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Spin coating method deposited nickel oxide thin films at various film thickness

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Abstract

The objective of this research is to study the influence of the film thickness on the optical and electrical characterizations of the prepared NiO thin films. For this, we used thin films such as nickel oxide, which has been prepared on the glass substrates by a spin-coating technique using nickel nitrate hexahydrate (Ni (NO3)2.6H2O) as source materials. The coating process was repeated for 13, 14-, 15-, 16- and 17-layer times to obtain a good NiO thin film. The optical and electrical characterizations were observed to be dependent on each film's thickness. For smaller film thickness the thin films have a high optical transmission (over 88 %) in the visible of the longer of the wavelength higher than 400 nm. The bandgap energy was found to be in the range of 3.94–4.06 eV depending on the film thickness. The lowest value of Urbach energy was 0.182 eV. In the end, the electrical measurements are investigated by the four-point method, the results show that the good electrical conductivity was found at 171 nm.

Keywords: NiO, thin films, spin coater method, polycrystalline structure, electrical conductivity

Introduction

Recently, semiconductors as oxides metallics are essential compounds for the development of the ultra-high frequencies' components, gas sensors, photocatalysis, optoelectronics, lithium-ion micro batteries, enamels and cathode materials for alkaline batteries. Among these, nickel oxide (NiO) is a semitransparent p-type semiconducting material of a large gap direct, and has a wide range of applications, such as gas sensors, photocatalysis, dye-sensitized, electrochromic coatings, UV photo-detector, light weight structural components in aerospace, in ceramic structures, a counter electrodes and anode layer of solid, counter electrodes oxide fuel cells [1,2].

Nickel oxide NiO is a semiconductor material with a nature of p-type, which belongs to the part of this family of TCO; this renders possible a several potential applications in the gas sensors due to the range of bandgap energy (3.6-4.0 eV), for the organic solar cell applications due to the p-type semiconducting. It is used in transparent diodes due to the good transparency, also it can be used in the transparent transistors owing to the best optical transmission and electrical conductivity, also NiO can be used for defrosting windows due to the good conductivity. Fabricated NiO is used in UV photodetectors and touch screens on account of the good responsiveness [3,4].

The thin films of NiO can be obtained by various deposition methods such as electrochemical deposition, pulsed laser deposition, technique of magnetron sputtering, molecular beam epitaxy (MBE), reactive evaporation, sol-gel process, chemical vapor deposition, and spray pyrolysis [5,6]. NiO has been intensively studied as a promising material for gas sensors because of its wide band gap (3.6–4.0 eV) and high stability that are similar to ZnO [7].

The aim of this tutorial work is to present some information of TCOs films, and a detailed description of the optical and electrical characterizations of NiO. The films were deposited with different film layers times, then the NiO was crystallized at 600˚C for 2 hours in the air.

Experimental

Spin coating method

In the experimental work, the choice of sol-gel method to deposit NiO thin films aims at obtaining the best quality results. It has the following characteristics in order to achieve good properties. Following this technique, in our work we will deposit the thin films by a spin coating method, which is a method suitable for fabrication of the nanocrystalline thin films with high purity. In this method, the surfactants, solvents, reaction, time and temperature are the main factors to watch in order to obtain suitable quality solution with remarkable electrochemical performance of the NiO solution. It mainly consists in four steps as expressed below:

1) Preparation of the NiO solution precursor solutions.
2) Formation of the intermediate solution of NiO.
3) Conversion from NiO solution to gelatin NiO.
4) Calcinations [8].

The spin coater used to deposit the NiO thin films is presented in Fig. 1.

Figure 1: The spin coating method

Table 1: The characterization of nickel nitrate

Property	Value
Chemical name	Nickel nitrate
Molecular formula	Ni $(NO_3)_2.6H_2O$
Molecular weight	290.8 g/mol
Color	Green
Density	2.05 g/cm^3
Melting point	˚C

Preparation of the solution

The prepared solutions NiO have dissolved 0.8 M of the nickel nitrate hexahydrate NiCl2.6H2O (see Table 1) in the absolute H2O, HCl was used as a stabilization solution of NiO, and the HCl has been used to stabilize the NiO solution. The final mixture solution has been stirred in a heat at 40 ˚C to have a solution with high transparency. The film coating was deposited two days after the preparation.

Depositing of thin films

NiO thin films were synthesized by the spin coating process using one solution:

The first sample was prepared by dropping the coating solution on a glass substrate, which was rotated between 2000 and 3000 rpm for 30s by using spin coater. The coating process was repeated for 13, 14, 15, 16 and 17 times to obtain a thin film. The preheat-treatment temperature of 200 ˚C is required for the complete evaporation of organics and the initiation of formation and crystallization of the NiO film. After the deposition of the thin layers, the resulting thin films were annealed at 600 ˚C in air for 2 h.

Crystallization layers

Finally, a thin film was placed into a furnace and crystallized at a temperature of 600 ˚C for 2 hours in air, to obtain the surface homogeneous of NiO thin films and to improve the electrical conductivity of NiO.

Characterization of the films

The optical and electrical properties of nickel oxide thin films were evaluated using several characterization techniques such as:

The optical transmittance of fabricated NiO:Cu films was measured by an UV-visible (25-LAMBDA) in the range of 300–1000 nm. The crystalline structure of fabricated films was obtained by X-ray diffraction (Bruker-XRD AXS-8D, λCuKα = 0.15406 nm with 2θ varying between 30° and 50°).

The electrical conductivity was measured by injection current-voltage by four-point method into the deposited film surface. All characterizations have been made at stable conditions.

Results and discussion

Transmittance spectra

The optical transmission spectra of NiO thin films at several film thicknesses are presented in Fig .2. Here the optical transmission is measured as a function of the longer wavelength in the field ranging between 300 to 1000 nm. As can be seen at lower deposition with film thickness which were used present a highly transparent material (<72%) in the visible range. However, in the lower wavelengths (< 400 nm) the NiO thin films have a weak transparency less than 60 % at high film thickness due to the material nature of NiO.

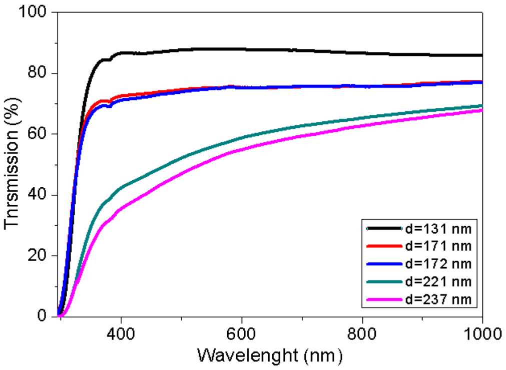

Figure 2: Optical transmission spectra of NiO thin films

The minimum reflectance in NiO thin films was obtained at lower film thickness (see Fig. 3). As can be seen that the film becomes transparent and no light is scattered or absorbed at the non-absorbing region (i.e. R+T+D=l), the inequality (R+T < 1) at shorter wavelengths.

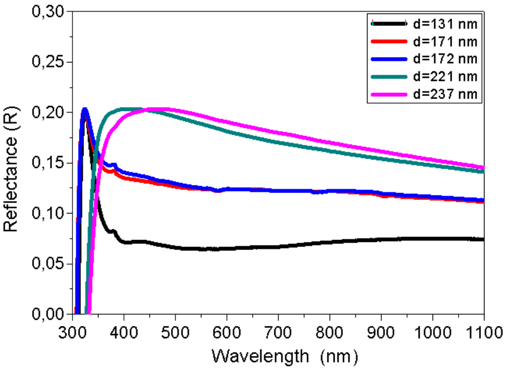

Figure 3: Reflectance spectra of NiO thin films

Optical gap

The optical band gap E_g was determined from optical transmission spectra of NiO thin films which was obtained by extrapolating the linear portion of the plot $(\alpha h\nu)^2$ versus $(h\nu)$ to $\alpha = 0$ [11]. See Fig. 4, the method to design the extrapolating was used according to the following equation [11]:

$$A = \alpha d = -LnT \qquad (1)$$

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

where A is the absorbance, C is a constant, $h\nu$ is the photon energy ($h\nu = \frac{1240}{\lambda}$) and E_g the band gap energy of the semiconductor. As it was shown in (see Fig. 4) a typical variation of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) used for deducing optical band gap E_g, it is determined by extrapolation of the straight-line portion to zero absorption ($\alpha = 0$) [11] the values of E_g are presented in Table 2.

The disorder (Urbach energy)

D (nm)	131	171	172	221	237
E_g (eV)	3.96	4.04	4.06	3.94	3.97
E_u (eV)	0.182	0.228	0.223	0.288	0.260

As it was shown in the Fig. 5, a typical variation of $(Ln\alpha)$ vs. photon energy of NiO thin film for deducing the Urbach energy, which is related to the disorder in the film network, is expressed as [12]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \qquad (3)$$

where α_0 is a constant and E_u is the Urbach energy was 196.7 meV. The optical band gap energy E_g and the Urbach energy E_u are presented in Table 2.

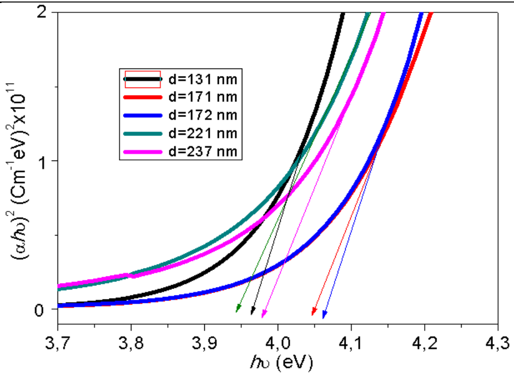

Figure 4: The variation of $(\alpha h\nu)^2$ as a function of $h\nu$ for each films thickness

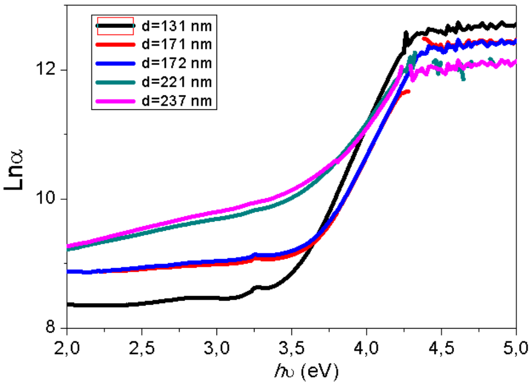

Figure 5: The variation of $Ln\alpha$ as a function of $h\nu$ for each films thickness

Table 2: The bandgap energy Eg and the Urbach energy Eu

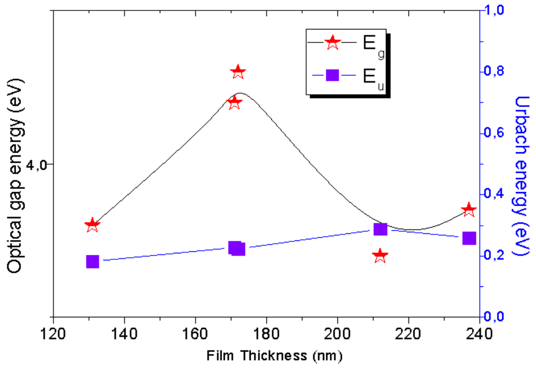

Figure 6: The changes of the bandgap energy Eg and the Urbach energy Eu as a function of films thickness

Fig. 6 shows the variation of the band gap energy E_g and the Urbach energy E_u as a function of the films thickness. The optical gap and disorder vary inversely; it is observed that the band gap energy and Urbach energy of NiO thin films increased with increasing films thickness up to 172 nm and the optical gap energy decreased at 221 nm. This result can be explained by decreasing the optical transmission of the films (see Fig. 2).

Refractive Index (n)

The refractive index is an important parameter for characterization of optical materials design, and it includes valuable information for higher efficiency optical materials. In this work the refractive index (n) can be calculated by using the following formula [13]:

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

where n is the refractive index, R is the reflectance and K *is* the extinction coefficient of NiO thin films.

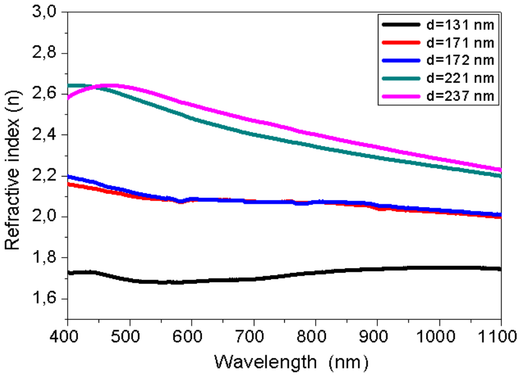

Figure 7 relation between the refractive index and the longer of wavelength for nickel oxide thin films at several film thickness

The variation of refractive index as a function of wavelength for spectrum range (400-1100 nm) of nickel oxide thin films is shown in Fig. 7. It can be seen that the refractive index value decreases towards the long wavelengths. As can be seen the index of refraction increases with increasing the film thickness up to 237 nm, the results show that the refractive index values of prepared films have values in the range of (1.7- 2.6).

Extinction coefficient (K)

The extinction coefficient (K) was calculated using the following relation [13].

$$K = \frac{\alpha\lambda}{4\pi} \qquad (5)$$

where λ is the wavelength and α is the absorption coefficient can be estimated from the absorbance using the formula [13]:

$$\alpha = 2.303 \times \frac{A}{d} \qquad (6)$$

where d is the thickness of the NiO thin films. Fig. 8 represents the relationship between extinction coefficient and wavelength.

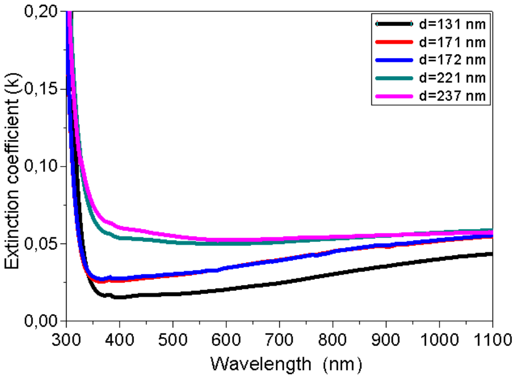

Figure 8: The relation between the extinction coefficient and the longer of wavelength for nickel oxide thin films at several film thickness

Electrical properties

The four-point method was used to determine the sheet resistance (Rsh); which was applying a variation in the current (I) between the outer two leads and measuring the potential difference (V), this model was applied in the linear. This method is important in electrical property for comparing with other methods. The sheet resistance Rsh was calculated from the following relation [14]:

$$R_{sh} = \frac{\pi}{\ln(2)} \cdot \frac{V}{I} \tag{7}$$

where I is the applied current = 5.10-8 A and V is the measurement voltage.

Table 3 and Fig. 9 give the sheet resistance R_{sh} of the NiO thin films as a function of films thickness.

The electrical direct conductivity σ equals inverse of resistivity as the following equation [14]:

$$\sigma = \frac{1}{\rho} \tag{8}$$

with the probes centered on a very wide (lateral dimension d >> s) and very thin (Thickness d << S) sample, with s the probe spacing, the resistivity is given by [14]:

$$\rho = \frac{\pi}{\ln(2)} d \frac{V}{I} = 4.5324 d \frac{V}{I} \tag{9}$$

Table 3: The electrical resistivity ρ and the electrical conductivity σ in several films' thicknesses

D (nm)	131	171	172	221	237
R_{sh} (Ω)	743248	287848	571213	540818	1407941
σ (Ωcm)	0.103	0.203	0.102	0.084	0.0299

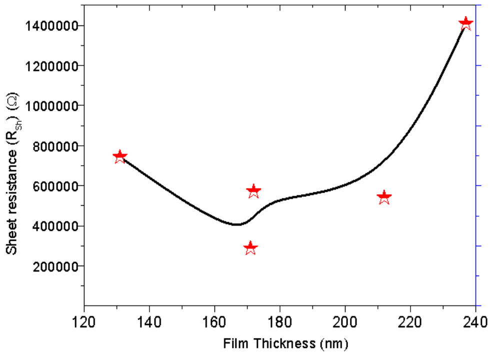

Figure 9: The changes of the sheet resistance NiO films in several films' thicknesses

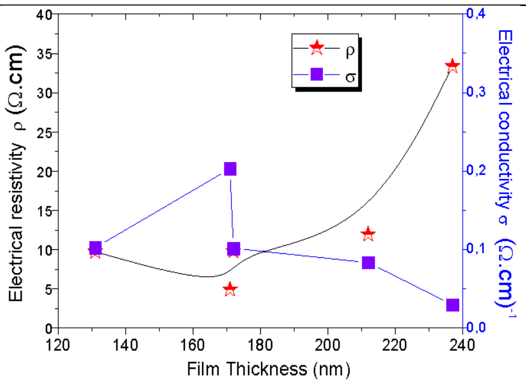

Figure 10: The changes as a function of NiO film thickness of the electrical resistivity and the conductivity

Fig. 10 shows the changes as a function of NiO film thickness of the electrical resistivity and the conductivity. It is observed that the conductivity increases up to 171 nm then decreases with increasing film thickness up to 237 nm. This observation in the increase of conductivity has been explained by the potential barriers with the Urbach energy. A decrease in the resistance can be expected with an increase in the film thickness. As can be seen from the curve NiO film of 237 nm exhibits a good electrical property.

Figure of merit

Information about prepared NiO thin films can be presented by the figure of merit for the good quality, which is measured from the optical transmission and sheet resistance by using Haacke formula [14]:

$$FOM = \frac{T^{10}}{R_{sh}} \tag{10}$$

where T and R_{sh} are the transmittance and the sheet resistance. The variation of the calculated FOM values of the prepared NiO thin films at several film thicknesses is shown in Fig. 11. We noted that an enhancement of the values of figure of merit in the visible region with the mentioned above was obtained in this study whereas a maximum value of medium figure of merit was achieved at 131 nm.

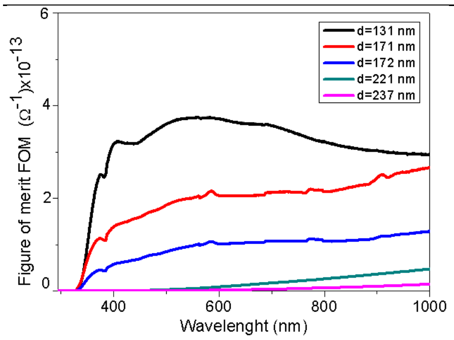

Figure 11: Figure of merit of NiO thin films with several film thickness

Conclusion

NiO thin films with different thicknesses have been deposited using a sol-gel spin coating method on glass substrates. We varied the number of coatings in order to produce different thicknesses of the thin films. The coating process was repeated for 13, 14, 15, 16 and 17 times to obtain a thin film. The optical and electrical properties were found to be dependent for each film's thickness. For smaller film thickness the thin films showed high transmission property (over 88 %) in the visible wavelength region. The optical band gap was found to be in the range of 3.94–4.06 eV depending on the film thickness. The minimum value of Urbach energy was 0.182 eV. The resistivity decreased for film thickness of 171 nm, due to an increase in carrier mobility. The good electrical conductivity was found at 171 nm.

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