Study of the Structural and Optical Properties of Ni-doped Co₃O₄ Thin Films Using Chemical Spray Pyrolysis Technique

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Abstract. Undoped and Ni-doped Cobalt oxide thin films (Co₃O₄:Ni) with doping percentage (3, 6, and 9%) have been prepared by chemical spray pyrolysis technique on glass substrates at (400 ºC). The structural, surface morphology and optical properties were studied. XRD results showed that all the films were polycrystalline and had a cubic structure with preferred orientation (111) plane for all doping. The AFM images appear to be smooth and homogenous films. The optical properties showed that the transmittance decreased by increasing the percentage of Ni, and the direct optical band gap decreased from (2.53 eV) to (2.32 eV) for undoped Co₃O₄ with increasing the doping percentage to (9%).

Keywords: Co₃O₄, thin films, XRD, AFM, doping, chemical spray pyrolysis.

1. Introduction
Thin films are used to describe one or a number of layers of atoms whose thickness does not exceed one micrometer, and which is deposited on solid substrate such as glass, silicon and aluminium [1]. The researchers have become increasingly interested in studying the transparent conductive oxides because of their important properties, combining electrical conductivity with optical transparency in the visible spectra. These properties have attracted the attention for their numerous applications in devices such as solar cells, gas sensor, and electrochromic devices [2,3]. Thin films can be prepared by many techniques, such as APCVD [4], Spin-coating [5], Sol-Gel [6], and Chemical Spray Pyrolysis (CSP) [7]. Cobalt oxide is one of the transition metal oxides which has wide applications in various fields. It is a p-type semiconducting [8], and found in three crystalline forms (CoO), (Co₂O₃) and (Co₃O₄). The form (Co₃O₄) is the most chemically stable compound [9]. Researchers have increased their efforts to prepare and study the chemical and physical properties of cobalt oxide thin films (Co₃O₄) because of their possible applications in many techniques. They are used in the manufacture of solar cells as selective absorbers of solar energy [10], lithium battery [11], as well as electrochromic applications like smart windows [12]. In this research, CSP technique was used to prepare cobalt oxide thin films because they are characterized by easy preparation, low cost and the possibility of preparing thin films for large area deposition. The present research aims to study the effect of Ni doping on the structural, morphological and optical properties of (Co₃O₄) thin films deposited on glass substrate at substrate temperature of (400 ºC).
2. Experimental Details

2.1. Thin Films Preparation

Undoped and Ni-doped Cobalt oxide films (Co$_3$O$_4$:Ni) with doping percentages (3, 6, and 9 %) have been deposited by CSP technique on glass substrates at (400 °C). Briefly, two different solutions of (0.1M) cobalt chloride (CoCl$_2$) and nickel chloride (NiCl$_2$.6H$_2$O) were prepared by dissolving in suitable amount of distilled water. In order to remove the contaminants over the surface of the substrates it is dried at (100 °C) for (10 min), and then is put on the heater plate. The precursor solution was loaded in the spray nozzle. The distance between the substrates and spray nozzle was (35± 1 cm), with spray rate of (5 ml/min). The possible formation of (Co$_3$O$_4$) thin films can be written as the equation [13, 14]:

\[
3\text{CoCl}_2 + 2\text{H}_2\text{O} + \text{O}_2 \xrightarrow{400^\circ\text{C}} \text{Co}_3\text{O}_4 \downarrow + 3\text{Cl}_2 \uparrow + 2\text{H}_2 \uparrow \\
\text{NiCl}_2.6\text{H}_2\text{O} \xrightarrow{400^\circ\text{C}} \text{NiO} \downarrow + 2\text{HCl} \uparrow + 5\text{H}_2\text{O} \uparrow
\]

2.2. Characterizations

All films were characterized by different techniques. The structural properties of the films were analyzed using (Shimadzu XRD-6000), Japanese origin with a X-ray source which uses Cu K$_\alpha$ radiation with wavelength of (1.54056 Å), in the 2θ range of (10-80°). The surface morphology of the deposited films was characterized by atomic force microscopy (AFM) model (SPM-AA3000). The optical properties were measured using (Shimadzu UV-Visible1800 Spectrophotometer).

3. Results and Discussions

3.1. XRD results

Figure 1 Shows XRD patterns of undoped and Nickel doped Cobalt oxide (Co$_3$O$_4$:Ni) thin films. By analysing and studying the XRD curves, several reversal peaks such as (111), (311), (222) and (511) were observed with preferential orientation along the (111) direction and polycrystalline with cubic structure. The XRD results for prepared films are consistent with the results of the International Standard Diffraction Card (ICDD 43-1003) [15].

The XRD results do not show any parasitic phase of nickel clusters or nickel oxides, which indicate the great purity of the prepared films. These results have previously been proven by many researchers [16, 17]. The Ni atoms enter into the matrix of the films as an substitution or interstitial atom [18]. The lattice constant (a$_0$) was calculated for the preferential orientation (111) by using the Bragg's formula for cubic system [19]:

\[
(1)d_{(hkl)} = \frac{(a_0)}{\sqrt{(h^2 + k^2 + l^2)}
\]

Where $hkl$ is miller indices and $d_{(hkl)}$ is an interlinear spacing calculated from Bragg's law.
The average Crystallite size \((D_{avg})\) for the preferential orientation (111) is calculated by Scherer's formula [20]:

\[
(2) D_{avg} = \frac{K \lambda}{\beta \cos \theta}
\]

Where \(K\) is the shape factor (0.94), \(\lambda\) is the wavelength of the x-ray source (Cu K\(\alpha\)) radiation (1.5406Å) and \(\beta\) is the full-width half maximum (FWHM) for the preferential orientation (111). The texture coefficient \((T_c)\) is used to describe the preferential orientation of the prepared thin films. It can be calculated from the relation [21]:

\[
(3) T_c = \frac{I_{(hkl)}}{I_{(hkl)}} \frac{I_{(hkl)}}{\sum I_{(hkl)}}
\]

Where: \(I_{(hkl)}\) is the intensity of the ICDD, \(I(hkl)\) is the measured intensity, \(N_{r}\) is the number of reflections. Table (1) shows that the values of \(T_c\) were \(>1\) for all the samples, thereby indicating that there were numerous grains in the (111) plane.

The density of dislocations \((\delta)\) was calculated for the prepared films using the relation[7]:

\[
\delta = \frac{1}{D_{avg}}^2
\]
While the number of crystallites per unit area ($N_o$) was calculated using the relation[7]:

$$N_o = \frac{f}{D_{avg}}$$  \hspace{1cm} (5)

It was found that the average crystallite size ($D_{avg}$) of pure ($\text{Co}_3\text{O}_4$) thin films was (25 nm) and it is decreasing with the increase of doping percentage, knowing that the value of (FWHM) increases as the average particle size decreases. This effect is due to the fact that the doping inhibits the grain growth, these results decreases of the crystallite size.

The results showed that increasing values of ($d$, $\delta$ and $N_o$) with decreasing values of average crystallite size with increasing of doping percentage, as given in Table 1.

### 3.2. AFM results

The AFM results assist us in studying the topography of prepared films on glass substrate for scanning area of up to (2x2 $\mu$m$^2$). AFM 3D-images of undoped and Ni-doped Cobalt oxide thin films ($\text{Co}_3\text{O}_4$:Ni) showed smooth and homogeneous thin films, as shown in Figure 2.

| Sample          | $h$  | $k$  | $l$  | 2$\theta$ (deg) | d spacing (Å) | FWHM (rad) | $a_0$ (Å) | $D_{avg}$ (nm) | $T_c$ (nm$^2$) | $\delta$ (nm$^2$) | $N_o$ (nm$^2$) |
|-----------------|------|------|------|----------------|--------------|------------|----------|----------------|----------------|----------------|-------------|
| $\text{Co}_3\text{O}_4$-Pure | 1    | 1    | 1    | 18.96         | 4.675        | 0.0057     | 8.098    | 25             | 2.14          | 0.0016         | 0.0131      |
| $\text{Co}_3\text{O}_4$:Ni (3%) | 1    | 1    | 1    | 18.93         | 4.683        | 0.0062     | 8.109    | 23             | 2.17          | 0.0019         | 0.0171      |
| $\text{Co}_3\text{O}_4$:Ni (6%) | 1    | 1    | 1    | 18.93         | 4.682        | 0.0065     | 8.114    | 22             | 2.31          | 0.0021         | 0.0197      |
| $\text{Co}_3\text{O}_4$:Ni (9%) | 1    | 1    | 1    | 18.95         | 4.677        | 0.0064     | 8.101    | 22             | 2.33          | 0.0020         | 0.0188      |

**Figure 2.** AFM 3D-images of ($\text{Co}_3\text{O}_4$:Ni) thin films.

Table 2. Shows the decreasing value of the average roughness and root mean square (RMS) roughness for Ni doped films comparing with undoped films.
Table 2. AFM results of undoped and Ni-doped (Co₃O₄:Ni) thin films.

| Sample          | Roughness Average (nm) | RMS (nm) |
|-----------------|------------------------|----------|
| Co₃O₄ pure      | 6.74                   | 7.72     |
| Co₃O₄: Ni (3%)  | 2.3                    | 2.65     |
| Co₃O₄: Ni (6%)  | 2.4                    | 2.7      |
| Co₃O₄: Ni (9%)  | 2.59                   | 3        |

3.3. Optical properties

The Optical properties of undoped and Ni-doped Cobalt oxide thin films (Co₃O₄:Ni) were calculated from analyzing the variation of the transmittance spectra in the wavelength range of (300-900nm). Figure 3 shows the optical transmittance spectra curves of the prepared films. The results indicate that the transmittance decreases by increasing the doping rate. This decrease in transmittance spectra by doping is due to entry of nickel atoms into the matrix of cobalt oxide. This would lead to creating new spot levels at the bottom of the conduction band. These new levels are ready to receive electrons from Valence band and generate tails in and reduce the optical energy gap, knowing that the transmittance spectra behaves in a way opposite to the behaviour of absorbance spectra. Figure 4 shows the change of the absorption coefficient (α) for undoped and Ni-doped (Co₃O₄:Ni) thin films. The relationship between photon energy (hu) and absorption coefficient (α) can be written from the solid band theory, as given by [7,22]:

\[(αhu) = A(hu − E_g)^n\]  

Where (α) is absorption coefficient, (hu) is photon energy, (E_g) is band gap, (A) is edge parameter and (n) constant (dependent on type of electronic transitions) equal to (0.5) for allowed direct electronic transitions.
As it is observed, the absorption coefficient increases with the increase in the percentage of Ni doping. The reason for the increase in the absorption coefficient when increasing the doping ratio is likely to be a result of the entry of Ni atoms into the crystalline structure of (Co$_3$O$_4$).

![Absorption coefficient of (Co$_3$O$_4$:Ni) thin films.](image)

**Figure 4.** Absorption coefficient of (Co$_3$O$_4$:Ni) thin films.

Figure 5 Shows the optical energy gap of undoped and Ni-doped Cobalt oxide thin films (Co$_3$O$_4$:Ni) with doping percentage (3, 6, and 9%). The results show the decrease in value of the optical energy gap compared to undoped (Co$_3$O$_4$) with the increase of ratio doping percentage. This shifting may be due to the system distortions caused by the introduction of Ni ions into (Co$_3$O$_4$) structure which in turn leads to the creation of new impurity energy levels below the conduction band within the energy band gap. On the other hand, Ni works to create new holes which contribute to the conductivity, given that (Co$_3$O$_4$) is a p-type semiconductor which was in agreement with the findings of other studies [23, 24].

4. Conclusion
The results of XRD showed that the prepared samples were polycrystalline in nature with cubic structure. The average crystallite size decreased from 25 to 22 nm. The AFM results pointed to the films were smooth and homogenous, and the average roughness and RMS roughness decreased with the increase of Ni percentage. Results of UV Spectrophotometer showed that the transmittance of the doped films decreases in comparison with that of the undoped films. Also, the results showed the decrease of direct optical band gaps with the increase of Ni percentage, with values range between (2.53eV) and (2.32eV). This makes it suitable to use as solar selective surfaces.
Figure 5. Energy gap of (Co$_3$O$_4$:Ni) thin films.
References

[1] K. D. Leaver & B. N. Chapman "Thin Films" Wykeham Publications London, UK, 1971.
[2] Z. T. Khodair, N. A. Bakr, A. M. Hassan, A. A. Kamil " Influence of substrate temperature and thickness on structural and optical properties of CZTS nanostructures thin films" Journal of Ovonic Research, Vol. 15, No. 6, p. 377 – 385, 2019.
[3] A. M. Saleh, N. A. Bakr, Z. T. Khodair. "Effect of oxygen flow rate on structural and optical properties SnO2 thin films prepared by APCVD technique" Digest Journal of Nanomaterials & Biostructures (DJNB) 13, no. 3, 2018.
[4] Abdul Hameed R. Al-Sarraf, Ziad T. Khodair, M. I. Manssor, Rola Abdul AlKhader abbas , Auday H. Shaban" Preparation and characterization of ZnO nanotripods and Nano flowers by atmospheric pressure chemical vapor deposition (APCVD) technique" AIP Conference Proceedings 1968, 030005, 2018.
[5] Ahmed H. Abed, Ziad T. Khodair, Tagreed M. Al-Saadi, Tariq A. Al-Dhahir, “Study the evaluation of Williamson–Hall (WH) strain distribution in silver nanoparticles prepared by sol-gel method” AIP Conference Proceedings 2123, 020019, 2019.
[6] Ahmed H. Abed, Tagreed M. Al- Saadi and Ziad T. Khodair “Structural, electrical and magnetic properties of the (CexFe0.03Mg0.97-xO) nano compound synthesized via sol-gel/ auto combustion technique” ARPN Journal of Engineering and Applied Sciences, Vol. 13, No. 19, 2018.
[7] Ziad T. Khodair, Mushtaq Abed Al-Jubbori, Abdulsalam M. Hassan, Mutaz Salih Aljuboori and Fadhil I. Sharrad," Structural Properties of Sn1-xMg xO Thin Films and Optical Parameter Dependence with Gamma Ray Irradiation Journal of Electronic Materials, vol. 48, no.1, pp. 696-678, 2019.
[8] Kandalkar, Sunil G., C. D. Lokhande, R. S. Mane, and Sung-Hwan Han. "A non-thermal chemical synthesis of hydrophilic and amorphous cobalt oxide films for supercapacitor application" Applied surface science 253, no., pp. 83952-3956, 2007
[9] Barrera, E., L. Huerta, S. Muhl, and A. Avila. "Synthesis of black cobalt and tin oxide films by the sol–gel process: surface and optical properties" Solar energy materials and solar cells 88, no. 2, pp. 179-186, 2005.
[10] Shaju, Kuthanapillil M., Feng Jiao, Aurélie Débart, and Peter G. Bruce. "Mesoporous and nanowire Co3O4 as negative electrodes for rechargeable lithium batteries." Physical Chemistry Chemical Physics 9, no. 15, pp.1837-1842, 2007.
[11] Xia, X. H., J. P. Tu, J. Zhang, J. Y. Xiang, X. L. Wang, and X. B. Zhao "Cobalt oxide ordered bowl-like array films prepared by electro deposition through monolayer polystyrene sphere template and electrochromic properties" ACS applied materials & interfaces 2, no. 1, pp. 186-192, 2009.
[12] El Bachiri, A., L. Soussi, O. Karzazi, A. Louardi, A. Rmili, H. Erguig, and B. El Idrissi. "Electrochromic and photoluminescence properties of cobalt oxide thin films prepared by spray pyrolysis" Spectroscopy Letters 52, no. 1, pp. 66-73, 2019.
[13] Ravindra, N. M. "Energy gap-refractive index relation -some observations" Infrared Physics 21, no. 5 ,pp. 283-285, 1981.
[14] Raid A. Ismail, Sa’ad Ghafori, Ghada A. Kadhim" Preparation and characterization of nanostructured nickel oxide thin films by spray pyrolysis" Appl Nanosci, 3, pp. 509–514, 2013.
[15] Seyed Javad Davarpanah, Ramin Karimian, Farideh Piri "Synthesis and Characterization of Co₃O₄ Nanotubes to Prepare Variety of Electrochemical Biosensors" Journal of Applied Biotechnology Reports, 1, 3, pp.117-120, 2014.

[16] Santos, Gustavo A., Camila MB Santos, Sebastião W. da Silva, Ernesto A. Urquieta-González, and Patricia P. Confessori Sartoratto. "Sol–gel synthesis of silica–cobalt composites by employing Co₃O₄ colloidal dispersions" Colloids and Surfaces A: Physicochemical and Engineering Aspects 395, pp. 217-224, 2012.

[17] Jacobs, Jean-Paul, Annemarieke Maltha, John GH Reintjes, Jiri Drimal, Vladimir Ponec, and Hidde H. Brongersma. "The surface of catalytically active spinels" Journal of Catalysis 147, no. 1, pp. 294-300, 1994.

[18] Manickam, M., V. Ponnumswamy, C. Sankar, R. Suresh, R. Mariappan, and J. Chandrasekaran "The effect of solution pH on the properties of cobalt oxide thin films prepared by nebulizer spray pyrolysis technique." Int. J. Thin Films Sc. Technol 5, pp. 155-161, 2016.

[19] Ziad T. Khodair, Ali M. Mohammad, Anees A. Khadom "Investigations of structural and magnetic properties of Cu₁₋ₓVₓO nanostructures prepared by sol-gel method " Chemical Data Collections 25,100315, 2020.

[20] Ziad T. Khodair, Anees A. Khadom, Hassan A. Jasim, "Corrosion protection of mild steel in different aqueous media via epoxy/nanomaterial coating:preparation, characterization and mathematical views" Journal of Materials Research and Technology, vol. 8, no. 1, pp. 424-435, 2019.

[21] Ziad T. Khodair, A. A. Kamil and Y. K. Abdalaah, " Effect of annealing on structural and optical properties of Ni₃₋ₓMnₓO nanostructures thin films ", Physica B503,55–63, 2016.

[22] Ziad T. Khodair, Buthainah Abdulmunem Ibrahim, Mayada Kaream Hassan, "Investigation on the structural and optical properties of copper doped NiO nanostructures thin films"Materials Today: Proceedings 20, pp. 560–565, 2020.

[23] Lakehal, Abdelhak, Benrabah Bedhiaf, Amar Bouaza, Benhebal Hadji, Abdelkader Ammari, and Cherifia Dalache "Structural, optical and electrical properties of Ni-doped Co₃O₄ prepared via Sol-Gel technique." Materials Research 21, no. 3, 2018.

[24] Svetlana Vladimirova , Valeriy Krivetskiy, Marina Rumyantseva, Alexander Gaskov ,Natalia Mordvinova , Oleg Lebedev, Mikhail Martyshov and Pavel Forsh," Co₃O₄ as p-Type Material for CO Sensing in Humid Air" Sensors, 17, 2216, 2017.