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Optical properties of chemical bath deposited nickel oxide (NiO) thin films

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Thin film of NiO was deposited on glass slide from aqueous solutions of nickel chloride, and ammonia in which ammonia was employed as complexing agents in the presence of hydroxyl solution. The film was studied using XRD and photomicrograph for the structure and spectrophotometers for its optical properties. The optical characterization shows that the band gap of the film is between 2.10 eV and 3.90 eV, while the indirect band gap is between 0.50eV and 3.20eV and thickness that ranged between 0.061 and 0.346μm. The average transmittance of films was found to be between 50% and 91% in the UV-VIS-NIR regions. The films could be effective as coatings for poultry houses.

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Keywords: Chemical bath deposition technique, NiO thin films, Poultry house coating

1. Introduction

Transition metal oxides like nickel oxides have found wide application in materials applications such sensors [1], transparent electrode [2], efficient control of energy inflow-outflow of buildings or automobiles and aerospace [2,3], smart window [4], solar thermal absorber [5], electrodes for batteries [6], large scale optical switching glazing and electronic information display [7].

Thin film of nickel oxide can be produced by various techniques, which include evaporation, sputter deposition, sol gel, spray pyrolysis, electrochemical and chemical techniques [1, 8-20]. There are a few reports on the deposition of NiO thin films by chemical bath deposition. Pramanik and Bhattacharya [21] deposited NiO thin films using nickel sulfate, ammonia, and persulfate aqueous solution at room temperature. The obtained films were polycrystalline NiO with a black appearance. Varkey and Fort [22] deposited nickel oxide thin films using nickel sulfate and ammonia solution over the temperature range 60–80°C. Pejova et al. [23] used a bath containing nickel nitrate and urea at a temperature of 100°C.

This paper reports on an investigation of the optical properties of chemical bath deposited nickel oxide thin film. The optical properties investigated include the Absorbance (A), and Transmittance (T), which were used to calculate extinction coefficient (k). These optical and solid state properties and the band gap of the films were deduced from equations given in literatures [24-31] while the film thicknesses were obtained by optical methods [28, 32].

2. Experimental details

The preparation of NiO thin films on glass slide was carried out using chemical bath deposition technique, the glass substrates were previously degreased in HNO_3 for 48 hours, cleaned in cold water with detergent, rinsed with distilled water and dried in air. The degreased cleaned surface has the advantage of providing nucleation centers for the growth of the films, hence yielding highly adhesive and uniformly deposited films.

The reaction bath for the deposition of NiO contained 0.2M-1.0M 2ml-10ml nickel sulphate, 1ml-5ml 100% ammonia, and 25ml-27ml water, which were added in that order and allowed for 20-48hours deposition time. The pH range is between 10 and 13. The complexing agents used slow down the precipitation action and enables the formation of NiO. The step wise reaction involved in the complex ion formation and film deposition process for NiO here is:

$$NiSO_4.6H_2O + NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + (SO_4)^{2-}$$

$$[Ni(NH_3)_6]^{2+} \rightleftharpoons Ni^{2+} + 6NH_3$$

$$Ni^{2+} + 2OH^- \rightleftharpoons Ni(OH)_2$$

Hydroxyl ions are released by hydrolysis but Ni^{2+} ions form tetra amine nickel ($[Ni(NH_3)_6]^{2+}$) complex ions by combining with NH_3 in the alkaline medium [33]. The complexes adsorb on the glass, then a heterogeneous nucleation and growth takes place by ionic exchange of reaction OH^- ions. This process, referred to as ion-by-ion process resulted in the deposition of NiO on glass slide in form of greenish-bluish uniform and adherent thin film. The films were then annealed to 423K and 473K in air.

After the films were deposited and annealed they were characterized using a Unico UV-2102 PC spectrophotometer at the scan intervals of 3nm, Philips

PW1800 diffractometer and the photomicrograph carried out using Olympus PMG.

The Absorbance -Transmittance spectra of the films were obtained in UV-VIS-NIR regions by means of Unico UV-2102 PC double beam spectrophotometer with uncoated glass slide as reference.

3. Results and discussion

The XRD pattern and the values related to peaks are shown in Fig. 1 and Table 1. As-deposited NiO films were amorphous. After heating at 150°C in air for 1 h, a weak reflection attributable to cubic NiO was detected. On heating at 200°C for 1 h, this peak was observed to be stronger. The most intense peak is at 2θ = 37.12^o with the preferential orientation of the films being (111).

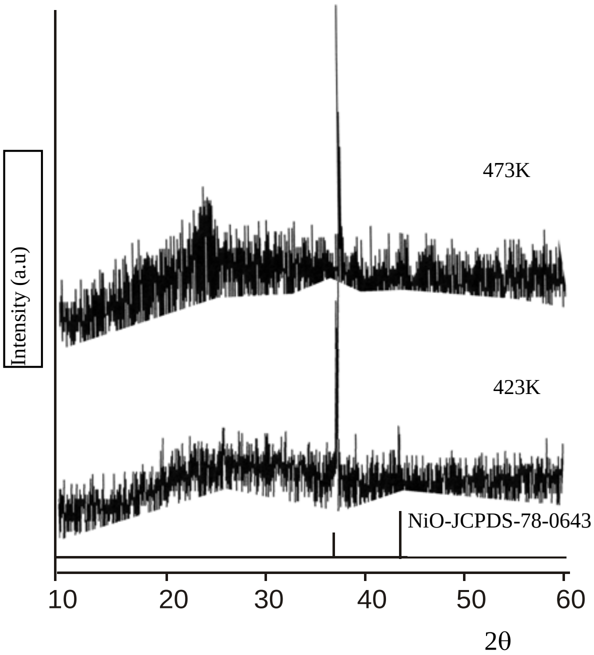


Fig. 1. XRD Pattern for NiO Thin Films Deposited and Annealed at Various Temperatures.

Two peaks at a 2θ value of 37.26 and 43.28 matched the (111) and (200) peaks of cubic NiO phase (JCPDS-ICDD card No. 78-0643) [10]. Similar XRD patterns have been observed for NiO films after annealing [20, 34]

For film annealed at 473K there are more peaks than the film annealed at 423K, however most of them are within the signal noise of spectrum. As the film is annealed there are more but poor crystalline peaks.

The difference between α-phase and β-phase $Ni(OH)_2$ is the location of the lowest 2θ diffraction peaks. For the β-phase $Ni(OH)_2$, the (001) diffraction peak appears at 2θ=19.2, while the lowest diffraction located at 2θ = 11.0 corresponds to α-phase $Ni(OH)_2$ [35]. As shown in shown in Fig. 1, the presence of (001) diffraction at 2θ = 19.2 confirms the presence of β-phase $Ni(OH)_2$ for film annealed 150 ^{o}C

Diffraction peaks of at 2θ=19.2^o, 33.62^o, 38.93^o and 57.77^o are values reported for β-$Ni(OH)_2$ [36]. The diffraction peaks arising from NiO appear at 2θ= 36.98^o, 37.17^o and 43.34^o, which are values reported for cubic NiO [20,35,37-38]. These indicates that at 150 and 200^{o}C is the coexistence of β-$Ni(OH)_2$ and NiO phases. The diffraction peaks were higher than the peaks that were annealed at lower temperature, implying the high orientation and well crystalline [36].

The spectral absorbance of NiO film prepared at 300K and annealed to 423K and 473K with different thickness is displayed in Fig. 2.The film Samples absorb heavily within UV-VIS regions but moderately in the NIR regions for the film deposited at room temperature (300K). The maximum absorbance for the films occurred within the UV region from where the absorbance decreased with the wavelength towards the NIR region. The maximum absorption peak shifts from the short wavelength regions of the UV region for the annealed films towards the longer wavelength of the same region for the as-deposited film.

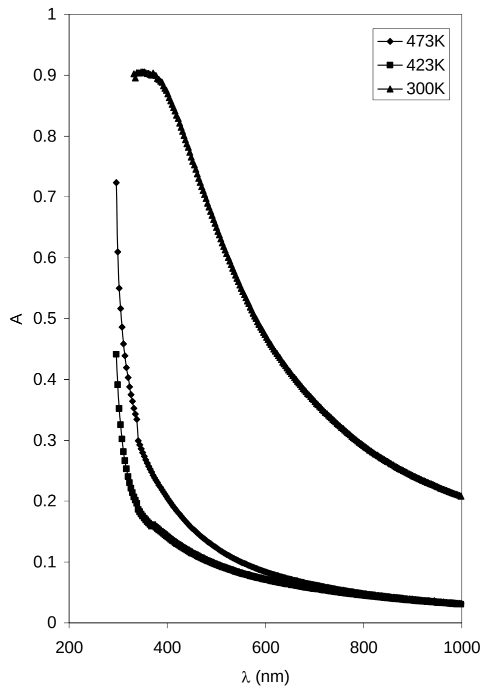


Fig. 2. Absorbance (A) against Wavelength (λ) for different Thickness of NiO Thin Film at (a) 300K (0.346μm) (b) 423K (0.062μm) (c) 473K (0.061 μm).

In high absorption region, the form of absorption coefficient with photon energy was given in a more general term [24, 39]: For direct transitions

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

and for indirect transitions

$$\alpha h\nu = B(\alpha h\nu - E_g)^n \quad (2)$$

Where ν is the frequency of the incident photon, h is Planck's constant, A and B are constants, E_g is the optical energy gap and n is the number which characterizes the optical processes. n has the value ½ for the direct allowed transition, 3/2 for forbidden direct allowed transition and 2 for the indirect allowed transition. When the straight portion of the graph of $(\alpha h\nu)^n$ against $h\nu$ is extrapolated to $\alpha = 0$ the intercept gives the transition band gaps.

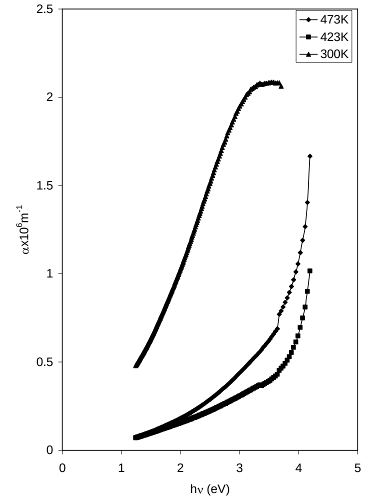


Fig. 3. Plots of α as a function Photon Energy (hν) for NiO Thin Film at (a) 300 K (0.346 μm) (b) 423 K (0.062μm) (c) 473K (0.061μm).

The plots of α against hν are shown in Fig. 3. These show sharp absorption edges, which are the characteristics of the crystalline state of the film but however poor as deduced from XRD analysis. The region of higher values of α that is $\alpha > 10^6 m^{-1}$ correspond to transition between extended state in both valence and conduction bands while the lower values that is $\alpha \leq 10^6 m^{-1}$ is the region where absorption present a rough exponential behaviour [40]. The plots for location of the direct and indirect transition band gaps are shown Figs. 4 and 5.

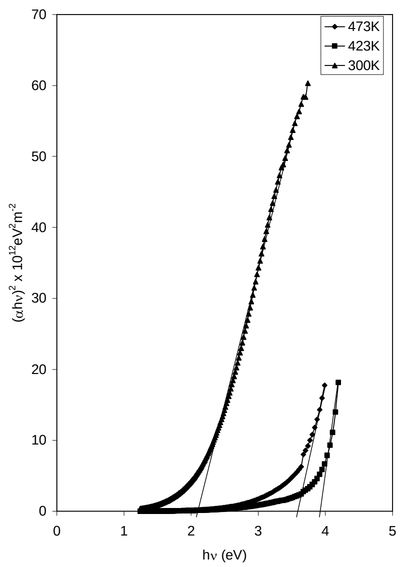


Fig. 4. Plots of $(\alpha h\nu)^2$ as a function Photon Energy (hν) for NiO Thin Film at (a) 300 K (0.346 μm) (b) 423 K (0.062μm) (c) 473K (0.061μm).

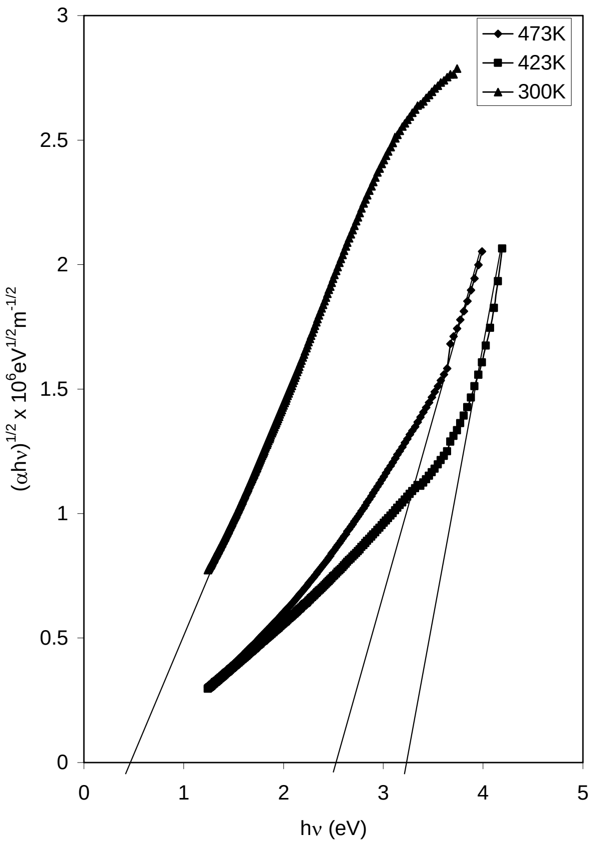


Fig. 5. Plots of $(\alpha h\nu)^{1/2}$ as a function Photon Energy (hν) for NiO Thin Film (a) at 300 K (0.346 μm) (b) 423 K (0.062μm) (c) 473K (0.061μm).

The direct band gap values range between 2.10 and 3.90eV while indirect band gap range between 0.50eV and 3.20 eV. Though this direct bandgap value disagrees with the optical gap of 1.75eV reported by Pramanik and Bhattacharya [21], it falls well within the range of 3.40–4.00eV as reported in literatures [8, 10, 13, 17, 19, 22, 23, 41].

When spectral absorbance of the film is compared with the band gap location of the film it is observed that as the thickness increased the band gap decreased. The absorbance of the film increased with the thickness of the film which shows that thicker films have more atoms present so that more states are available for the photon energy to be absorbed. An optical band gap narrowing from 3·90 to 2·10eV with increasing film thickness was deduced from the films, this is in good agreement with optical band gap narrowing from 3·90 to 3·80eV, which were reported as suitable for use as electrochromic films [17] and thin films deposited by chemical bath deposition and by spray pyrolysis [19] .

The transmittance spectra (Fig. 6) showed that the films annealed to 423K and 473K have transmittances higher than 72% in the VIS-NIR regions. These films agree fairly with report of films deposited on glass substrates prepared by the sol-gel technique, which were very transparent in the visible region, with optical transmittance >85% [16]. The as-deposited film (300K) showed transmittance of less than 62% within the VIS-NIR regions. However both the as-deposited and annealed films show transmittance that increased exponentially from the UV region towards the NIR region. The properties of poor transmittance in the UV-VIS but moderately high transmittance in the VIS-NIR exhibited by film sample 300K make the film good material for screening off UV portion of electromagnetic spectrum which is dangerous to human health and as well harmful to domestic animals. The film can be used for coating eye glasses for protection from sunburn caused by UV radiations. Since they show moderately high VIS-NIR transmittance it can be used for coating of poultry roofs and walls. This will ensure that young chicks which have not developed protective thick feather are protected from UV radiation while the heating of the poultry house is maintained by the heating portion of the electromagnetic spectrum, and as well allows for admittance of VIS light in the house.

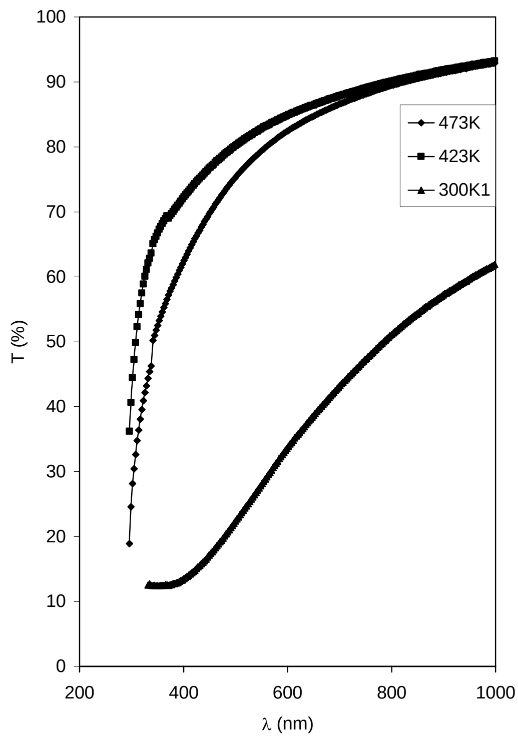


Fig. 6. Transmittance (T) as a function of wavelength (λ) for different thicknesses of NiO thin film at (a) 300 K (0.346μm) (b) 423K (0.062μm) (c) 473K (0.061μm)

The annealed film at 423K exhibited high transmittance of greater than 73% within the VIS region and has a wide band gap of 3.90eV. The film annealed to 473K has a transmittance of greater than 63% in the VIS region with a band gap of 3.60eV. The transmittance values exhibited by the annealed films agree fairly with that reported by Svensson and Granqvist [15] which were prepared by sputtering technique.

There is a relationship between k and α given by [24, 42-45].

$$k = \alpha\lambda/4\pi \quad (3)$$

where α is the absorption coefficient of the film and λ is the wavelength of electromagnetic wave. Equation 3 was used to determine the extinction coefficient.

Plots of k against hν are displayed in Fig. 7.

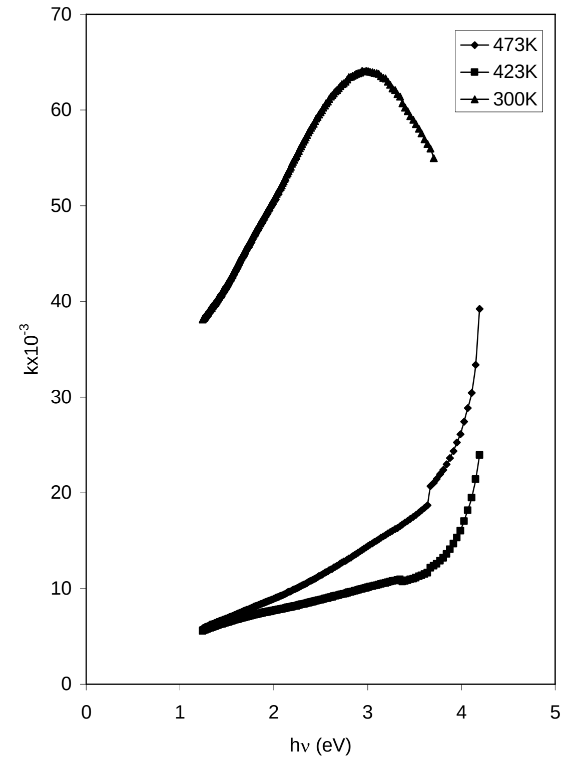


Fig. 7. Extinction coefficient (k) as a function Photon Energy (hν) for NiO Thin Film at (a) 300K (0.346μm) (b) 423K (0.062μm) (c) 473K (0.061μm)

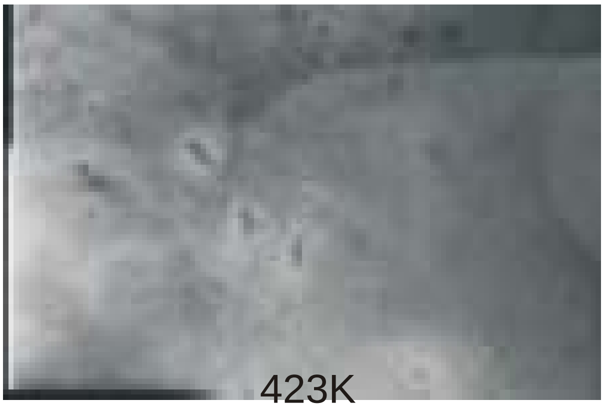
Maximum k values range between 2.45×10^{-2} and 6.41×10^{-2} with minimum values ranging between 5.57×10^{-3} and 2.33×10^{-2}.

Table 1 is the average optical properties of the film deposited and annealed at different temperature.

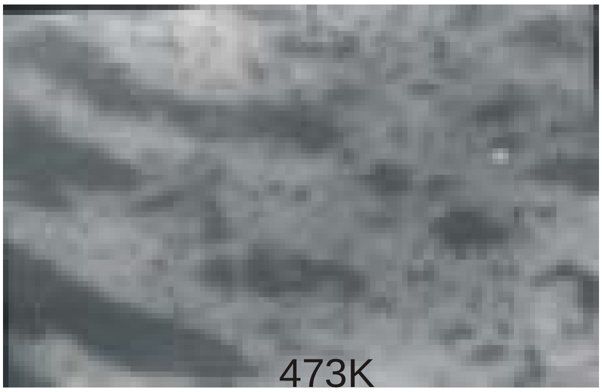
Table 1. Average Optical Properties of the Film Deposited and Annealed at Different Temperature.

Sample No	$\alpha\times10^{6}$ m^{-1}	%T	$k\times10^{-2}$	E_g	t(μm)
473 K	0.112	89	0.707	3.90	0.061
423 K	0.104	90	0.655	3.60	0.062
300 K	0.676	51	4.278	2.10	0.346

From the table it is observed that as temperature increased, the band gap increased but the thickness decreased.



a



b

Fig. 8a-b. Optical micrograph of NiO thin films annealed at various temperatures.

Fig. 8a-b shows the optical micrograph of NiO thin film deposited and annealed at different temperatures. The optical micrographs (magnification 100×) of the as deposited films at different annealed temperatures reveal difference in surface texture and good film uniformity over significant surface area of a continuous phase. The variations in the morphology of the film show that the annealing of the film affect the structure of the film and as well the absorption coefficient. The variation observed in the band gap could be attributed to changes observed in the micro-surface texture of the films when annealed as seen in the photomicrograph.

4. Conclusion

Thin films of NiO were deposited, using chemical bath deposition techniques. The spectral analysis revealed that some of the films grown are poor transmitter of UV but transmit highly in the VIS – NIR regions. The transmittances show between 63 and 87% in the VIS – NIR regions with a band gap that ranged between 2.10 and 3.90 eV. The films therefore have potential applications for poultry protection and warming coatings, solar control and antireflection coatings.

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