Optical and Structural properties of Ni-doped Co3O4 Nanostructure Thin films Via CSPM

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Abstract—In this research, Co3O4:Ni thin films have been prepared by a chemical spray pyrolysis method (CSPM). The synthesized samples, structure and morphology of creating Co3O4:Ni thin films were characterized by X-ray diffractions (XRD), and Atomic Force Microscopy (AFM). The impacted of Ni concentration were changed from 0 to 4 % by XRD results cause increasing the crystallite size, while the Microstrain and the dislocation density are decreasing. Furthermore, the AFM imaging shows of Co3O4:Ni thin films involving a classic amorphous polymer-metal complex synthetic route where Co3O4 films are uniformly embedded with 3D nanoparticles Ni skeleton. The optical properties approve that the energy gap increased from 2 eV to 2.5 eV at 4% Ni doping.

Keywords: Co3O4:Ni thin films, Co3O4 particle size, Ni doping, Co3O4 films energy gap.

1. Introduction

The transparent conductive oxides (TCO) materials have acquired a massive attention in many areas due to their interesting properties. Their characterization are promising to use them such as photovoltaic solar cells, electrochromic sensor, and optoelectronics devices [1,2].

Among the TCO, The cobalt oxide (Co3O4) is one of the most studied oxides in scientific fields and energy storage owing to its electrochemical stability [1,3] such as supercapacitors when the stable cobalt oxide system is mixed-valence compound [Co2⁺Co3⁺O4] with a normal spinel structure [4], solar selective absorber, large surface area and high conductivity [5]. The several direct band gap energies and optical studies have exhibits that Co3O4 a high opposition to thermal shocks, oxidation, UV radiation [6].

Recently, several methods was used to deposit cobalt oxide nanostructured with adjustable characterization for broad range of applications. Various routes of synthesis of Co3O4 films have been considered such as CVD [7], spray pyrolysis [8], sol-gel technique [7,9,10], MOCVD [11].

In this regard, Nickel (Ni) doped Co3O4 thin films and powders was deposit on glass substrates via CSP technique, in order to check and understand their enhanced properties. A small change indoping concentration (0-4%)affect the value energygaps, The morphology of Co3O4: Ni samples shows continuous and uniform 3D nanoparticles, and its minimum nanoparticle size can achieve at 4%. The treated sample shows a hierarchical nanoparticles that in situ formed Co3O4 nanosheets doping with Ni nanopowder.
2. Experimental

The Cobalt oxide and Nickel doped cobalt oxide Co$_3$O$_4$:Ni thin films were prepared onto glass slide substrates via chemical spray pyrolysis method. Aqueous solution of 0.1 M of cobalt chloride was used as a matrix solution to obtain Co$_3$O$_4$ thin. The doping material was 0.1 M of nickel chloride (NiCl$_2$.6H$_2$O) to get Ni of 2% and 4%. The matrix solution was deposited on preheated substrate. After many trials, the following optimization parameters were taken into account: substrate temperature of 400 $^\circ$C was kept constant during deposition process; the distance between nozzle and substrate was 29 cm. Flow rate 5 mL/min, spraying rate was 8 s followed by 1.5 min to avert redundant substrate cooling. Ni was used as a Carrier gas. Double beam UV-Vis spectrophotometer was used to record the transmittance and absorbance spectra in wavelength range (400 - 700) nm. High-resolution X-Ray was used to measure the structural specifications of thin films using D8 Advance Bruker, CuKa ($\lambda = 0.154056$ nm). The AFM was used to introduce surface topography using a digital tool, Nanoscp III and Dimension 3100.

3. Results and discussion

A. Structural properties

Figure (1) shows X-Ray diffraction pattern for Co$_3$O$_4$ with different Ni doping by (CSPM). The Co$_3$O$_4$ films at 0% doing exist in cubic crystal structure [12]. At the 4% Ni doping leads peak intensity elaboration height at the reflection, indicating that increasing Ni doing decreases the crystallinity of the film. In Figure (1) the standard (222) reflection at $2\theta = 38.54^\circ$ used to calculate the crystallite sizes from the XRD pattern, As observed, increasing the Ni doping causes a sharpening of the Bragg reflections, uncover a decrease in film crystallinity. The valuation of crystallite size was done using Scherrer’s formula [13, 14].

$$D = \frac{k\lambda}{\beta \cos\theta}$$  \hspace{1cm} (1)

Where K is the shape factor =0.9, $\beta$ is full width at half maximum in radians, $\lambda$ is X-ray wavelength , and $\theta$ is Bragg angle. The lattice parameter values were estimated using the equations [13].

$$a = d \left( h^2 + k^2 + l^2 \right)^{1/2}$$  \hspace{1cm} (2)

$$\frac{1}{d^2} = \frac{4}{a^2} \left( h^2 + h k + k^2 \right) + \frac{l^2}{c^2}$$  \hspace{1cm} (3)

The crystallite size of the CO$_3$O$_4$ films was 17.53 nm and it increases to 38.25nm with the Ni doping increasing steadily up to 4% to be 33.66 nm. The dislocation density the number of crystallites per unit area and Microstrain ($\varepsilon$). The Microstrain ($\varepsilon$) reduction caused by varying the displacement of the atom with respect to their reference lattice position. Dislocation density ($\delta$) is represent crystal imperfection related with the misregistry of the lattice. The dislocation density ($\delta$) was obtained using equation (5). These values were listed in Table (1).

$$\varepsilon = \frac{\beta \cos\theta}{4}$$  \hspace{1cm} (4)

And strain [13] in the films was determined by:

$$\delta = \frac{1}{D^2}$$  \hspace{1cm} (5)

The FWHM values of the preferred reflections, are shown in Table 1, which gives high precision values.
Fig. 1: X-Ray diffraction pattern of $\text{CO}_3\text{O}_4$ with different Ni doping by (CSPM).

Table 1: structural data of $\text{CO}_3\text{O}_4$ with different Ni doping by (CSPM).

| Ni Doping % | (hkl) Plane | $2\Theta$ (Deg.) | Lattice constant (Å) | FWHM (Deg.) | Crystallite size D (nm) | Microstrain $\times 10^{-4}$ | Dislocation density (δ) $10^{-4}$ (1/nm²) |
|-------------|-------------|------------------|----------------------|-------------|-----------------------|----------------------------|---------------------------------|
| 0           | (222)       | 38.54            | 8.087 a              | 0.48        | 17.53                 | 20.91                      | 32.52                           |
| 2           | (222)       | 38.54            | 8.091 a              | 0.22        | 38.25                 | 9.58                       | 6.83                            |
| 4           | (222)       | 38.54            | 8.083 a              | 0.25        | 33.66                 | 10.89                      | 8.82                            |
The transmission spectra for different Ni doping are shown in Fig.2 (a). The deposited film is highly transparent with an average transmittance reaching values up to 23% at 4% doping but the transmittance decreases at 2 or 0% doping decreases, as in the research [15], and it is due to an increase in film thickness. As expected, inversely proportional with absorption coefficient values in Fig.2(b).

Bandgap energy ($E_g$) can be estimated from the optical absorption measurements. The plot of $(\alpha h\nu)^2$ with photon energy ($h\nu$) is shown in Fig.2(c). The optical bandgap energy was calculated by flowing equations [16]:

$$ (\alpha h\nu) = A(h\nu - E_g)^n $$  \hspace{1cm} (6)

Where $h\nu$ is the photon energy and $n$ is a constant, which depends on the probability of transition. The value of $n$ of direct allowed transition is $\frac{1}{2}$. The direct bandgap energy values of the Co$_3$O$_4$·Ni thin films are found to decrease with increase in Ni deposited the result of the change in film thicknesses, decrease in crystal size and it may be attributed to the quantum confinement [17].

Fig.2(b) represents the values of the absorption coefficient that gives an explanation that the type of bandgap is direct. In addition to their dependence in drawing the relationship between the values of $(\alpha h\nu)^2$ and the photon energy ($h\nu$) as in Fig.2(c) where the bandgap value is estimated from this figure, which are observed to decrease at 4% deposited.

![Fig.2: (a) Transmittance as Function to The Wavelength for Co$_3$O$_4$ with different Ni doping by (CSPM), (b) absorption coefficient, (c) band gap.](image)

Where:  
- **(a)** Transmittance %  
- **(b)** Wavelength (nm)  
- **(c)** $(\alpha h\nu)^2$, $h\nu$ (eV)
4. AFM

Surface topography was observed from 2D and 3D AFM images as shown in Figure 4, showing incremental increase in the columnar size, roughness and surface area related to time deposition and thickness. This increase in surface area is a feature of photocatalytic activity [18, 19]. However, the average particle size decreases linearly with time coating but the surface area also increases.

As observed from the figures (4a, b and c) there is a decrease in the rate of the average particle size with an increase roughness average that increased.

Fig.3: Atomic force microscopy, 3D image of Co3O4 :Ni thin films (a, b and c) RMS, Roughness Average and Avg. Diameter, AFM images of Co3O4 with % depositions of (d) 0%, (e) 2% and (c) 4%.

5. Conclusions

The Co3O4 films are prepared under different Ni dopants, it is clear that the films are cubic phase at 0% and at 4% of Co3O4:Ni thin films, turns from the hundred particle size and decreased to nanoparticle size and the crystallization improved. The decreased particle to nano size with Ni doping increasing, selected such as a model for the optoelectronics devices.
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7. References

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