Effect of Calcinations Temperature on ZnO:Co Nanostructured Thin Films Prepared By Sol – Gel Method.

Dr. Shaima’a J.Kareem¹, Dr. Elham Abd Al-Majeed¹, Afnan Salam¹
¹Department of Ceramics and building materials Engineering, College of Materials Engineering, University of Babylon, Babylon, Iraq
mat.shiamaa.jaber@uobabylon.edu.iq, mat.elham.abdulmajeed@uobabylon.edu.iq, afnansalam1995@yahoo.com

Abstract. Nanostructured ZnO thin films were developed on medical-glass substrates using a sol gel dip coating process and calcinated at various temperatures (350, 450, and 550 °C). The impact of Co doping and effect temperature calcination on the structural, optical and electrical properties of ZnO:Co nanostructured thin films were investigated using XRD, SEM, Hall effect, and UV-Visible spectra measurements. Both nanostructured films have hexagonal-wurtzite crystals composition according to XRD analysis with the average crystallite sizes of ZnO:Co nanostructured thin films are of (26.7-102.1) nm. The FESEM findings show that the undoped ZnO thin film has the smoothest and more regular surface compared to the doped ZnO films, indicating that both films with nanoscale ZnO particles. The average transmittance of all films is about 69–91 % in the visible range and the band gap energy decreased from 3.283 to 3.205 eV with increase of temperature calcination. The Hall impact indicates that all thin films are n-type and the electrical conductivity increase from (12.4-16.2) in the ZnO:Co thin films. This one of the outstanding property of ZnO thin films, both undoped and doped with cobalt, enables the fabrication of transparent electrodes for flat panel displays, metal-insulator-semiconductor diodes, and solar cells.

1. Introduction
Transparent semiconductors consisting of conductive oxides may be coated with antireflection materials to increase solar cell absorption [1]. Now, different nanostructured materials are being investigated for their ability to monitor light and thus improve absorption in photovoltaic (PV) cells [2].
Zinc oxide thin films have garnered as much interest as clear conducting oxides due to their advantageous properties such as strong optical clarity in the visible field, low electrical and electrochemical resistive properties, abundance in existence, and lack of toxicity [3]. Numerous coworkers have studied the preparation of zinc oxide thin films and shown that temperature calcination and dopant inclusion can be used to tune the optical, magnetic, and electrical properties of ZnO nanostructure thin films [4, 5]. Due to its similar ionic radius, abundance of electronic states, and divalent state, cobalt is a promising material for doping ZnO among transition metals [6]. Numerous deposition techniques have been used to fabricate thin films of cobalt-doped ZnO nanostructures, including solvothermal [5], ultrasonic spray [7], spin coating [8], sputtering [9], and pulsed laser deposition [10]. Although simplified synthesis techniques that can be conducted in the ambient environment have the advantage of being more accessible and cost effective, it is critical that the resulting
(doped) ZnO is of high quality, exhibiting comparable properties and functionality to that generated by other methods. Sol-gel processing is a common method for fabricating low-cost materials [8, 11]. This article delves into the effects of dopant concentration and thermal treatment on the structural, morphological, optical, and electrical properties of ZnO thin films.

2. Experimental procedure
On medical glass substrates, doped and undoped ZnO nanostructure thin films were created using the dip coating technique. Zinc nitrate hexahydrate (Zn (NO$_3$)$_2$6H$_2$O) and cobalt nitrate hexahydrate (Co(NO$_3$)$_3$6H$_2$O) is dissolved in DMF (No$_7$H$_3$C) to form a solution. After 1 hour of magnetic stirring at room temperature, addition of mono-ethanolamine (MEA) drop by drop at a molar ratio of $n$(MEA)/nitrate = 1 increases the solubility of nitrate in the solvent and results in a transparent solution. The collected solution was dried at 80°C for 2 hours with magnetic stirring. Following that, both solutions were aged at room temperature for 24 hours to achieve homogeneity. Prior to deposition, dilute hydrochloric acid, ammonia, and deionized water is used to clean medical glass substrates to eliminate any contaminants that may damage the thin film's properties. On washed substrates, the readily prepared ZnO:Co solutions were deposited. Following that, both films were dried for 5 hours at 200 °C in air to ensure that all organic organisms were removed from the films. Finally, the grown nanostructure thin films were calcined at temperatures of (350, 450, and 550) °C at a heating rate of 5°C/min. The XRD patterns for the prepared films were collected using a copper objective (CuK$_1$, 1.5418) in a goniometer (XRD 6000, Shimadzu). To investigate the microstructure and elemental distribution of samples, FESEM tests were performed using MIRA3 (TESCAN) equipped with an Energy Dispersive X-Ray detector. UV-VIS-NIR spectroscopy was used to analyze optical properties in the wavelength range (350-650) nm (UV-1800, SHIMADZU). The relative transmittance and absorbance of as-deposited ZnO and Cobalt doped ZnO thin films is determined using this spectrophotometer.

3. Results & discussions
3.1 Analysis of X-ray diffraction

Figures (1), (2) and (3). show the X-ray diffraction graphs of undoped ZnO and Co doped ZnO films (1 wt.% Co). The direction of these peaks (002) is prevailing in terms of relative strength (0 wt. percent and 1 wt percent Co). In theory, the line (002) of pure ZnO is extreme than the line (002) of 1% Co. The amplitude of the peaks steadily decreases with increasing cobalt contented, which is caused by the deterioration of the crystal quality caused by the replacement of Zn$^{2+}$ ions by Co$^{2+}$ ions [6].

The crystallite sizes of the samples were determined using the (002) plane of the XRD results. In this experiment, the full width at half height (FWHM) was used in accordance with the Debye–Scherrer formula [11].

$$D = \frac{0.9\lambda}{\beta \cos \Theta}$$  \hspace{1cm} (1)

Where D denotes the crystallite scale in nanometers, $\lambda$ denotes the wavelength of the Cu K$_\alpha$ line ($\lambda$= 1:5406 Å), $\Theta$ denotes the Bragg diffraction angle and $\beta$ is the diffraction peak's complete width at half limit (FWHM) in rad. Table 1 contains values of the Average of crystalline size of undoped ZnO thin film at 350°C, 450°C and 550°C. This table shows that both samples have a grain size of nanometric.
Fig. (1). Spectra of XRD of thin films at 350 °C.

Fig (2). Spectra of XRD of thin films at 450°C.

Fig (3). Spectra of XRD of thin films at 550°C
Table 1: Values of the Average of crystalline size of undoped ZnO thin film at 350°C, 450°C and 550°C

| Calcination | Co doped ZnO | Average of crystalline size |
|-------------|--------------|----------------------------|
| 350 C       | 0%           | 49.300                     |
|             | 1%           | 26.784                     |
| 450 C       | 0%           | 70.733                     |
|             | 1%           | 37.384                     |
| 550C        | 0%           | 102.124                    |
|             | 1%           | 50.133                     |

3.2 Field Emission-Scanning Electron Microscopy.
Using a field emission scanning electron microscope, we examined the surface morphology of cobalt-doped ZnO thin films accumulated at varying concentrations and calcinations. The FESEM photos in Figures (4), (5) and (6) demonstrate that the nanoscale ZnO particles are uniformly distributed over all films. Additionally, it can be found that the particle size appears to increase with increasing ZnO and cobalt-doped ZnO concentrations during calcinations. According to the FESEM photographs, the grain size of films calcined at 350 °C is smaller than calcined at 450 °C and 550 °C.

FESEM photographs of the undoped and co-doped ZnO films are included in the figures (4), (5) and (6). The ZnO FESEM photographs resemble a granular surface. Co ions were incorporated into the dirt, resulting in the forming of a wrinkled network. Increased dopant accumulation resulted in the incorporation of additional impurities into the ZnO crystal, resulting in increased crystal defects and affecting the crystallinity of the films, as found by XRD. The film morphology shifted to a network at 1% Co concentration, which is consistent with the literature [10].

Fig. (4): FESEM image of thin film at 350°C
3.3 Optical properties analysis
The optical transmittance spectra of pure ZnO and Co doped ZnO [1 wt %] thin films at various calcification temperatures [350°C, 450°C, 550°C] are shown in Figures (7) and (8). At 350 °C, the transmittance of the samples is equivalent to 90%, 87 % at 450 °C, and 76 % at 550 °C. We noticed that light radiation with a wavelength less than 370 nm has a high absorption and a low transmittance. Additionally, we observe that the 1% Co doped substrate has the maximum transmittance while the undoped ZnO substrate has the lowest, suggesting an area of high visibility between 375 and 500 nm (visible light). The transmittance in this field increases sharply.
Estimate the band gap of ZnO nanostructured films using the Tauc relationship and the following term. [13]:

\[ \alpha h\nu = C(h\nu - E_g)^{1/2} \]  

(2)

where \( E_g \) denotes the band gap energy, \( C \) denotes an energy-independent constant, and \( \alpha \) is the absorption coefficient determined by the following relationship:

\[ \alpha = \frac{2.303A}{t} \]  

(3)

where \( A \) denotes the absorbance of the ZnO nanofilms and \( t \) denotes their thickness. The optical band gap was calculated via extrapolating to the the linear area in the \((\alpha h\nu)^2\) versus \((h\nu)\) plot to the horizontal axis. The plots of \((\alpha h\nu)^2\) versus photon energy for (0% - 1%) Co doped ZnO nanofilms are seen in the figures. It is found that even a trace amount of Co in the films has a significant impact on the optical band gap of ZnO. The band gap energy reduces as the temperature of calcination rises.
3.4 Hall Effect

By detecting and investigating the Hall Effect, charge carrier mobility, type, and accessibility of nano-films, as well as knowing and measuring the charge carrier concentration, can be detected and investigated. The findings of the Hall effect experiment indicate that all undoped and doped ZnO nano-films prepared at various temperatures calcified is (n-type), and that the charge carriers are electrons, as shown in tables [2,3,4], and that the negative charge in the average Hall coefficient indicates that the material is n-type.

The electrical conductivity of ZnO and Co doped ZnO thin films improved with rising calcification temperature, which is consistent with an improvement in carrier concentration.

Figure 9. The relation between $(\alpha h \nu)^2$ and $(h \nu)$ for ZnO and Co doped ZnO thin films at 350 °C, 450 °C and 550 °C.
Fig. (10) Difference of electrical conductivity for different temperature.

Table 2: The result of Hall measurement for Co-doped ZnO thin films at 350°C

| Concentrations | n (cm)^{-3} | μ (cm^2V^{-1}s^{-1}) | R_H (cm^3C^{-1}) | σ (o.cm)^{-1} | Type |
|----------------|-------------|-----------------------|------------------|---------------|------|
| 0              | -101*10^{14} | 9268.292              | -612.903         | 15.122        | n    |
| 1              | -96*10^{14}  | 8000                  | -645.161         | 12.4          | n    |

Table 3: The result of Hall measurement for Co doped ZnO thin films at 450°C

| Concentrations | n (cm)^{-3} | μ (cm^2V^{-1}s^{-1}) | R_H (cm^3C^{-1}) | σ (o.cm)^{-1} | Type |
|----------------|-------------|-----------------------|------------------|---------------|------|
| 0              | -957*10^{14} | 11454.49              | -651.61          | 17.58         | n    |
| 1              | -460*10^{14} | 21374.045             | -1354.838        | 15.7761       | n    |

Table 4: The result of Hall measurement for Co doped ZnO thin films at 550°C

| Concentrations | n (cm)^{-3} | μ (cm^2V^{-1}s^{-1}) | R_H (cm^3C^{-1}) | σ (o.cm)^{-1} | Type |
|----------------|-------------|-----------------------|------------------|---------------|------|
| 0              | -88*10^{14}  | 12899.408             | -703.23          | 18.3432       | n    |
| 1              | -537*10^{14} | 18604.65              | -1161.29         | 16.02         | n    |

3.5 Measurement of thickness

Thin film thickness (t) is measured by using laser interferometer and applying the following equation [14].

\[
\varepsilon_c = \frac{\Delta x}{x} \cdot \frac{\lambda}{2}
\]  

(4)

Where x is the fringes spacing, Δx is the displacement between two fringes and λ is the wavelength of the used laser light (632.8nm). In this work it noted when increase temperature of calcification, decreases Thickness Co doped ZnO thin films Measurement as show in figure(10) and table 5.
Fig.(11) The variation of thickness (nm) and different Temperature of calcification for ZnO and Co doped ZnO thin films

Table (5): Measurement of thickness of ZnO and Co doped ZnO thin films

| Samples | Thickness (nm) |
|---------|----------------|
|         | 350°C | 450°C | 550°C |
| 0 %     | 305 nm | 233 nm | 265 nm |
| 1%      | 390 nm | 304 nm | 230 nm |

4. Conclusion

In conclusion, we used the sol–gel dip coating process to deposit undoped and co-doped ZnO thin films on medical-glass substrates. The structural, electrical, and optical properties of TCO nano-films were studied in order to determine the feasibility of manufacturing them using a low-cost method. The impacts of doping concentration and calcination temperatures on the films' structural and optical properties were thoroughly investigated. The XRD findings show that the crystallinity increased as the annealing temperature was increased. Meanwhile, the cobalt doped ZnO degrades the crystallinity. FESEM photos were used to describe the evolution of grain size and texture caused by Cobalt dopant. At 350 ° C , the maximum transmittance and strongest ultraviolet emission was seen in ZnO and co-doped ZnO thin films. The optical distance of our ZnO samples reduces as the calcination temperature increases. ZnO and Co doped ZnO thin films are n-type semiconductors, as determined by Hall measurements.

5. References

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