Int. j. adv. multidisc. res. stud. 2023; 3(5):68-72

Received: 14-07-2023
Accepted: 24-08-2023

International Journal of Advanced Multidisciplinary Research and Studies

ISSN: 2583-049X

Optical Properties of Nanostructured NiO Thin Films Prepared by Spray Pyrolysis Method

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Abstract

In this work, nickel oxide thin films was fabricated on glass substrate at different temperature by spray pyrolysis technique. The NiO layers were obtained with different molar concentrations. The NiO thin films were crystallized with a cubic structure that can be related to obtaining peaks in the XRD diffraction of NiO thin films. The optical transmission of the deposited films was measured in the range of (300–900nm) by using an ultraviolet-visible spectrophotometer (LAMBDA 25).The transmission spectra shows that the NiO thin films have a good optical transparency in the visible region. The optical gap energy varied between 3.28 and 3.82 eV. The NiO thin films prepared with a molar concentration C=0.2mol/l at a temperature of T=460°C has the best transmittance of 90% and has a band gap energy value of 3.41eV. The $Ni_{1-x}Zn_xO$ thin films prepared with a molar concentration C=0.05mol/l at a temperature of T=480°C and x=0.13 has a transmittance of 82% and has a band gap energy of 3.72 eV. The pure NiO thin films prepared with a molar concentration C=0.1mol/l at a temperature of T=360°C has the largest refractive index value of 1.98.

Keywords: Nickel oxide, Thin films, Spray Pyrolysis Method, Optical Properties, Band Gap Energy

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 of 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 NOx, SOx, CO, CO_2…, at high temperature. Because of its semiconductor nature with controlling optical transparency and electrical conductivity, finding 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 molecular beam epitaxy (MBE), electrochemical deposition, pulsed laser deposition (PLD), chemical vapor deposition and spray Sol–Gel methods, spray pyrolysis method [11-17].

The optical transmission of the deposited films was measured in the range of (300–900nm) by using an ultraviolet-visible spectrophotometer (LAMBDA 25).

The mean objective of this research is to study the optical properties of NiO thin films based on past research. In this work; we have proposed a review of original research to nanostructured NiO prepared by spray pyrolysis method.

2. Optical Properties of NiO Thin Films

Nickel oxide is one of the most promising low cost, polarisable materials that exist since it is characterized as having excellent durability, electrochemical stability and high transmittance of 80%-90% at the spectrum range of 400-900 nm [18]. It is known as a good transparent conducting material because it's of wide band gap [19].

The analysis optical observation spectrum is one of the most productive tools for understanding and developing the band structure and energy band gap E_g of crystalline structure. Optical characterization was carried out using a UV-VIS-NIV spectra photometer [20].

In situ transmittance measurement was carried out during the electrochemical measurement at the wavelength (λ = 550 nm) using an UV-Vis-Nir spectrophotometer (λ= 950nm) [21] from variant spectral transmittance of the lingers in the three electrodes cell at normal incident angle against a reference cell that ave a global glass substrate in the devices is measured in the spectral range from 300 to 3000 nm against air as a reference.
The variation in optical density (Δ OD) was calculated by the measured transmittance of the layer or device in the colored (Tc) and bleached (Td) state by the application of this equation [21].

$$\Delta \mathrm{OD} = \log 10(\mathrm{Tb}/\mathrm{Tc}) \quad (1)$$

2.1 The transmittance of NiO thin films

The transmittance of NiO thin films obtained by many researchers confined between 40 to 80%, in the range of visible these values vary from substrate to substrate according to conditions of the experiment, they many experiments obtain the transmittance of NiO thin films equal to 80%.
Pathal *et al* [22], in their own experiences found when increased the concentrate solution of NiO it leads to decreases of transmittance, latter because of increase atoms of Ni in solution, and when we study, we found that samples, when prepared in high temperature are characterized by good transmittance because of crystallization in the good case [23], in the other direction and from researchers, they spokes about thickness are found the transmittance affected by length of thickness NiO thin films, if the transmittance high so the NiO thin films have superfine thickness these NiO thin films found by many researchers [24], finally there is an effect, the doping by more materials such as Ag, Zn, Li, Co, Cu and Na *et al*. Eachelement has a special effect:

- Several researchers have found if the value of Zn in the solution of $Ni_{1-X}Zn_XO$ is law, so the transmittance have big values [25-26].
- Many experiments affirm that, if the high value of Mn in the solution $Ni_{1-X}Mn_XO$, so the transmittance is law [27].
- We found several research, the law percentage of Li in the solution of NiO makes big transmittance of NiO thin films [28].

Table 1: The relation between grain/crystallite size and transmittance NiO films deposited at the different conditions

S.N.	Condition	Grain \ Crystallite size (nm)	Transmittance (%)	Ref
NiO-Ag	400°C Ni : 42.13 % atomic Ag: 11.06 % atomic O: 47.13 % atomic P : 5.10^{-4} mbar	11.00 (nm)	39 **%**	[29]
NiO-B	NiO:97 % B:3% 400°C C = 0.1 M	30.00 (nm)	12 **%**	[30]
NiO	C = 0.5 M T=500°C	1100 (nm)	40 **%**	[31]
NiO	C = 0.5 M T=500°C Precusor = 10 mL	73.62 (nm)	70 **%**	[32]
$Co_xNi_{1-x}O$	C =0.1 M T = 573°K X = 0.15 Nozzl = 28 cm	124 (nm)	70 **%**	[33]
$Ni_{1-x}Zn_xO$	C =0.05 M T = 480°K X = 0.12	13.31 (nm)	82 **%**	[26]
NiO:8Li	C = 1 M T = 600°C	17.7 (nm)	75 **%**	[34]
NiO:8Li	C = 0.1 M T = 400-430°C	20 (nm)	73 **%**	[35]
NiO	Ni = 58.80 w % O = 22.26 w % C = 18.93 w % T = 470°C	50 (nm)	68 **%**	[36]
NiO	T = 300°C C = 0.03 M	20 (nm)	30 **%**	[37]
$NiCo_2O_4$	T = 300° C = 0.1 M	10 (nm)	59 **%**	[38]
NiO	T = 360°C C = 0.1 M T_a = 30 min	116 (nm)	76 **%**	[39]
NiO	T = 460°C C = 0.2 M	350 (nm)	75 **%**	[40]
$NiO_{1-x}Zn_X$	T = 623°K C = 0.1 M X = 0.05	18.75 (nm)	75 **%**	[41]
NiO	T = 350°C C = 0.75 M	12.82 (nm)	65 **%**	[42]
NiO	T = 450°C C =0.01	92 (nm)	71 **%**	[43]

2.2 Absorbance of NiO thin films

In the last years, many researchers' spokes to absorbance, they found that the value of absorbance for NiO thin films between 0.1 and 0.8 in the range 380 to 800 nm of the wavelength visible.
Akl and Mahmoud [44], however, the absorbance it's affected by more property such as temperature, she superfast in the law temperature on account of miss-class of atoms, this is last prevented passing the light, they found other researchers [45], that absorbance affected by concentration, so the absorbance law in the highest molarities because of there is no stacking of the grain thin films which facilitate passage of light. And in the other article [46], they found influence to absorbance by thickness, so small values of absorbance resulting from large thickness, finally we saw on other influential it's doping by many materials, such as Ag, Zn, Co, Cu and Na, *et al*, each element has a special effect :

- The higher the percentage of Zn in $Ni_{1-X}Zn_XO$ solution of thin films, so the decreased value of the absorption NiO thin films [47-26].
- In decrease that value of Mn with NiO, so higher the percentage of absorption [48].
- The solution of NiO:Li if the concentration Li is law, so the absorption of NiO thin films is also weak [49].

2.3 Optical band gap of NiO thin films

In solid-state physics, a band gap, also called an energy gap or band gap, is an energy range in a solid where no electron states can exist. In graphs of the electronic band structure of solids, the band gap generally refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. It is the energy required to promote a valence electron bound to an atom to become a conduction electron, which is free to move within the crystal lattice and serve as a charge carrier to conduct electric current. It is closely related to the HOMO/LUMO gap in chemistry. If the valence band is completely full and the conduction band is completely empty, then electrons cannot move in the solid; however, if some electrons transfer from the valence to the conduction band, then the current can flow. Therefore, the band gap is a major factor determining the electrical conductivity of a solid. Substances with large band gaps are generally insulators, those with smaller band gaps are semiconductors, while conductors either have very small band gaps or none, because the valence and conduction bands overlap (see Table 2) [50].

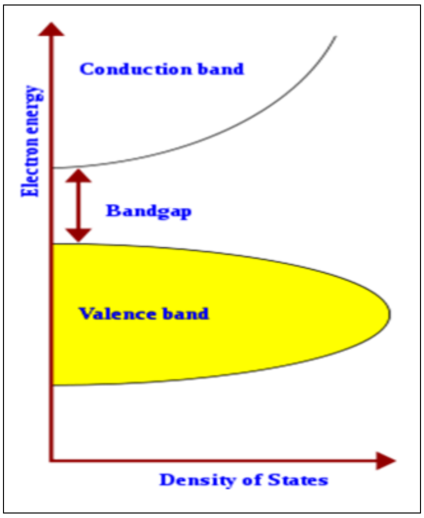

Fig 1: Band gap in semiconductor

That absorbance and the optical band gap energy E_g of fabricated NiO thin films were determined by the following relations [51-52]:

$$A = \alpha d = -\ln T \quad (2)$$

$$(Ah\upsilon)^2 = C\,(h\upsilon - E_g) \quad (3)$$

Where A is the absorbance of fabricated NiO thin films, α is the absorption coefficient, d is the film thickness, T is the transmission of fabricated NiO thin films, C is a constant, hυ is the energy of photon ($h\upsilon = \frac{1240}{\lambda(\mathrm{nm})}\,(\mathrm{eV})$) and E_g is the band gap energy of the semiconductor.

Table 2: Band gap energy and transmittance values of NiO thin films deposited at different conditions

S.N.	Condition	Band gap energy (eV)	Transmitence (%)	Ref
Li-NiO	T= 420°C C = 0.1 M	Eg=3.51 Ev	68 %	[53]
NiO-Ag	400°C Ni : 42.13 % atomic Ag: 11.06 % atomic O: 47.13 % atomic P : 5.10^{-4} mbar	Eg=3.00 eV	39 %	[29]
NiO-B	NiO:97 % B:3% 400°C C = 0.1 M	Eg=3.58 eV	12 %	[30]
NiO	C = 0.5 M T=500°C	Eg=3.28 eV	40 %	[31]
NiO	C = 0.05 M T=450°C	Eg=3.51 eV	78 %	[17]
NiO	C = 0.5 M T=500°C Precusar = 10 mL	Eg=3.64 eV	70 %	[32]
$Co_xNi_{1-x}O$	C =0.1 M T = 573°K X = 0.15 Nozzl = 28 cm	Eg = 3.26 eV	70 %	[33]
$Ni_{1-x}Zn_xO$	C =0.05 M T = 480°K X = 0.13	Eg = 3.72 eV	82 %	[26]
NiO:8Li	C = 1 M T = 600°C	Eg = 2.28 eV	80 %	[34]
NiO	Ni = 58.80 w % O = 22.26 w % C = 18.93 w % T = 470°C	Eg = 3.11 eV	85 %	[35]
NiO	T = 300°C C = 0.03 M	Eg = 3.56 eV	68 %	[36]
Zn_XNiO_{1-x}	T = 460° C = 0.1 M X = 0.6	Eg = 3.66 eV	30 %	[54]
NiO	T = 360°C C = 0.1 M	Eg = 3.48 eV	86%	[39]
NiO	T = 460°C C = 0.2 M	Eg = 3.41 eV	90 %	[40]
$NiO_{1-x}Zn_X$	T = 623°K C = 0.1 M X = 0.05	Eg = 3.48 eV	75 %	[41]
NiO	T = 350°C C = 0.75 M	Eg = 3.70 eV	65 %	[42]
NiO	T = 450°C C =0.01	Eg = 3.82 eV	84 %	[43]
NiO-Cu	T = 1737°F Cu = 16.17 at%	Eg = 3.6 eV	45 %	[55]
$(NiO)_{1-x}(ZnO)_x$	T = 400°C C = 0.05 M X = 0.25	Eg = 3.67 eV	60 %	[56]

2.4 Refractive index

The optical reflectance spectra (R) have been used to determine the refractive index (n) (see table 3) of the film through the relation [57-58].

$$n = \frac{1+R}{1-R}\sqrt{\frac{4R}{(1-R)^2} - K^2} \quad (4)$$

Where K is the extinction coefficient, R is the reflection; n is the refractive index [59- 60]:

Table 3: Refractance index values of NiO thin films deposited at different conditions

N.S	Condition	N	Ref
Li-NiO	T= 420°C0 C = 0.1 M	1.72	[53]
NiO	T = 360°C C = 0.1 M	1.98	[39]

3. Conclusion

Nickel oxide (NiO) has attracted a great deal of attention due to its wide direct band gap of (3.5-4.2 eV), which exhibits p-type conductivity. Stoichio metric NiO is an insulator with a resistivity of the order of $10^{13}\Omega$.cm at room temperature. NiO is one of the most important oxide materials due to its excellent chemical stability and durability, low toxicity, large span optical density, low cost and good thermal stabilityand high stability that are similar to ZnO. NiO can be used in various potential applications such as solar cells due to the p-type semiconducting, transparent diodes, transparent transistors, displays and defrosting windows because their transparency can be used for the UV photo detectors and touch screens due to the good responsively. NiO can be produced by several techniques such as reactive evaporation, molecular beam epitaxy (MBE), magnetron sputtering technique, pulsed laser deposition (PLD), spray pyrolysis, sol–gel process, chemical vapor deposition, and electrochemical deposition. The NiO thin films prepared with a molar concentration C=0.2mol/l at a temperature of T=460°C has the best transmittance of 90% and has a band gap energy value of 3.41eV. The $Ni_{1-x}Zn_xO$ thin films prepared with a molar concentration C=0.05mol/l at a temperature of T=480°C and x=0.13 has a transmittance of 82% and has a band gap energy of 3.72 eV. The pure NiO thin films prepared with a molar concentration C=0.1mol/l at a temperature of T=360°C has the largest refractive index value of 1.98.

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