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ARTICLE

Study of Optical and Structural Properties of NiO Thin Films Prepared by Chemical Spray Pyrolysis (CSP) Method

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Abstract: In this study, NiO thin films with molarity of 0.1 M have been successfully deposited on glass substrates by chemical spray pyrolysis (CSP) technique at a substrate temperature of 400 ^{o}C and a deposited thickness of about 350 nm. The structural and optical properties of these films have been studied using Ultraviolet-visible (UV-Visible) spectroscopy and X ray diffraction (XRD). The absorbance and transmittance spectra have been recorded in the wavelength range of 300-900 nm in order to study the optical properties. The optical energy gap for allowed direct electronic transition was calculated using Tauc's equation. It is found that the band gap is equal to 3.58 eV for the prepared thin films. The optical constants, including absorption coefficient, were also calculated as a function of photon energy. Refractive index and extinction coefficient for the prepared thin films were estimated as a function of wavelength in the wavelength range 300-900 nm. The XRD results showed that the studied films are polycrystalline in nature with a cubic structure and a preferred orientation along (111) plane. The average crystallite size of the film was estimated for (111) direction by Scherrer formula and was equal to ~ 10nm.
Keywords: Thin film, NiO, Optical properties, CSP, XRD.

Introduction

Nickel(II) oxide is a chemical compound with the formula NiO. It is notable as being the only well characterized oxide of nickel. The mineralogical form of NiO, bunsenite, is very rare. NiO can be prepared using different methods. Upon heating above 400 °C, nickel powder reacts with oxygen to give NiO. In some commercial processes, green nickel oxide is made by heating a mixture of nickel powder and water at 1000 °C. The rate for this reaction can be increased by the addition of NiO [1]. The simplest and most successful method of preparation is through pyrolysis for compounds of nickel (II), such as: hydroxide, nitrate and carbonate, which yields a light green powder. The synthesis from the elements by heating the metal in oxygen can yield grey to black powders, which indicates nonstoichiometry [2]. NiO adopts the NaCl structure, with octahedral Ni(II) and O_2. Nickel oxide (NiO) has a density of 6.67g/cm^3, a molecular weight of 74.69 g/mol and a melting point of 1955 °C [3]. Nickel oxide thin films have different applications, such as: an antiferromagnetic material [4], p-type transparent conducting films [5], electro catalysis, positive electrode in batteries, fuel cell, a material for electro-chromic display devices and solar thermal absorbers [6].

Experimental Procedure

Chemical spray pyrolysis technique was used to deposit NiO thin films on glass substrates at a temperature of 400 ºC. In the preparation of NiO films, an aqueous solution with a molarity of 0.1M was prepared $Ni(NO_3)_2.6H_2O$ and mixed with distilled water by using a magnetic stirrer for 40 minutes. The resultant solution was sprayed on glass substrates. Other deposition

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conditions, such as spray nozzle substrate distance (30 cm), spray interval (2 minutes) and pressure (p bar), were kept constant for each concentration. The X-ray diffraction patterns for the prepared films were obtained by using a Shimadzu XRD-6000 diffractometer using copper target (Cu Kα, 1.5418 Å) and optical properties in the wavelength range of 300-900 nm were investigated by using a Shimadzu UV-1800 UV-Visible spectrophotometer.

Results and Discussion

Optical Analysis

The optical absorption spectra of the films in the spectral range of 300-900 nm were recorded by using UV–Visible spectrophotometer. The analysis of the dependence of absorption coefficient on photon energy in the high absorption regions is performed to obtain the detailed information on the energy band gaps of the films [1]. Fig. 1a shows the relation between transmittance and wavelength for Nickel Oxide thin films. From this figure, the transmittance increases with wavelength. The spectrum shows a high transmittance in the visible and infrared regions and a low transmittance in the ultraviolet region. Fig. 1b shows the relation between absorbance (A) and wavelength for the deposited thin films. The absorbance decreases rapidly at short wavelengths corresponding to the energy gap of the film. This evident increase of energy is due to the interaction of the material electrons with the incident photons which have enough energy for the occurrence of electron transitions.

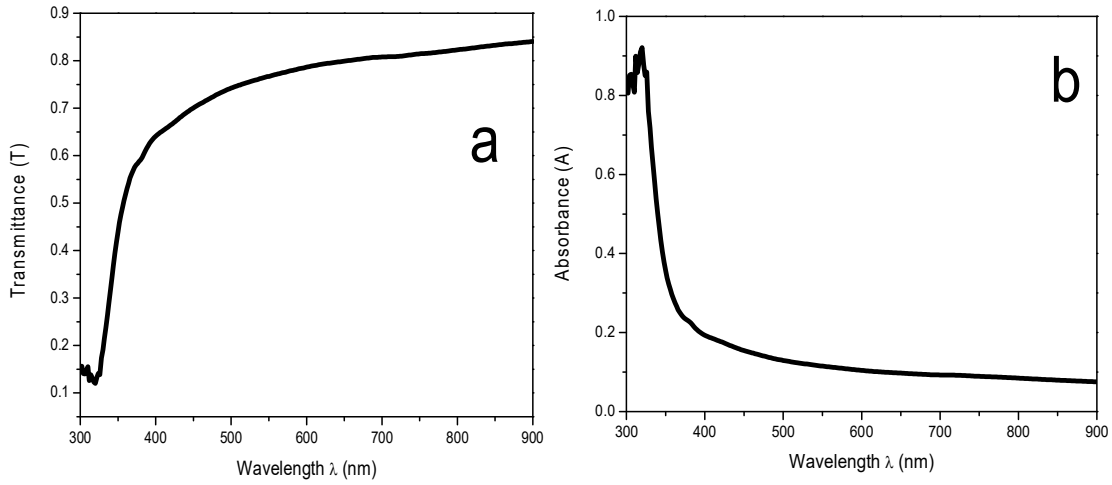

FIG. 1a. Transmittance (T), b. Absorbance (A) *versus* wavelength (λ) for Nickel Oxide thin film.

The absorption coefficient can be estimated from the absorbance using the well-known formula [7]:

$$\alpha = (2.303 \times A)/t, \quad (1)$$

where A is the absorbance**,** t is the thickness and α is the absorption coefficient. It has been noticed that all the prepared thin films have a high absorption coefficient in the visible range of the spectrum and this could be seen in Fig. 2. The absorption coefficient increases with the increase in photon energy (hυ). The optical energy band gap (Eg) is given by the well known Tauc's relation [7]:

$$\alpha hv = A(hv - E_g)^r \quad (2)$$

where α is the absorption coefficient, hv is the photon energy, Eg is the optical band gap, A is a constant which does not depend on photon energy and r has four numeric values (1/2) for allowed direct, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions. In this work, direct band gap was determined by plotting a graph between $(\alpha\, hv)^2$ and (hv) in eV units, where a straight line is obtained which gives the value of the direct band gap. The extrapolation of straight line to $(\alpha\, hv)^2 = 0$ gives the value of the direct band gap of the material and this could be seen in Fig. 3. From this figure, the band gap value is equal to 3.58eV, which is in agreement with Sriram and Thaymanavan [8].

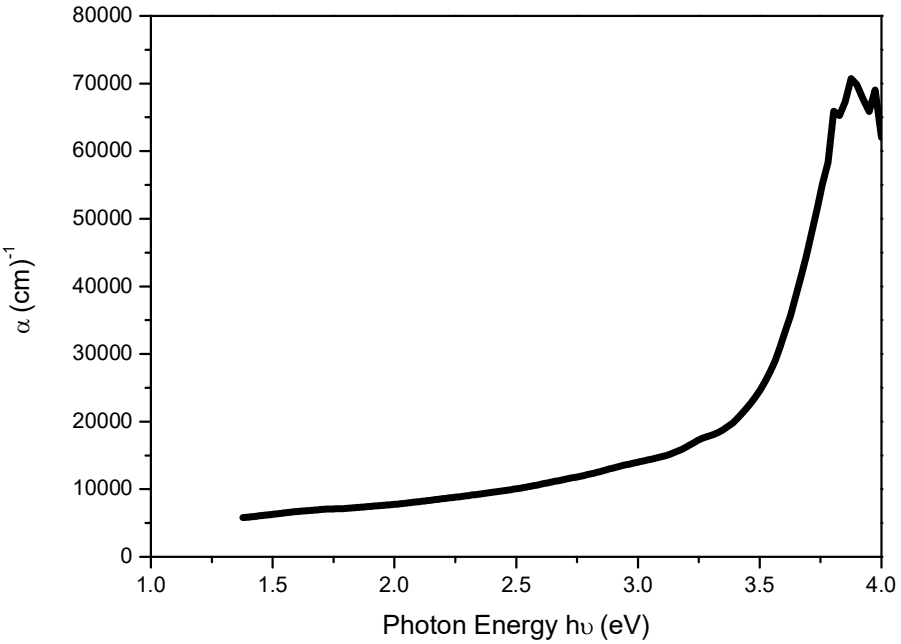

FIG. 2. Absorption coefficient *versus* photon energy for Nickel Oxide thin films.

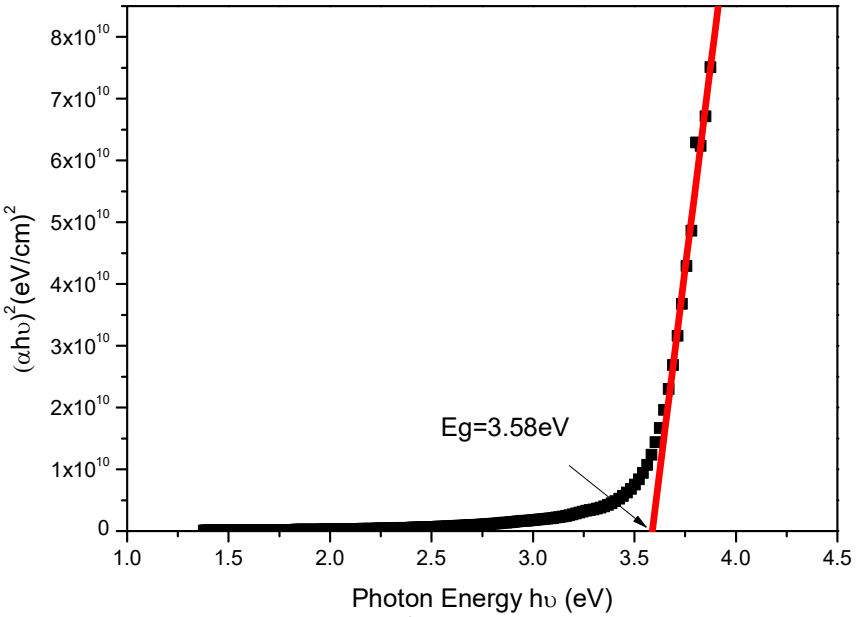

FIG.3. The relation between $(\alpha h\nu)^2$ and $(h\upsilon)$ for Nickel Oxide thin film.

The refractive index has been calculated using the relation [1]:

$$n = \left[\frac{(1+R)^2}{(1-R)^2} - \left(k_o^2 - 1\right)\right]^{1/2} + \frac{(1+R)}{(1-R)} \qquad (3)$$

where, n: is the refractive index, R: is the reflectance (calculated from $R + A + T = 1$) and k_o: is the extinction coefficient. The relation between refractive index and wavelength for NiO thin films is shown in Fig. 4a. It can be seen that the refractive index of the prepared films decreases with the increase in wavelength, which is in agreement with other reports [1, 9].

The extinction coefficient (k_o) was calculated using the relation [10]:

$$k_0 = \frac{\alpha\lambda}{4\pi} \qquad (4)$$

where: k_o **:** is the **e**xtinction coefficient and λ: is the wavelength of the incident photon. The extinction coefficient (k_o) decreases rapidly at short wavelengths (300-400) nm and after that the value of (k_o) remains almost constant. The rise and fall in the value of (k_o) is directly related to the absorption of light. In Fig. 4 (b), the lower value of (k_o) in the wavelength range (400-900) nm implies that these films absorb light in this region very easily.

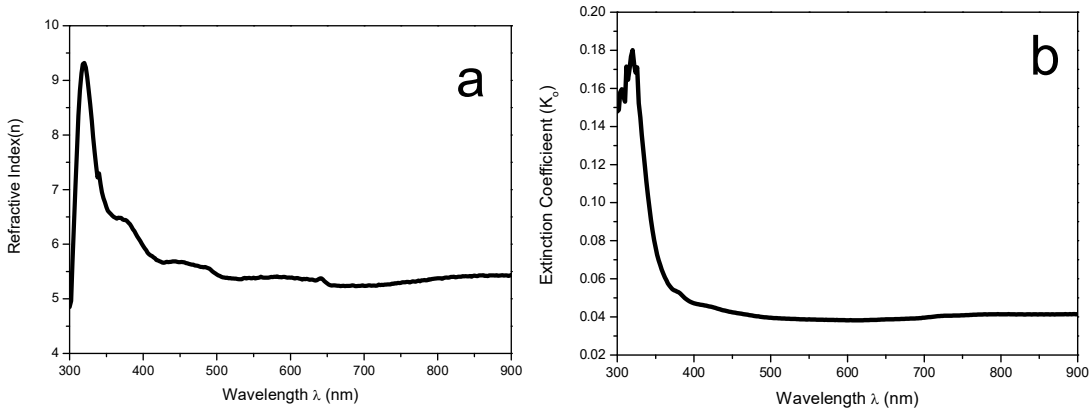

FIG.4a. Refractive index. b. Extinction coefficient *versus* wavelength of Nickel Oxide thin films.

Structural Analysis

XRD patterns of the nickel oxide films is shown in Fig. 5. It can be noticed that all the patterns exhibit diffraction peaks around (2θ~37°, 43° and 63°) referred to (111), (200) and (220) favorite directions, respectively, which is in agreement with the Joint Committee of Powder Diffraction Standards (JCPDS) card number (04-0835). The strongest peak occurs at (2θ~37°), which is referred to as (111) plane, which is in agreement with Khoder *et al*. [7]. The positions of the peaks and the presence of more than one diffraction peak lead to the conclusion that the films are polycrystalline in nature with a cubic crystalline structure, which is in agreement with other reports [11]. The lattice constant is (a_o=4.179 Å). It should be mentioned here that the standard a_o value for NiO is (4.176 Å).

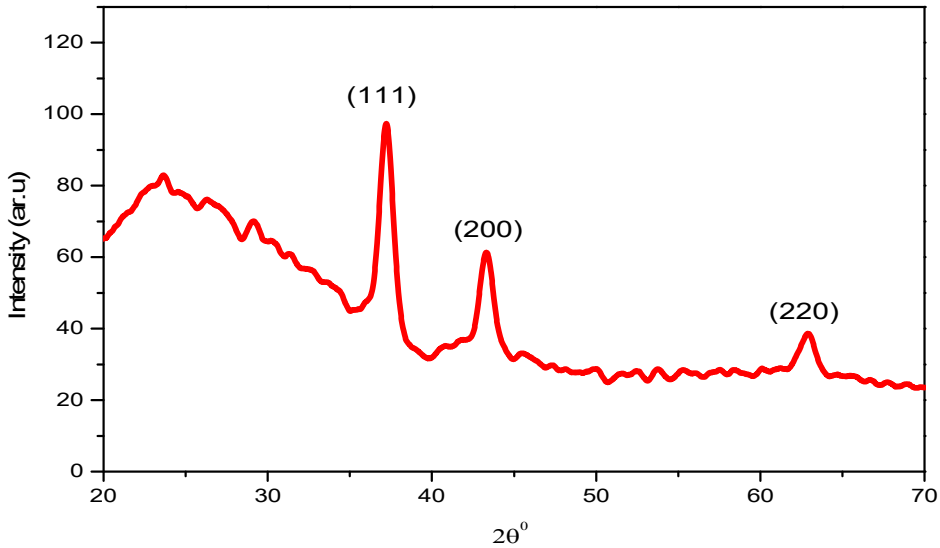

Figure 5. XRD patterns of Nickel Oxide thin films.

The average crystallite size for the films can be determined using Williamson-Hall (WH) formula [9]:

$$\beta_{hkl} \cos\theta = k\lambda / D + 4 S \sin\theta \quad (5)$$

where β_{hkl} is full width of half maximum, D is the average crystallite size, k is a constant which

was assumed to be equal to 0.9, λ is the wavelength for the Cu target of the XRD instrument, θ is Bragg's angle for all peaks and S is the micro-strain in the film. If $\beta_{hkl}\cos\theta$ is plotted with respect to 4sinθ, strain and crystallite size can be calculated from the slope and y-intercept of the fitted line, respectively, as shown in Fig. 6. It is observed that the crystallite size value is equal to (7.38 nm) and (S=-0.00411).

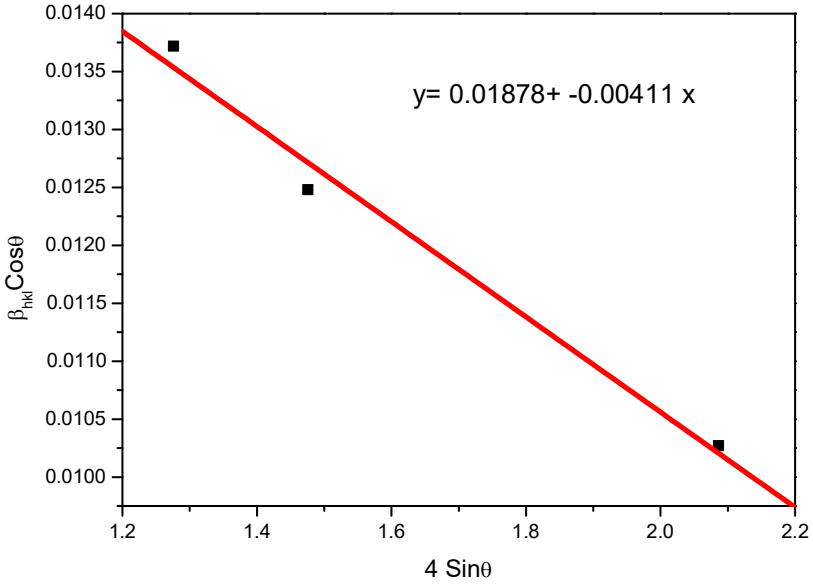

FIG. 6. The W-H analysis of NiO thin film.

The average crystallite size for all the films is also calculated for (111) direction by Scherrer's formula [11]:

$$D_{av} = k\lambda / \beta \cos\theta \qquad (6)$$

where:

k: is a constant which was assumed to be equal to 0.9.

λ: is the wavelength of incident X-ray radiation, (λ =1.5406Å for CuK_α).

β: is the full width at half maximum of the peak (in radians).

θ: is Bragg's diffraction angle of the XRD peak.

It is observed that the crystallite size for the Nickel Oxide thin films is 10 nm. These results agree qualitatively with the results of crystallite size obtained by Williamson-Hall method.The micro-strain in the films is induced during the growth of thin films by varying displacements of the atoms with respect to their reference lattice position [1]. The larger crystallite size values indicate better crystallization of the films; values of micro-strain were negative, which indicates the occurrence of compression in the lattice.

The texture coefficient (*Tc*) represents the texture of a particular plane, in which greater than unity values imply that there are numerous grains in that particular direction. The texture coefficients Tc*(hkl)* for the sample have been calculated from the X-ray data using the well-known formula [7]:

$$T_C(hkl) = \frac{I(hkl)/I_0(hkl)}{N_r^{-1}\sum I(hkl)/I_0(hkl)} \qquad (7)$$

where, I(*hkl*) is the measured intensity, I_o(*hkl*) is taken from the JCPDS data, (Nr) is the reflection number and (*hkl*) represents Miller indices. The texture coefficient is calculated for crystal plane (111) of the NiO films. The value of texture coefficient was greater than 1, which indicates the abundance of grains in the (111) direction.

The Specific Surface Area (SSA) is the Surface Area (SA) per unit mass. It is a very important factor in the field of nanoparticles because of large surface to volume ratio of such small particle size materials. SSA is used in materials to determine their types and also used in case of reactions on surfaces, heterogeneous catalysis and adsorption. Mathematically, SSA can be calculated using the formula [12]:

$$SSA = 6 \times 10^3 / D.\ \rho \qquad (8)$$

where, D is the crystallite size (W-H and Scherrer) and ρ is the density of NiO (6.67 g/cm^3).

The values of the Specific Surface Area from W-H is equal to (121901m^2/g) and from Scherrer is equal to (89955m^2/g). According to Eq.(8), the Specific Surface Area increases with decreasing the crystallite size. There is an inverse relation between them so that Specific Surface Area was large.

Conclusion

In this study, NiO thin films with a molarity of 0.1 M were successfully deposited on glass substrates at (400 ºC) by chemical spray pyrolysis technique using Nickel nitrates as the Ni source. XRD patterns of the NiO thin films indicate that all films are polycrystalline with a cubic crystal structure. The main characteristic peaks are assigned to the (111), (200) and (220) planes and the transmittance for NiO thin films increases when wavelength increases. The band gap value is (3.58 eV).

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