band gap for CdO thin film from 2.8 to 2.3 after annealing at 500 °C. Hong et al.[17] found that the optical band gap of ZnO thin film decreases from 3.31 to 3.26 eV after annealing. And attributed this because of the increasing of the ZnO grain size. Table (3) The effect of pH value on the optical properties of Co_3O_4 thin films, Table(4) The effect of Annealing temperature on the optical properties of Co_3O_4 thin films.



Figure(6) The effect of annealing Temperatures on the energy band gap

Table(3) The effect of pH value on the optical properties of Co_3O_4 thin films

pH value	Energy band gap (eV)	λ = 625	
		Absorption coefficientX 105 cm-1	Extinction coefficient
9.5	2.75	6.4	0.273
10.5	2.5	6.31	0.313
11.5	2.42	6.34	0.315

Table(4) The effect of Annealing temperature on the optical properties of Co_3O_4 thin films

Annealing Temperatures(°C)	Energy band gap (eV)	λ = 625	
		Absorption coefficient X 10^5 cm^{-1}	Extinction coefficient
300	2.5	3.3	0.168
400	2.2	4.4	0.222
600	2	8.9	0.444

CONCLUSION

Co_3O_4 was deposited well on the substrate by sol-gel technique dipping method. The films has a good nanocrystalline cubic spinal structure. Crystalline size increase with increase the annealing temperature and alter with pH value with spherical shape as revealed the SEM result. Transmission was decrease with increase both pH value and annealing temperature due to increase the films thickness and improved the film structure respectively. The calculated band gap decrease from 2.7 to 2.4 eV with increase the pH from 9.5 to 11.5 and from 2.5 to 2 eV with increase annealing temperatures.

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