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Characterization of sol-gel derived NiO thin films: Effect of post-heat treatment

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ABSTRACT

Nickel Oxide (NiO) thin films have a wide range of applications in the field of photovoltaics and optoelectronics technology, due to their excellent properties. By modifying the composition and state of the structure with heat treatments, most of the properties of the film are improved. Thus, this study aim to show the behavior of NiO thin films with the post-heat treatment. We prepared thin films of nickel oxide (NiO) by the spray pyrolysis method, deposited on glass substrates and heated to different temperatures (200 ° C, 250 ° C and 300 ° C). The obtained samples were characterized by UV-Visible spectroscopy, contact angle measurement and Raman spectroscopy. We found that the transmittance of films increases with the annealing temperature and Urbach energy (disorder) decreases with increasing optics gap and annealing temperature. Also, the contact angle increases with the temperature of the annealing, but the surface remains hydrophilic. Furthermore, the Raman spectrum has shown the presence of the crystalline state and amorphous carbon (graphite).

Keywords: NiO, Thin films, Spray pyrolysis, sol-gel, heat treatment .

INTRODUCTION

Transparent conductive oxides with a wide band gap (>3eV) such as nickel oxide (NiO) are very attractive and of great interest due to their various applications in the microelectronics and optoelectronics devices including radiation detection diodes, photovoltaic cells, diodes emitters, lasers, gas sensors, solar cells and photocatalytic cells [1]. Nickel oxide has p-type oxide semiconductor character with large band gap energy. It provides an antimagnetic arrangement based on the properties of face-centered cubic (Perovskite) crystal symmetry [2]. The lattice parameter is 0.417 nm, which is 18% larger than that of metallic nickel [3]. Nominally pure stoichiometric NiO is an insulator with a resistivity at room temperature of the order of 1013 □-cm 68. NiO is characterized by high chemical and thermodynamic [4] stability and high oxidation resistance. Also, It is non-toxic, inexpensive, easy to produce and very abundant in nature,. Depending on the method of preparation, it comes in the form of a more or less dense and less black greenish-gray powder [5]. Structural properties are very sensitive to the nature and number of point (interstitial, substitute, vacant), line (dislocation) and plane (grain boundary...) defects that may exist inside the crystalline structure [6]. As a semiconductor thin films, it opened new ways of artificial structures for electronic and optical devices [7].

There are various thin film deposition methods that are under continuous development and improvement. The sol-gel process is the best alternative to partially costly and complex techniques which makes possible to produce thin layers by spin-coating, dip-coating and spraying [8]. Sol-Gel is a process for developing materials from precursors in solution. It allows, within the framework of soft chemistry approaches, to produce thin layers consisting from a pile of metal oxides nanoparticles [9]. The simplest deposition technique used in the field of thin layers is spray pyrolysis. in this method, the layers are obtained by atomizing the precursor into fine droplets and transporting these drops onto a heated substrate [10].

Metal oxide thin films like NiO deposited by sol-gel usually require heat treatment in order to induce crystallization and remove inorganic/organic residues. The annealing temperature mainly depends on the nature of the Ni precursor and the solvent [11]. The particles become highly crystalline, resulting in a reduction in pore and grain boundary density. Therefore, the optical band gap (Eg) of films decreases with increasing annealing temperature [12].

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However, Madhavi et al. [13] claimed that the optical band gap of NiO thin films increased with increasing annealing temperature up to 400°C (from 3.43 eV to 3.68 eV) and then decreased to 3.48 eV at a higher annealing temperature of 500°C due to better crystallization of NiO films. On the other hand, in the study of Mallick [14] a NiO film annealed at 400°C showed an optical band gap of 3.52 eV which increased to 3.62 eV with increasing annealing temperature at 600°C. In another study [15], NiO films were annealed for 2 h between 100°C and 400°C in ambient air. As the annealing temperature increased, the film became transparent in the visible and near infrared region. On the other hand, the duration of the heat treatment in the atmospheric environment also affects the structure in two different aspects. As the annealing time increases the particle size of the structure increases, In addition, with the increase in the interaction time of the transparent conductive oxide layers with the heat treatment atmosphere, the quantity of oxide phase increases due to the amount of oxygen in the structure. The chemically absorbed oxygen reduces the carrier concentration by acting as a trap against free carriers. Due to the decrease in carrier concentration, the band gap narrows [16].

In this work, we report the results of characterization of the thin layers of NiO deposited by the spray pyrolysis technique on the glass substrates, while showing the effect of post-heat treatment study the hydrophilic properties.

EXPERIMENTAL METHOD

The experimental part of our study was carried out in two parts: The elaboration of the samples and the characterization of the NiO thin films. The experimental procedure that we adopted in this study is summarized by the concept map below (Figure 1).

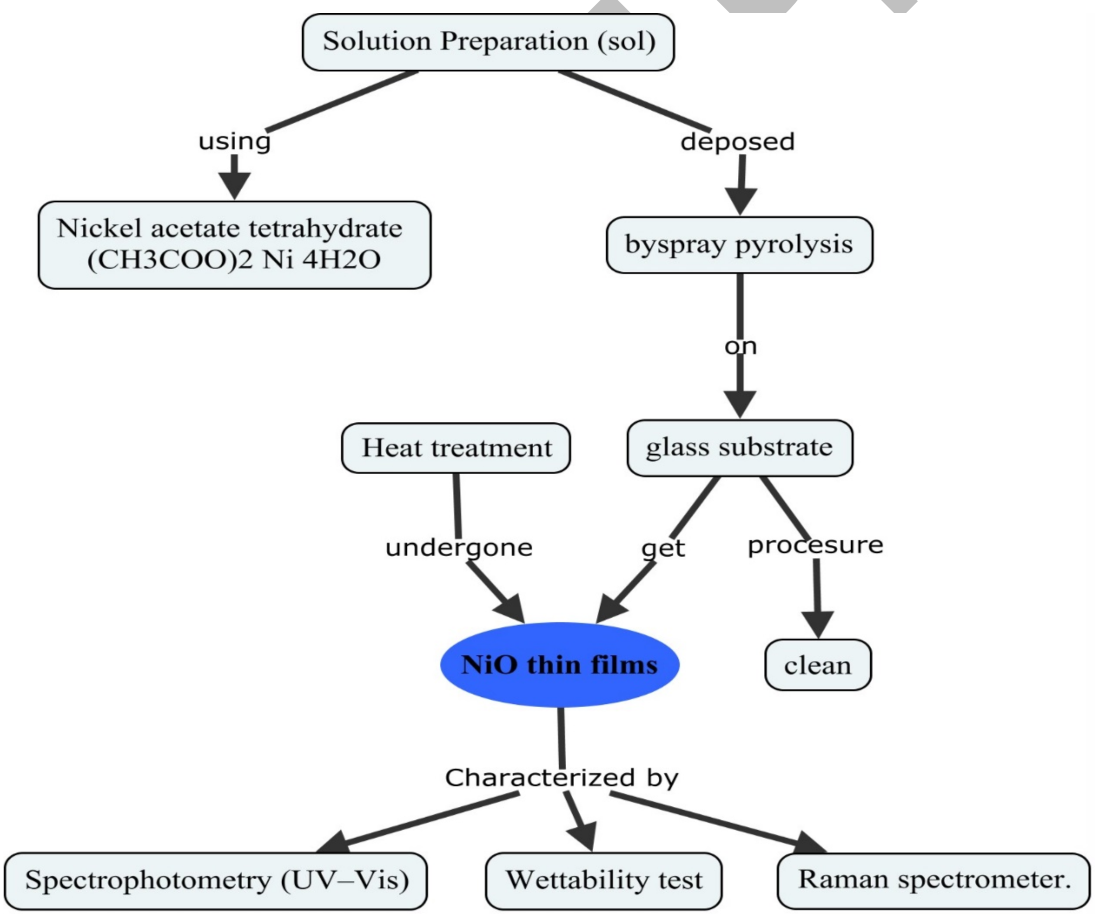

Figure 1. The experimental procedure

Sample preparation

The precursor solution (sol) with a concentration of 0.1 M was obtained by dissolving a few grams (m=2.49 g) of nickel acetate tetrahydrate (CH3COO)2 Ni 4H2O (Biochem, 99.5%) in a volume of 100 ml of distilled water (solvent). After stirring for one hour with a magnetic stirrer at 60°C, "a few drops" of Monoethanolamine C2H3NO (MEA) was added to stabilize the solution. The suspension is left stirring for 2 hours at 60° and 4 hours at ambient temperature. We added a few drops of HCL (Sigma Aldrich 35%) to lower the pH and obtain a transparent solution of bluish color and slightly viscous. The sol is left to stand for 72 hours in a beaker, covered to prevent any sort of contamination and evaporation, before being used for the deposition of NiO thin films.The commercial transparent glass slides (1.5 cm x 2.5 cm, 1 mm thickness) used as substrates in our study were cleaned using the following steps:

- Cleaning with warm water and soap
- Immersion in acetone (C3H5OH) for 10 minutes, in an ultrasonic bath to eliminate all traces of oil.
- Rinse with distilled water under ultrasound for 5 minutes.
- Soaking in ethanol (C2H5OH) for 10 minutes in an ultrasonic bath to remove impurities that remain stuck to the surface.
- After Rinse with distilled water and drying, the substrates are kept free from all kinds of impurities.

In this simplified spray technique, atomization is based on hydraulic pressure. Pulsed solution feed with an interval of 5s of spraying and 60 s of pause was used. A volume of 30 ml of the solution was sprayed at a distance of 20 cm from the substrate heated to 250°C. The thin layers were deposited on several glass substrates at the same time and under the same conditions.

The samples prepared by technical spray were thermally annealed in air for 2 hours at different temperatures (200, 250 and 300° C.). We have chosen to use temperatures which are not very high and extend the annealing time. We used a digital muffle furnace . Our samples underwent slow cooling to room temperature after the oven was turned off.

Sample Characterization

After annealing, the NiO films were characterized using UV–Visible Spectrophotometer (JENWAY 6715) to record the transmission spectrum of the films. To study the hydrophilic properties of NiO films, we measured the contact angle of water drop on the layers using a standard goniometer and ImageJ software. A micro-Raman spectrometer (Lab-Ram HR) was used as a qualitative structural and molecular analysis technique. This device uses He-Cd laser (325 nm, 32 mW). The thickness of the films has been measured using Stylus profilometer (MUTITOYO).

RESULTS AND DISCUSSION

The effect of post-heat treatment on the thickness of thin layers:

The values of the thicknesses of the NiO thin films after post-heat treatment are shown in the table 1. We notice that the values of the thickness of the nickel oxide decrease with the increase of the annealing temperature. According to Godse et al. [17], this decrease in thickness is due to the increase in crystal grain size with increasing annealing temperature. In their study, they found that the thicknesses of nanocrystalline NiO thin films produced by the sol-gel spin coating method using nickel acetate Ni(CH3COO)2 4H2O as the Ni source, vary from 906 nm to 642 nm for the annealing temperature of 400°C and 600°C respectively.

Table 1. The effect of annealing on thickness.

	Annealing temperature	Annealing time	Thickness
Sample 1	200°C	2H	225 nm
Sample 2	250°C	2H	223 nm
Sample 3	300°C	2H	218 nm

The effect of post-heat treatment on water contact angle

The ImageJ software was used to measure the contact angles between the water drop and the sample surface (figure 2). The angle values are shown in the table 2. Knowing that the contact angle with surface water is inversely proportional to the wettability, we deduce that all the layers of NiO produced are hydrophilic because the contact angles with water are less than 90°. This may be due to the strong cohesive force between the water droplet and the NiO oxide [18].

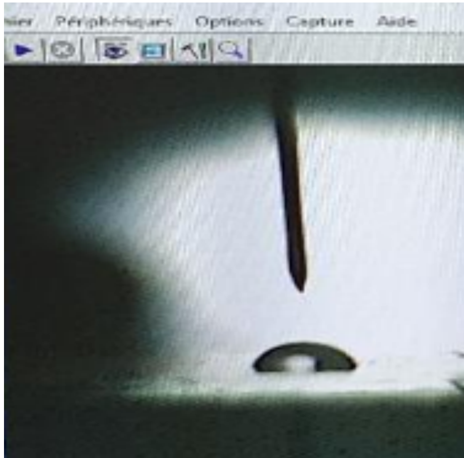

Figure 2. Contact angle measurement

It is important to emphasize that the contact angle between the water drop and the sample surface is strongly influenced by the topological structure, directly implying the wettability state of the film. the data obtained show that with the increase in the annealing temperature, the wettability decreases, which reveals that the structure of the samples has a more crystalline character [19].

Table 2. Water contact angle variation

	Galss	*Sample 1*	*Sample 2*	*Sample 3*
Annealing temperature	NO ANNEALING	*200°C*	*250°C*	*300°C*
Contact angle	35,305	61.2	73	86

The effect of post-heat treatment on optical properties

The spectra of the transmittance of thin layers of NiO as a function of the wavelength for the three annealing temperatures that we have chosen are presented in figure 3 In the absorption region (280-380 nm) corresponding to the near UV region, there are sharp drops in the measured transmittances due to the light absorption induced by the

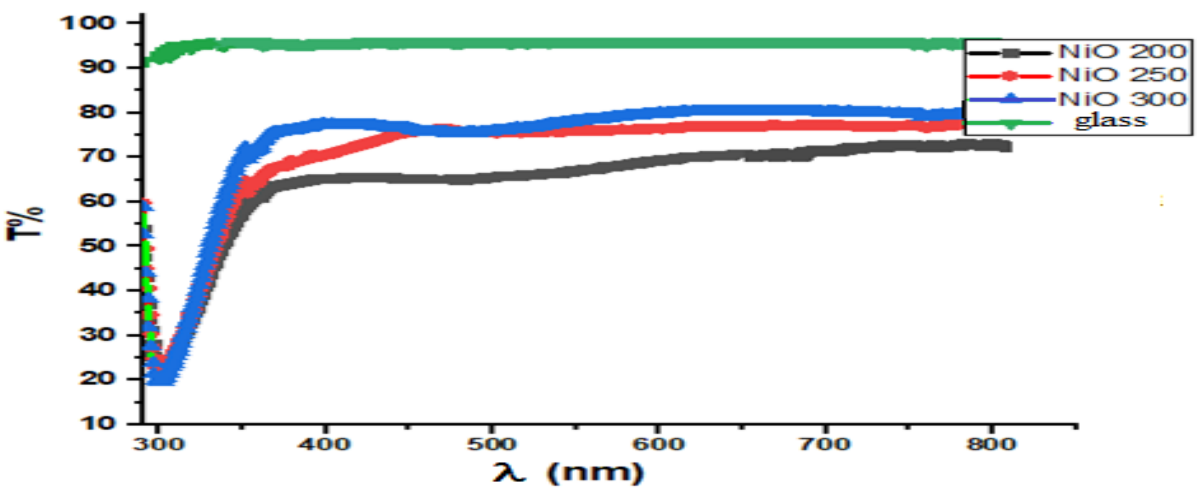

Figure 3. Transmittance spectra as a function of wavelength

electronic excitation [17]. In addition, it can be observed that the transmission level increases with increasing annealing temperature. The variation in transparency can be attributed to the change in structure from amorphous to crystalline caused by the increase in temperature [20].

To determine the energy of the band gap (Eg), we used Tauc Method for a direct transition [14]. Figure 4 shows the variation of $(\alpha h\nu)^2$ (α is absorption coefficient) as a function of incident photon energy ($h\nu$) for (NiO) thin films deposited on glass substrates at 200°C, 250°C and 300°C. We observe that the Eg increases with increasing annealing temperature from 3.42 eV to 3.63 eV. These results are in good agreement with the values obtained in previous researches [14,17, 21-25] as shown in Table 3. The blue shift Eg is due to the enhancement of crystal quality [4]. Due to the effect of temperature, the widening of the band gap is produced by the filling of electrons near the bottom of the valence band Ev which have moved to the upper part of the conduction band Ec. The increase in the forbidden bandwidth by the additional electrons in Ec, favors an increase in the concentration of charge carriers [26].

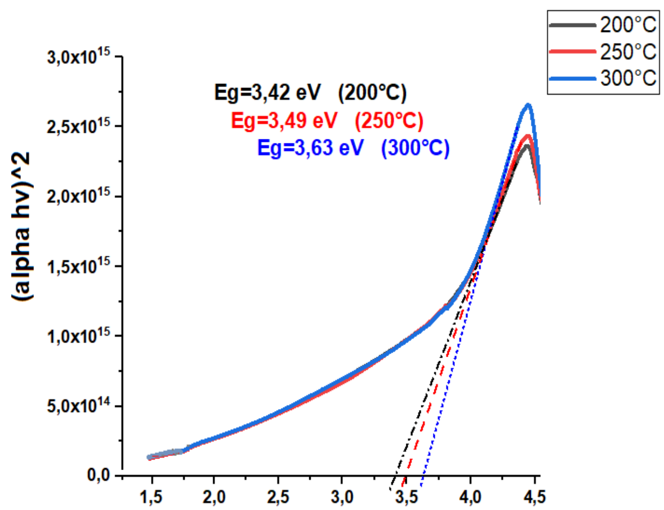

Figure 4. Variation of ($\alpha h\nu$) as a function of incident photon energy ($h\nu$).

Table 3. NiO thin film gap value in previous research

Thin film deposition technique	precursor	T°C	Thickness	Gap (eV)	Reference
spin coating	$Ni(NO_3)_2\ 6H_2O$	400	/	3.52	[14]
spin coating	Nickel acetate	400	906 nm	3.86	[17]
Spray pyrolysis	nickel chloride	350	/	3,51	[21]
Spray pyrolysis	Nickel chloride	/	230	3,4	[22]
Spray pyrolysis	Nickel acetate	450	170	3,65	[23]
Spray pyrolysis	Nickel acetate	350	/	3.83	[24]
Spin-coating	Nickel acetate	450	/	3.7	[25]

the NiO thin films in our work were worked out by the sputtering technique, the atoms arriving on the substrate after the sputtering are not usually in an ideal position to form a desired compound, which can cause different types of defects in the structure. The existence of this disorder can be expressed by the Urbach energy (Eu). We observe in Figure 5 that the energy value of Urbach Eu decreases with the increase of the annealing temperature from 3.06 eV to

2.1 eV. While Ikhmayies et al. [27], stated that Eu interpreted as the tail width of band gap localized states is weakly temperature dependent.

We believe that the disordered and amorphous structure of our layers producing the extended localized states in the band gap has been reduced which has been reflected by the decrease in the values of Eu.

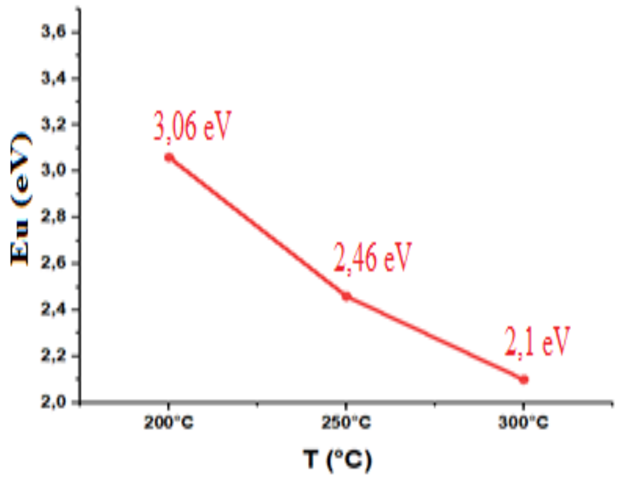

Figure 5. Variations of the optical gap with the Urbach energy as a function of the annealing temperature

The effect of post-heat treatment on the structural properties of thin NiO layers

The Raman spectrum of the NiO thin film in figure 6 shows the positions of the peaks corresponding to the characteristic vibrations of the molecular bonds. Ni-O bond peaks were observed at 574 and around 1094 cm^{-1} confirming the presence of NiO in crystalline state for all of the three thermal anneals. However, in the case of disordered semiconductors, such as amorphous and nanocrystalline, the phonons other than centered phonons on the area can also be observed in their Raman spectra [28]. The 547 cm^{-1} band is generally attributed to first-order one-phonon (1P) excitation related to nickel starvation point defects [29]. While the band at about 1090 $cm-^{1}$ corresponds to the second-order longitudinal two-phonon (2P) vibrational modes.

For the film annealed at 200°C, a peak at about 1583.2 cm^{-1} due to optical vibrations (mode) in the graphite (presence of amorphous carbon) [30].

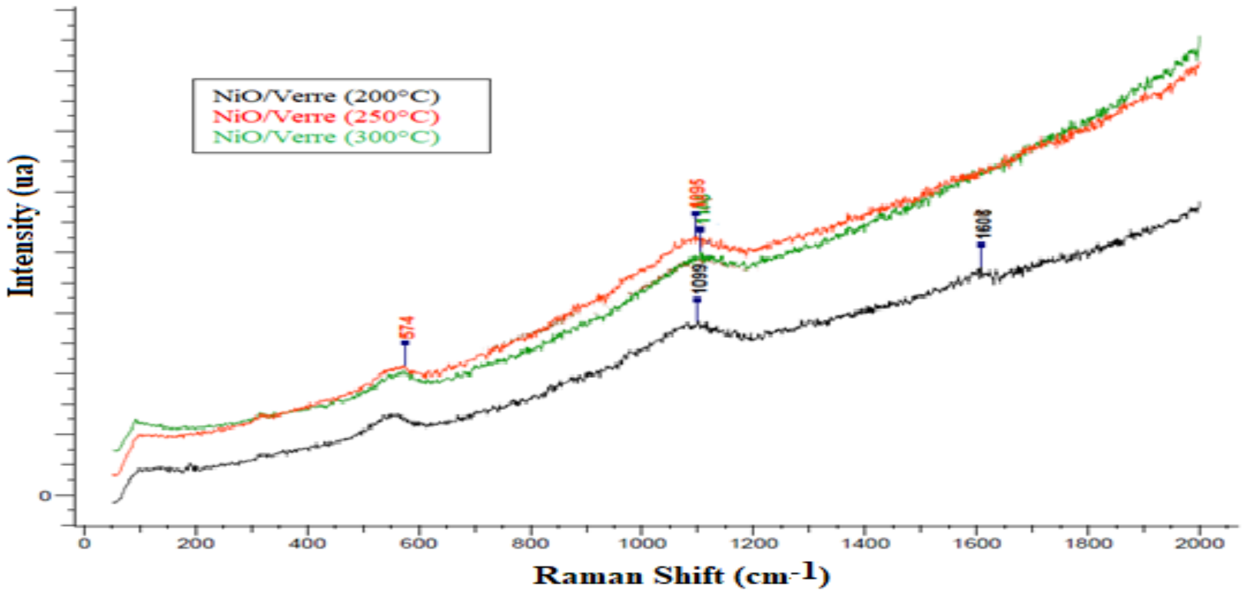

Figure 6. Raman photoluminescence emission spectra of NiO thin films

CONCLUSION

In order to demonstrate the behavior of thin layers of NiO, with subsequent heat treatment, we developed thin layers of nickel oxides by sputtering technique on glass substrates. We have chosen three annealing temperatures and several characterization technics. The optical properties carried out with spectrophotometry have shown that the transmittance of the NiO films increases with the annealing temperature. the values of the optical gap obtained(3.42 eV , 3.49 eV and 3.63 eV) increase with increasing annealing temperatures, which is in agreement with other studies. It was found that Urbach energy (disorder) decreases with increasing gap and annealing temperature. The measured water contact angles are all less than 90°, which indicates that the NiO films produced are hydrophilic. Raman spectrum confirms the presence of the crystalline state in all samples. It revealed also, the presence of carbon in the NiP thin film annealed at 200°C showed the presence of amorphous carbon (graphite).

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