

MESCon 2014 [4th -5th September 2014]
National Conference on Material for Energy Storage and Conversion- 2014

Optical dispersion characterization of NiO thin films prepared by nebulized spray technique

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Abstract : Nickel oxide (NiO) thin films were prepared by nebulized spray pyrolysis (NSP) technique. The films are having more uniform thickness and there is no pinhole. Nickel oxide thin films have been deposited using 0.3M aqueous solution of nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ onto microscopic glass substrates, which were chemically and ultrasonically cleaned before coating. The film depositions are carried out at various substrate temperatures from 350 to 450°C in 50°C step. The optical properties of the NiO films were studied using UV-Vis-NIR spectrometer. It is found that increase in the substrate temperature the transmittance decreases, consequently the band-gap energy wanes from 3.54eV to 3.37eV. The refractive index and the extinction coefficient have been calculated from the optical measurements. The dispersion of the refractive index is discussed in terms of the Wemple-DiDomenico single-oscillator model. The oscillator parameters such as optical dispersion energies, dielectric constant, the average value of oscillator strength, wavelength of single oscillator and plasma frequency have been evaluated.

Keywords: NiO thin film, refractive indices, dispersion of the refractive index.

1. Introduction

Nickel oxide may exist in various forms like NiO, NiO₂, NiO₄ and Ni₂O₃. Among them NiO is an anti-ferromagnetic material with a density of 6.67 g/cm³ and having a cubic structure. Bulk nickel oxide (NiO) has a very high resistivity and a high melting point (~2000°C) suggesting that it can be used in high temperature applications. NiO shows p-type semiconductivity when it is heated in air due to the generation of Ni²⁺ vacancies into the NiO structure[1]. NiO thin films have been fabricated by various physical and chemical deposition techniques, such as reactive sputtering[2], spray pyrolysis[3], sol-gel[4] and plasma-enhanced chemical vapor depositions[5], electron beam evaporation[6]. NSP technique is a very easy, low cost, safe, cheap, non-vacuum system of deposition method[7] for preparing transparent conducting oxides when compared with the other technique. The advantage of NSP over conventional pneumatic spraying is its low material consumption with better control of the spray and low carrier gas flow, which allows the deposition of very thin layers of uniform thickness[7].

Recently, the optical properties are necessary to study optoelectronic devices that use semiconductor thin films and interference devices (antireflection coating, laser mirrors and monochromatic filters). The optical constants of thin films provide us the information concerning with microscopic characteristics of the material. In this work the optical constants of NiO thin films were influenced by the substrate temperature (T_s) deposited

by simple NSP technique, whereas the optical absorption parameters, such as optical dispersion energies, dielectric constant, the average values of oscillator strength, wavelength of single oscillator, plasma frequency, etc., had been calculated under the effect of substrate temperature.

2. Experimental

Nickel oxide thin films had been deposited from 0.3M aqueous solution of nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ by nebulizer technique onto microscopic glass substrates, which were chemically and ultrasonically cleaned before coating. This technique has some advantages such as an atomization based on hydraulic pressure without using any carrier gas, intermittent spraying and fine atomization. During the film deposition the substrate temperature was kept at 350 °C, 400 °C and 450 °C. The volume of the solution for each deposition was 10 ml. Only the small amount was consumed and 10 mins was necessary for spraying 5 ml i.e 0.5 ml per min. The nozzle to substrate distance was ~7 cm and the optimized air flow rate was 1.2 kg/cm^2 . After deposition, the films were allowed to cool slowly to room temperature. NiO thin film properties were studied, the substrate temperature was kept at 350 °C, 400 °C and 450 °C. The optical transmittance and band gap were demonstrated by Ocean Optics HR-2000 (USA) UV-Vis-NIR spectrophotometer.

3. Results and discussion

3.1 Optical transmittance and Energy Band gap

Optical transmittance of the films deposited at various substrate temperatures are shown in Fig.1. The optical transmittance spectrum is recorded from 300 to 1100 nm wavelength regions. Transmittance spectrum indicates that the transmittance decreases as film thickness increases; the transmittance is varied from 30% to 90% as the film thickness is decreased. The optical band gap of the film was evaluated from the relation

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (1)$$

where n is equal to $\frac{1}{2}$ and 2 for direct and indirect transitions respectively, A is a proportionality constant, E_g is optical energy band gap and (α) is absorption coefficient. The optical absorption coefficient (α) is calculated using the following expression,

$$\alpha = \frac{1}{t} \ln T \quad (2)$$

From the plots of $(\alpha h\nu)^2$ versus $h\nu$, direct band gap was found (Fig.2.) by extrapolating the linear portion of the curve to energy axis for $(\alpha h\nu)^2 = 0$. The curves indicate the values of the direct band gap. The energy band gap values are found as 3.54, 3.43 and 3.37 eV for the NiO thin films with increasing the substrate temperature from 350, 400 and 450°C, which is in good agreement with the reported band gap values of 3.15-3.80 eV for NiO films[8].

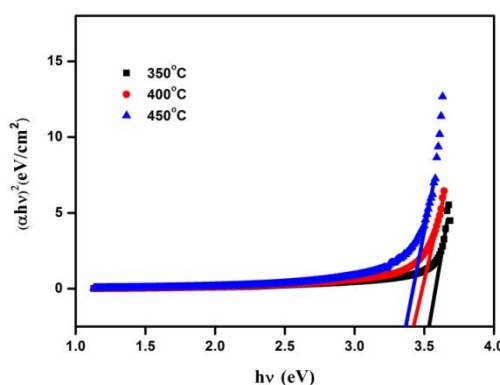
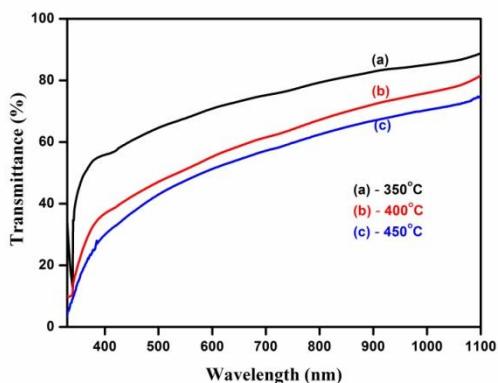


Fig. 1. Transmittance spectra of NiO thin films Fig. 2. $(\alpha h\nu)^2$ versus $h\nu$ plot of NiO thin films

3.2 Optical constants

Refractive index is an important parameter for optical materials design and it includes valuable information for higher efficiency optical materials, because it is closely related to the electronic polarization of ions and the local field inside materials. The complex refractive index (n^*) can be expressed as[9].

$$n^* = n - ik \quad (3)$$

Here, the real part of the refractive index (n) and imaginary part (k) can be calculated using the following relations.

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

$$k = \frac{\alpha \lambda}{4\pi} \quad (5)$$

Where, R is the reflectance of the film and λ is the wavelength of the incident beam. Fig.3. shows the spectral variation of the refractive index as a function of wavelength at various substrate temperatures. It can be seen that the maximum value of refractive index ($n \sim 2.8$ at $T_s = 450^\circ\text{C}$) at very low wavelength, $\lambda = 300\text{nm}$ (strong absorption region), was observed in all samples. The behavior of refractive index has a higher value at very low wavelength (strong absorption). This is due to the quality between the frequency of incident electromagnetic radiation and the plasma frequency of electrons. This leads to the coupling of electrons in NiO films to the oscillating electric field. Fig.4 shows the variation of extinction coefficient as a function of wavelength at various substrate temperatures. In the visible region, it indicates the better surface homogeneity of deposited NiO thin film [10]. The increase in k value with increase in substrate temperature may be due to surface roughness of the film, which enhanced the scattering losses thereby reducing the transmitting ability. This inference is consistent with our observed optical transmittance spectra decrease with increase of substrate temperature. In general, the index of refraction is higher for shorter wavelengths of light and decreases monotonically with increasing wavelength. However, some highly colored materials exhibit abnormal dispersion for those wavelengths of light that are strongly absorbed. Further, it may be mentioned that the refractive index and extinction coefficient depend on the atomic density and atomic masses of each component element. The refractive index is high for crystalline material than the amorphous one. This is due to the lower atomic density of each element in the amorphous state because of the higher average interatomic distance.

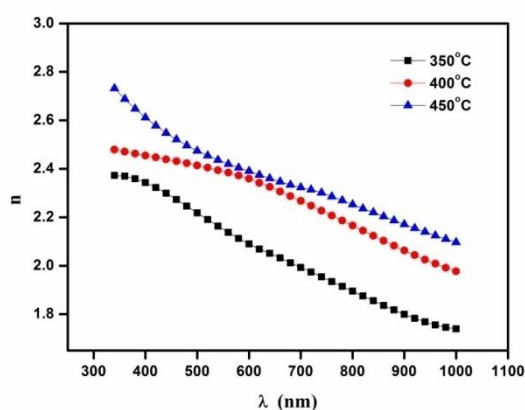


Fig. 3. Refractive index (n) of NiO thin films as a function of wavelength (λ)

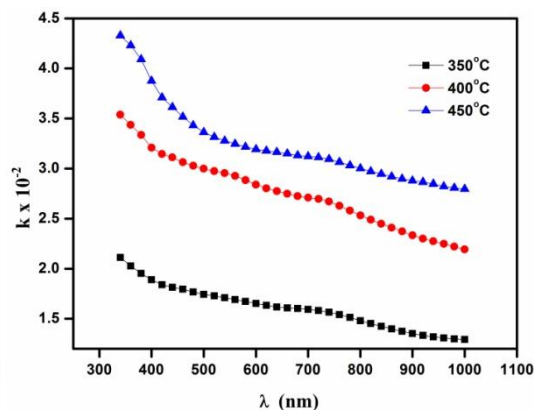


Fig. 4. Extinction coefficient (k) of NiO thin films as a function of wavelength (λ)

3.3 Dielectric constants

The calculated refractive index is used for the estimation of high frequency dielectric constant by adopting two procedures[11]: The first, describes the contribution of the free carriers and lattice vibration modes of the dispersion, while the second procedure is based upon the dispersion arising from the bound carriers in an empty lattice. However, both procedures were employed for obtaining lattice high frequency

dielectric constant. The following equation shows the relation between the lattice dielectric constant ($\epsilon_L=n^2$), wavelength (λ) and refractive index (n) [12].

$$\epsilon = n^2 = \epsilon_{\infty(1)} - \left(\frac{e^2}{4\pi c^2 \epsilon_0} \right) \left(\frac{N}{m^*} \right) \lambda^2 \quad (6)$$

where ϵ_L is the lattice dielectric constant, e is the electronic charge, c is the velocity of light, ϵ_0 is the permittivity of free space (8.854×10^{-12} F/m), N is the free carrier concentration and m^* is the effective mass of the charge carriers.

The nature of the dispersion of n^2 as a function of wavelength (λ^2) for different substrate temperatures are shown in Fig.5 which verifies the linearity of the above said expression (6). The intercept of the straight line to X-axis ($\lambda^2=0$) gives the value of lattice dielectric constant (ϵ_L). Whereas the slope of the graph results the N/m^* and these values are presented in Table 1. Mahmoud et al.¹¹ reported that the lattice high frequency dielectric constant varies from 3.34 to 3.54 and N/m^* lies between 6.25×10^{40} and $5.49 \times 10^{41} \text{ cm}^{-3} \text{ g}^{-1}$, for spray pyrolysed NiO thin films. A characteristic frequency at which the material changes from a metallic to a dielectric response is the plasma frequency (ω_p). In this frequency, the real part of dielectric function vanishes. The plasma resonance frequency (ω_p) of all valence electrons involved in the optical transitions was calculated using the following relation and reported in Table 1.

$$\omega_p^2 = \frac{e^2 N / m^*}{\epsilon_0} \quad (7)$$

According to this relation, plasma frequency depends on the concentration of free carriers. The plasma resonance frequency increases with increasing the substrate temperature. Determination of the dielectric constant could be defined using the dispersion relation of the incident photon. The refractive index was also fitted using a function for extrapolation towards shorter wavelength. The Moss model [12] stated that: "the free carriers contribution to dispersion are relatively small". This means that data corresponding to the wavelength range lying below the absorption edge of the material has to be used [11]. The properties of the investigated NiO could be treated as a single oscillator at wavelength λ_0 at high frequency. The following equation is used to calculate the high frequency dielectric constant ϵ_{∞} ,

$$n^2 - 1 = \frac{S_0 \lambda_0^2}{1 - (\lambda_0 / \lambda)^2} \quad (8)$$

where S_0 is the average oscillator strength and λ_0 is an average oscillator wavelength. The equation (8) can be expressed in a single term Sellmeier oscillator with the refractive index as [13]

$$\frac{n_{\infty}^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_0}{\lambda} \right)^2 \quad (9)$$

where n_{∞} is the static refractive index, which provides a good indication on the structure and density of the material. The above equation (9) can be used to calculate high frequency dielectric constant (ϵ_{∞}). However, according to Moss model¹², the free carriers contributions to dispersion are relatively small, which means that the data corresponding to the wavelength range lying below the absorption edge have to be used to evaluate ϵ_{∞} . Hence the graph between $(n^2-1)^{-1}$ and λ^{-2} as a function of substrate temperature is shown in Fig.6. The intersection with $(n^2-1)^{-1}$ axis is $(n_{\infty}^2 - 1)^{-1}$ and hence, n_{∞}^2 at λ_0 is equal to high frequency dielectric constant (ϵ_{∞}). The obtained λ_0 and S_0 values are found to be comparable with the observed NiO thin films deposited by spray pyrolysis at various substrate temperatures [11].

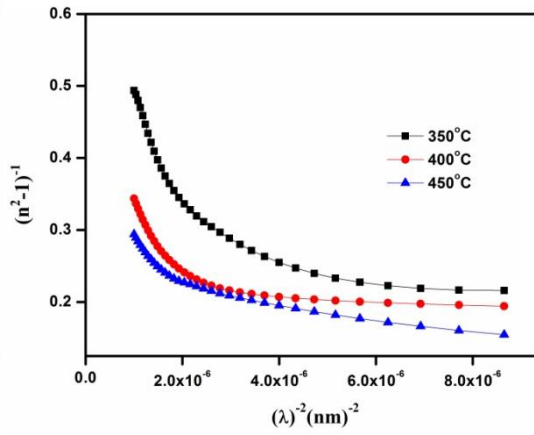
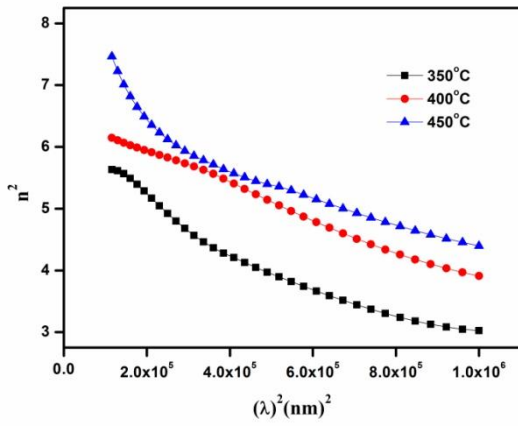


Fig. 5. Plot of n^2 versus λ^2 for NiO thin films

Fig. 6. Plot of $(n^2-1)^{-1}$ versus λ^{-2} for NiO thin films

Table 1:

Dispersion parameters of NiO thin films prepared at various substrate temperatures

Ts °C	ϵ_L	ϵ_∞	$N/m^3 \times 10^{20}$ ($cm^{-3} g^{-1}$)	$\rho_p(Hz) \times 10^8$	λ_0	$S_0 \times 10^{-13}$ (m^{-2})	E_0 (eV)	E_d (eV)	E_g (eV)	E_0/E_g	M_{-1}	M_{-3} (eV) ²
350	3.165	3.825	2.309	0.817	263	4.095	5.184	15.748	3.54	1.46	3.04	0.113
400	5.399	4.578	5.823	1.298	279	4.599	5.133	19.619	3.43	1.49	3.82	0.145
450	5.916	4.662	6.129	1.772	286	4.470	5.074	19.946	3.37	1.50	3.93	0.153

3.4 Dispersion energy parameter

The dispersion of refractive index for NiO films was analyzed using the concept of the single oscillator and can be expressed by Wemple and Di-Domenico (WD) model[14]. In this model, the refractive index data have been examined below the inter-band absorption edge, where the normal dispersion of the optical dielectric constant of the material and the energy dependence of refractive index satisfy the relation,

$$n^2 - 1 = \frac{E_o E_d}{E_o^2 - (h\nu)^2} \tag{10}$$

where $E=h\nu$ is the photon energy. E_o is the average oscillator energy (an average of the optical band gap) and E_d is the dispersion energy parameter of the material that measures the average strength of inter-band optical transitions. A plot of $(n^2-1)^{-1}$ versus $(h\nu)^2$ of NiO deposited films for various substrate temperatures is shown in Fig. 7. It is clear that, the effect of substrate temperature on the refractive index and semiconductor dispersion profiles were exhibited a linear displacement in the shape of the dispersion profile with decreasing refractive index. The refractive index value declines towards longer wavelengths. This is due to the influence of lattice absorption. The values of E_d and E_o are obtained from the intercepts, and slopes of the curves and presented in the Table 1. The variation of E_d and E_o with various substrate temperatures is shown in Fig. 7. The values of E_o was found to be decreased with increasing the substrate temperature, while the values of E_d increased with increasing the substrate temperature. The oscillator energy, E_o is related to the optical band gap (E_g) by $E_o \approx 1.5E_g$, as suggested by WD model[14]. It is evident from Table 1 that the average ratio of $E_o/E_g \approx 1.5$, which shows an agreement with this relation.

A simple connection between the single-oscillator parameters of E_o and E_d and the statistical weighting of the imaginary part of the dielectric constant ϵ_∞ , can be expressed in terms of moments of the ϵ_∞ as follows[15]

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \tag{11}$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad (12)$$

The oscillator energy E_0 is independent of the scale of ϵ_∞ , the evaluated values of M_{-1} vary from 3.04 to 3.93 (dimensionless) and M_{-3} lies between 0.11 and 0.15 (eV)² (Table 1).

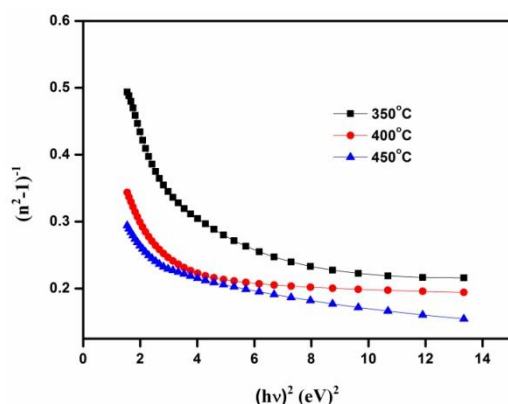


Fig. 7. Plot of $(n^2-1)^{-1}$ versus $(hv)^2$ for NiO thin films

4. Conclusion

Nickel oxide thin film was prepared on glass substrate by simple nebulized spray pyrolysis (NSP) technique using nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) solution at various substrate temperatures. The optical transmittance decreases, consequently the optical band gap energy of NiO film decreases from 3.54 eV to 3.37 eV with increase in substrate temperature. In addition, optical constants, dielectric constants, energy dispersion parameter using WD model, oscillator energy, lattice energy are correlated between obtained data and reported values.

Acknowledgement

One of the authors (Prof. C. Sanjeeviraja) deeply thanks the Council of Scientific and Industrial Research, New Delhi, India for sanctioning Emeritus Scientist Scheme.

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