The calculate of optical gap energy and urbach energy of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films

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Abstract. The effect of Co doping on optical, structural and electrical properties of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films has been successfully deposited on glass substrate by Sol–Gel Sping coating technique. The main objective of this research is to study the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films to determine the optical gap energy by various methods and compare of calculated values. The transmission spectra show that the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films have a good optical transparency in the visible region. The optical gap energy was varied between 3.8 and 4.05 eV, which was determined by various methods and equations. These are found in the drawn of A , A^2 , α , α^2 , $(Ah\nu)^2$ and $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$, the suitable method to calculate the optical energy was observed for $(Ah\nu)^2$ versus $h\nu$, but this method can not be related to the film thickness. The urbach energy of the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films also was determined by the curves of $\ln A$ and $\ln \alpha$ as a function of photon energy $h\nu$. The deduce by $\ln A$ versus $h\nu$ is also suitable to estimate the urbach energy. However, the $\text{Ni}_{0.96}\text{Co}_{0.04}\text{O}$ thin films have a few defects with minimum value of urbach energy. XRD patterns of the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films indicate that some films are polycrystalline with cubic structure. The electrical conductivity of our films is in the order of $8.2 \times 10^{-3} (\Omega \cdot \text{cm})^1$.

Keywords. NiO; thin films; co doping; TCO; sol–gel sping coating method.

1. Introduction

Nickel oxide is one of the most important semiconductor materials in the environmental field due to the detecting ability of toxic gases [1]. Nickel oxide (NiO) has a several different applications in the field pizoelectronic, optoelectronic, environmental and renewable energy such as sensors, fuel cell electrodes, catalysis, thermoelectric devices, dye-sensitized solar cells (DSSCs) and electrochromic material for displays [2–8]. Moreover, it is used to find suitable material with enhanced properties for gas sensing applications for detecting the sensibility in the environment such as NO_x , SO_x , CO , CO_2 ..., at high temperature. Because of its semiconductor nature with controlling optical transparency and electrical conductivity to find the form of the applied interaction is significant. However, several studies have been made to find that the NiO have a high optical transparency and good electrical conductivity at

various experimental conditions. NiO thin films have a direct band gap ranging from 3.5 to 4.3 eV [9, 10].

Nickel oxide is used as thin layers, which can be deposited in several methods, including pyrolysis techniques, molecular beam epitaxy (MBE), electrochemical deposition, sputtering technique, pulsed laser deposition (PLD), chemical vapor deposition and spray Sol–Gel methods [11–16]. The cobalet doped NiO thin films were used to enhance the optical and electrical properties of deposited thin films. This is a metal transition in the periodic table, which was used in the research because of some rare earth material quality due to the increase inf optical band gap energy (broadening).

The sol–gel spin coating method has been successfully employed to deposit the nanocrystalline $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films in our laboratory at room temperature. Co doped NiO thin films were synthesised with different doping levels (0, 2, 4, 6, 8 and 16 at.%), to study the changes in the structural, optical properties of Co doped NiO thin films. However, the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films were used to determine

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Figure 1. Transmission spectra of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films as a function of Co doping level.

the optical gap energy by various methods for comparing the experimental values.

2. Experimental procedure

$\text{Ni}_{1-x}\text{Co}_x\text{O}$ solutions were prepared by dissolving the nickel nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 0.8 mol l^{-1} and cobalt chloride dehydrate ($\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$) were used as the starting materials sources in the solvent containing equal volumes of absolute H_2O . In this work, we have used a Co doping with various concentrations in the range $\text{Co/Ni} = 0, 2, 4, 8$ and $16 \text{ at.}\%$ or ($x = 0, 0.02, 0.04, 0.08$ and 0.16). Then we have added a drop of HCl for stabiliz of heating solution, the mixture solution was stirred at room temperature and heated at 50°C for 3 h to yield a clear and transparency solution. The coating was made 1 day after the precursor was prepared.

The $\text{Ni}_{1-x}\text{Co}_x\text{O}$ samples were prepared by dropping the coating solution onto glass substrate, which was rotated at 3000 rpm for 30 s by using spin coater method, the depositions were repeated for 17 times to obtain a thin film. The prepared $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films at different Na doping levels are 0 at.%, 2 at.%, 4 at.%, 8 at.% and 16 at.%. The preheat-treatment temperature of 200°C is required for the complete evaporation of organics and the initiation of formation and crystallization of the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films. After the deposition of the thin layers, the resulting thin films were annealed at 600°C in air for 2 h.

The structural properties of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films were studied by means of X-ray diffraction (XRD Bruker AXS-8D) with CuK_α radiation ($\lambda = 0.15406 \text{ nm}$) in the scanning range of (2θ) was between 20° and 50° . The optical transmission of the deposited films was measured in the range of 300–1100 nm by using an ultraviolet-visible spectrophotometer (LAMBDA 25) and the resistance R was measured by four point methods.

3. Results and discussion

3.1 Optical characteristics of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films

Figure 1 shows the variation of transmittance of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films in the range of 300–1100 nm of the wavelength. The $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films prepared between 0 and 4 at.% have an average transmittance at 70–85%. However, the doped thin films with 8 at.% and 16 at.% of cobalt have a transmittance less than 60% in the visible region. The increase of optical transmission with Co doping can be explained by decreases in the film thickness. The high transparency was obtained in Co doped NiO thin film with 4 at.% due to the interstitial site of Ni and Co.

The optical energy gap (E_g) was derived assuming allowed direct transitions between the edge of the valence and conduction band. In this work, we have used six models to determine to optical band gap energy in the NiO thin films; which are presented in figure 2. These models were based on the absorbance and absorption coefficient, here the optical energy was determined by the extrapolation of linear curve of A , A^2 , α , α^2 , $(Ah\nu)^2$ and $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$. It has been noticed that all the prepared thin films have a different absorption coefficient in visible range of the spectrum (see figure 2c), the high absorption coefficient value can be explained by the film thickness with increasing of Co doping. Therefore, we have used these models to compare the calculated optical energy in the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films. Figure 2a–f show the drawn of A , A^2 , α , α^2 , $(Ah\nu)^2$ and $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$, respectively. As shown in figure 2a–f, the intersection of the linear region on the $h\nu$ axis gives the E_g . It is determined by the transmission spectra according to the following equations [17–19]:

$$A = \alpha d = -\ln T \quad (1)$$

$$(Ah\nu)^2 = B(h\nu - E_g) \quad (2)$$

or

$$(\alpha h\nu)^2 = C(h\nu - E_g) \quad (3)$$

where A is the absorbance, d is the film thickness; T is the transmission spectra of thin films; α is the absorption coefficient values; B and C is a constant, $h\nu$ is the photon energy and E_g the band gap energy of Co doped NiO thin films. The films thickness of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films are presented in table 1.

The variations of calculated optical gap energy of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films are presented in figure 3, which shows the variation of optical band gap energy of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films at various models. As clearly seen, the optical gap energy was varied in the range 3.8–4.05 eV, and for each one the variation of optical gap energy of Co doped NiO thin films and looks like fixed when Co increases from 0 to 4 at.%, then decreased at 8 at.%, the

Figure 2. (a)–(f) Plot of A , A^2 , α , α^2 , $(Ah\nu)^2$ and $(\alpha h\nu)^2$ versus $(h\nu)$, respectively, in $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films for different Co doping levels.

optical energy have a smaller value after doping at 4 at.%, can be explained by the transition d–d in Ni of Co. As can be seen, that the band gap energy E_g is related to the

calculation method and Co doping level, it is clear that the calculated optical energy by A and α it is less than of calculated by other methods. On other hand, the

Table 1. Variation of film thickness of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films as a function of Co doping level.

Co doped NiO thin film (at.%)	0	2	4	8	16
Film thickness (nm)	168.71	144.19	136.26	329.49	414.97

Figure 3. The variation of optical band gap of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films as a function of Co doping level.

suitable method to calculate the optical energy was observed for $(Ahv)^2$ versus $h\nu$.

The same thing as the optical gap, the urbach energy (E_u) is also related to the disorder in the film network, as it is expressed as follows [20, 21]:

$$A = A_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (4)$$

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (5)$$

where A_0 and α_0 are constants and E_u is the urbach energy, it was also determined by the curves of $\text{Ln}A$ and $\text{Ln}\alpha$ as a function of photon energy $h\nu$ are used to deduce the urbach energy of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films as presented in figure 4a and b.

In figure 5 we have reported the variation of the urbach energy in the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films as a function of Co doping level. As clearly see, the curve of $\text{Ln}A$ versus $h\nu$ also suitable to estimate the urbach energy of NiO thin films. However, the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films having a few defect with minimum value of urbach energy, it was decreased after doping, the minimum value was obtained at 4 at.% of Co doping.

3.2 Electrical properties $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films

The four-points probe method was used to determine the electrical conductivity of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films, it is based

Figure 4. (a) and (b) The drawn of $\text{Ln}A$ and $\text{Ln}\alpha$ as a function of photon energy ($h\nu$), respectively, for deduce the Urbach energy for $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films.

on measured the sheet resistance of the films as expressed by:

$$R_{sh} = \frac{\pi}{\ln(2)} \cdot \frac{V}{I} \quad (6)$$

where I is the applied current = 1 nA and V is the measurement voltage. However, the electrical conductivity σ also determined by the following equation:

$$\sigma = \frac{1}{d \cdot R_{sh}} \quad (7)$$

Figure 6 show the variation of the electrical conductivity of Co doped NiO thin films as a function of Co doping level. As can be seen, the electrical conductivity increases with increasing the Co doping level up to 4 at.%, it is a maximum conductivity value was $0.012(\Omega \cdot \text{cm})^{-1}$. However, in the increase of Co doping up to 16 at.%, we have obtained a reduction in the electrical conductivity. The increase in the conductivity of the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films can be explained by the displacement of the electrons, the

Figure 5. The variation of Urbach energy of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films as a function of Co doping level.

Figure 6. The electrical conductivity variation of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films as a function of Co doping level.

latter come from the Co^{+2} donor ions in the substitutional sites of Ni^{+2} , and formation of the molecular NiCoO existed on the surface. The decrease in the conductivity of deposited films after 4 at.% can be related by the increase of the potential barriers, because the introduced atoms are segregated into the grain boundaries [22].

3.3 Structural properties of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films

The structural characterization of the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films is carried out by X-ray diffraction method is shown in figure 7. It can be noticed that all the patterns exhibit diffraction peaks around ($2\theta \sim 38^\circ$ and 44°) referred to (111) and (200) crystal plan, respectively, the peaks position was in accordance with Rahman *et al* [23]. The positions of obtain peaks with and without presence in the XRD spectra indicating that the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films are

Figure 7. X-ray diffraction of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films as a function of Co doping level.

polycrystalline in nature with cubic structure, which is in agreement with other reports [24] of the cubic type of NiO (JCPDS) No. 73-1519) [25]. However, the good crystallinity was obtained in the lower doping.

4. Conclusion

In this study, cobalt doped Nickel Oxide thin films (Co/Ni = 0, 2, 4, 8 and 16 at.%) were successfully deposited on glass substrate by Sol-Gel Sping coating technique using Nickel nitrate and Cobalt nitrate. The transmission spectra of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films indicated that the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films become transparency in the visible region. The variation of the optical gap energy was located between 3.8 and 4.05 eV, it was determined by various methods to compare the calculate values. These are estimated by the drawn of A , A^2 , α , α^2 ($Ah\nu$)² and $(\alpha h\nu)$ ² as a function of the photon energy $h\nu$, the suitable method to calculate the optical energy was observed for ($Ah\nu$)² versus $h\nu$. The Urbach energy in the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films also was determined by the curves of $\text{Ln}A$ and $\text{Ln}\alpha$ as a function of photon energy $h\nu$. The deduce by $\text{Ln}A$ versus $h\nu$, it is also suitable to estimate the urbach energy. However, the $\text{Ni}_{0.96}\text{Co}_{0.04}\text{O}$ thin films having a few defects with minimum value of urbach energy. XRD patterns of the $\text{Ni}_{1-x}\text{Co}_x\text{O}$ thin films

indicate that some films are polycrystalline with cubic structure. The electrical conductivity of deposited films is in the order of $8.2 \times 10^{-3} (\Omega \cdot \text{cm})^{-1}$.

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