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Study of thin Films of Nickel Oxide (NiO) Deposited by the Spray Pyrolysis Method

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Abstract: In this work, thin films of nickel oxide (NiO) were deposited by a simple and inexpensive technique, which is spray pyrolysis on ordinary glass substrates heated to a fixed temperature of 500 °C, from a solution containing nickel nitrate hexahydrate as a precursor dissolved in distilled water with deferent values of concentrations. The NiO thin films obtained were characterized to determine the structure with X-ray diffraction technique (XRD), the absorption domain (UV-Visible Spectroscopy), and the surface morphology (SEM). The X-ray diffraction patterns confirm the presence of NiO phase with preferential orientation along the (111) direction. The optical gap for nickel oxide calculated with a concentration of 0.1 M from the measurement of optical absorption is 3.6 eV, which is quite comparable to the value of the ratio.

Key words: NiO, thin films, spray pyrolysis.

Nomenclature

c	Speed of light
h	Planck's constant
T	Temperature

Greek Letters

α	Absorption coefficient
λ	Wavelength
$h\nu$	Photon energy

1. Introduction

Advanced Oxidation Processes (AOPs) are among the most recent advances in the treatment of wastewater and industrial effluents that are a major concern today. The latter describes a novel treatment method, known as heterogeneous photocatalysis, which is a combination of a semiconductor catalyst with a light source. Metallic oxides are catalysts used for the degradation of some pollutants existing in water by the heterogeneous photocatalysis process such as ZnO, TiO2, CuO, NiO. Nickel oxide (NiO) is a binary compound that is an important material because of its large direct optical gap of the order of 3.6-4 eV [1], it is a very resistant to oxidation and has a high chemical stability [2], a density of 6.72 g/cm^3 [3]. The work presented in this manuscript is focused on the study of the thin films of nickel oxide developed by the pyrolysis spray technique which presented advantages such as simplicity, inexpensive, efficient and fast with wide surfaces and good uniformity [4, 5] with their characterizations by X-ray diffraction techniques (XRD), UV-Visible Spectroscopy (SEM), with gap calculation.

2. Experimental Setup

The preparations of thin films of NiO are made from a solution of hexa-hydrated nickel nitrate as precursor dissolved in distilled water was used to prepare all concentration solutions. The distilled water used as a reactant to supply the oxygen atoms. The substrates in ordinary glass are well adapted for the optical characterization of our films, these latter are cleaned before use with acetone solution in the ultrasound machine for 10 minutes under 40 °C, and in the ultrasound machine for 10 min and rinsed with distilled water, finally dried with a dryer. To obtain the desired

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molarity (0.05, 0.1, 0.15 M), the precursors will be weighed by an electronic scale, where the quantities measured are mixed with a volume of distilled water. The mixture heated to prevent breaking of the substrates, and ejected onto glass substrates placed in a spray pyrolysis equipment, the schematic of this latter is shown in Fig. 1. Spray pyrolysis chemical deposition involves causing chemical reactions of a solution to form a solid deposit on a substrate heated between T = 200 °C and 500 °C.

3. Experimental Results

The present chapter contains the results of our work concerning the characterization of thin films nickel oxide (NiO), which are deposited with spray method. The obtained thin films were analyzed by different characterization techniques such as X-ray diffraction, scanning electron microscope, optical microscope, spectrophotometer, and so on....

3.1 Structural Characterization

The characterizations with XDR techniques are useful for phase material identification, making it possible to have information on the crystallinity and structure of the prepared thin films.

The spectra of NiO thin films deposited at 500 ° C with a concentration of the fixed solution equal to 0.1 M, are shown in Fig. 2.

From the results of the diffractograms it can be noted that the presence of the peak (111) confirms the cubic structure of the NiO films with the intensity of the principal peak value of 37°.

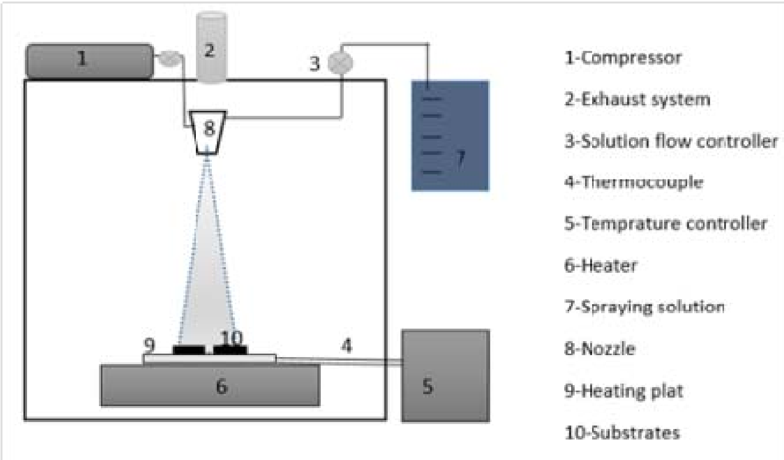

Fig. 1 Schematic the system chemical spray pyrolysis.

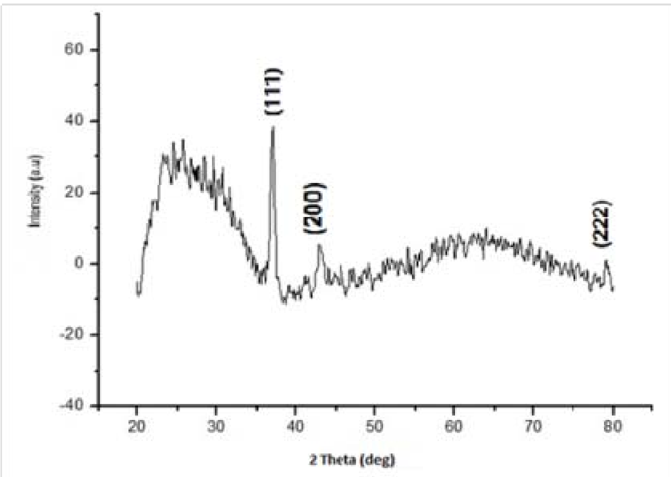

Fig .2 XRD patterns of NiO thin film.

3.2 Morphological Characterization

The morphology of the prepared NiO thin films has been investigated using Scanning electron Microscope (SEM). The SEM images are shown in Fig. 3.

The investigations obtained by this technique show that the surface of the elaborated layers is covered with material furthermore, the roughness of the surface. The particles of NiO are at the nano-metric scale.

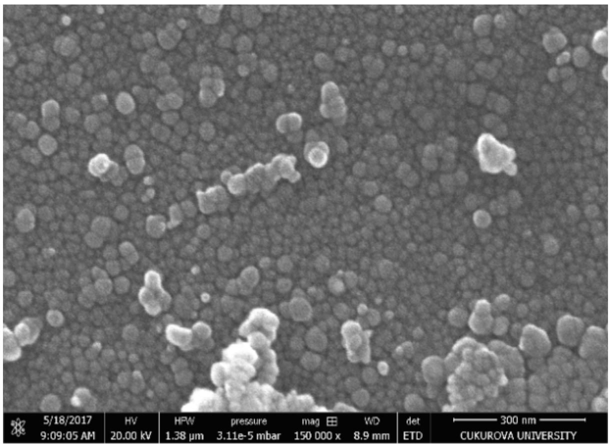

Fig. 3 SEM image of NiO thin films.

3.3 Absorption Domain

The UV-Visible adsorption spectrum of the NiO films (0.1 M) shows that the presence of a maximum adsorption band appears in the ultraviolet range at the value of 34,500 cm^{-1}.

Fig. 4 shows the UV-Visible transmission spectra of the NiO layers prepared with different concentrations of the precursor dissolved in water (0.05, 0.1 and 0.15 M).

From Fig. 4, we can note that the concentration has an influence on the transmission of the layers, therefore the optical gap of the NiO will affect with this variation.

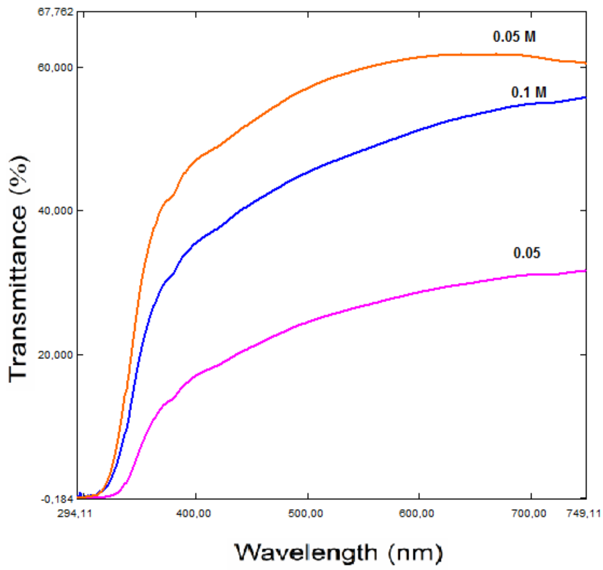

Fig. 4 UV-Visible transmission of NiO thin film with deferent value of concentration (0.05, 0.1and 0.15 M).

3.4 Determination of the Optical Gap

Nickel oxide has very interesting optical properties for various applications. For this, the study of optical properties is necessary for the characterization of thin films such as transmittance, energy gap, etc. To determine the width of the optical gap of nickel oxide, we need the model proposed by Tauc where Eg is connected to the absorption coefficient α and the photon energy $h\nu$ by the following equation [6] :

$$(\alpha h\nu)^2 = A(h\nu - Eg) \qquad (1)$$

where:

h : Planck's constant $h = 6.6\times10^{-34}$

The value of Eg can be obtained experimentally by extrapolating the plot of $(\alpha h\nu)^2 = f(h\nu)$ at $\alpha = 0$. The latter is calculated in eV by Ref. [7]:

$$h\nu = \frac{hc}{\lambda} = \frac{1,24}{\lambda}(eV) \qquad (2)$$

The values of the optical gap of NiO thin films deposited with deferent concentration of solution are shown in Fig. 5.

Table 1 gives the energy gap values obtained by using the concentration of diposit solutions with different concentrations.

Table 1 Values of Eg (eV) with deferent concentration.

Concentration (M)	0.05	0.10	0.15
Eg (eV)	3.63	3.6	3.57

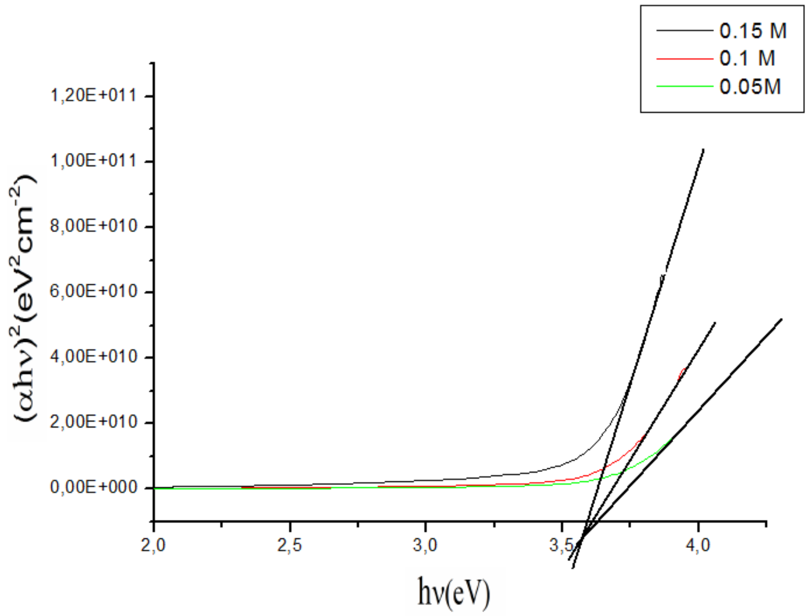

Fig. 5 Determination of the optical gap of NiO thin films (0.05 M, 0.1 M and 0.15 M).

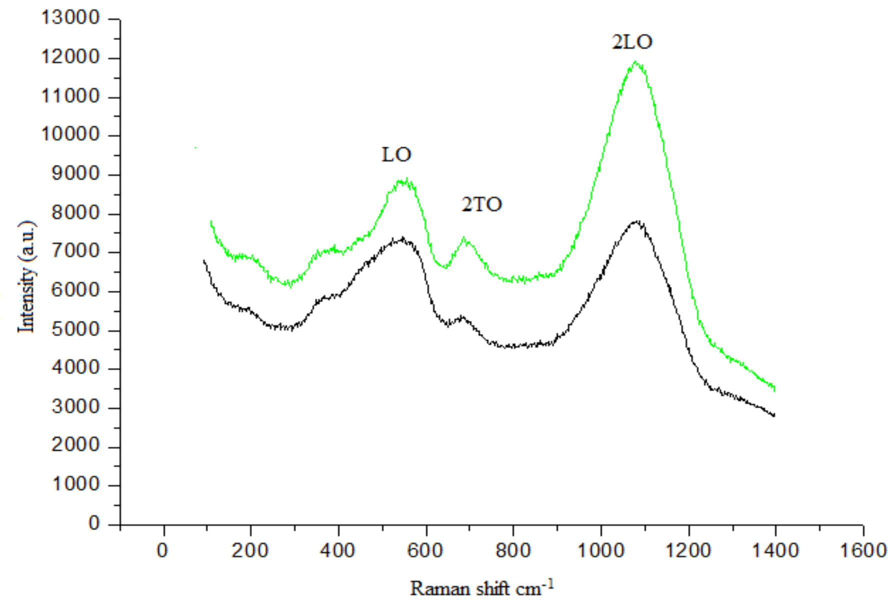

Fig. 6 Raman spectra of nickel oxide thin film (0.1 M).

3.5 Raman Spectroscopy

Raman spectroscopy (Raman analysis) is an optical spectrometry highlighting the molecular vibrations, allows us to determine the chemical structure of a sample and to identify organic molecules, polymers, biomolecules and inorganic compounds also. Fig. 6 represents the Raman spectrum of the thin film NiO where the band positions are expressed in (cm^{-1}) which correspond to the characteristic vibration frequencies of the molecular bonds, as a function of the intensity of these bands is expressed in arbitrary units (ua).

The Raman spectrum of the thin film NiO shows among several bands a strong peak at 540 cm^{-1} corresponds to the vibrations of Ni-O [8] (one-phonon

TO and LO modes), at ~700 cm^{-1} two-phonon 2TO modes. The last strongest band at ~1,100 cm^{-1} corresponds au 2LO modes.

The phonon related part of the Raman spectra indicate with (LO and 2TO modes) in Fig. 6 in nanosized NiO thin film is rather similar to that in the single-crystal (u.a.).

4. Conclusions

From the results obtained, we have led to the following observations

- Spray pyrolysis of aqueous Nickel Nitrate solutions is a simple and effective method for preparing NiO thin films at moderate temperatures.
- The formation of the nickel oxide phase by X-ray diffraction analysis, the film crystallites obtained have preferential orientation in the (111) direction.
- The UV-Visible spectra of thin films developed by deferent concentration values showed that the films show optical transmission in the ultraviolet.
- The observation of the state of the surface of our thin layers by SEM shows that the latter have a uniform distribution and cover the entire surface of the substrate furthermore; there is a roughness of the surface.
- The transmittance of NiO to a good range of transmittance, is between 30-60%.
- The use of Raman scattering spectroscopy to study the magnetic ordering in nanosized NiO thin film, is prepared by the pyrolysis spray method, and we observed the appearance of a characteristic band at the longitudinal vibration LO at 540 cm^{-1} corresponds to the vibration Ni-O, as well band corresponds to 2TO and 2LO modes at 700 and 1,100 cm^{-1}.

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