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

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Thin film of NiOx was deposited on glass slide from aqueous solutions of nickel chloride and ammonia. Ammonia was employed as complexing agent in the presence of hydroxyl solution. The film was studied using X ray diffraction, photomicrograph for the structure and absorption spectroscopy for its optical properties. The optical characterization shows that the film has band gap that ranged between 2.10eV and 3.90eV, 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 optical coatings for poultry houses.

Introduction

The composition of nickel oxide can be represented as NiO$_x$H$_y$ but for simplicity it is referred to as NiO$_x$ [1]. Analysis of pure crystalline phases of Ni(OH)$_2$ and NiOOH has revealed the existence of different structures which include a more stable β-Ni(OH)$_2$ and a more hydrated unstable α-Ni(OH)$_2$ [2]. Under oxidation processes in alkaline solutions Ni(OH)$_2$, oxidation products are described as nickel-oxi-hydroxides (NiOOH) and have different structures which include a more stable γ-NiOOH and β-NiOOH [2]. This is represented as follows [3]

Ni(OH)$_2$ ⇔ NiOOH + H$^+$ + e
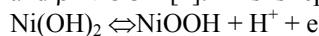
The electrochromic properties of the films show that NiOx exhibit coloration of the anode which is associated with the extraction of proton and formation of Ni^{3+} color centers. The electrical properties of NiOx thin films show that they are p-type semiconductors of which the resistivity can be lowered by an increase of the hole concentration. This lowering of the resistivity can achieved by increase of the number of native defects such as nickel vacancies and/or interstitial oxygen or by doping with monovalent ions such as lithium [1].

Metal oxides like nickel oxides have found wide application in materials applications such sensors [4], transparent electrode [3], efficient control of energy inflow-outflow of buildings or automobiles and aerospace [3, 5], large scale optical switching glazing and electronic information display [6]
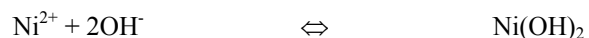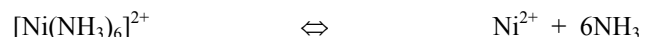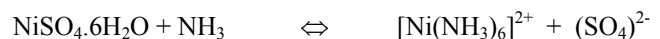
Thin film of nickel oxide can be produced by different methods such as evaporation, sputter deposition, sol gel, electrochemical and chemical techniques [4, 7-11].

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 literature [12-19] while the film thicknesses were obtained by optical methods [16, 20].

Experimental details

The preparation of NiO$_x$ 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$_x$ 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 and13. The complexing agents used slow down the precipitation action and enables the formation of NiO$_x$. The step wise reaction involved in the complex ion formation and film deposition process for NiO$_x$ here is:

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

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

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

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 [21]. 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 an ion-by-ion process resulted in the deposition of NiO$_x$ on glass slide in form of greenish-bluish uniform and strong adherence 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
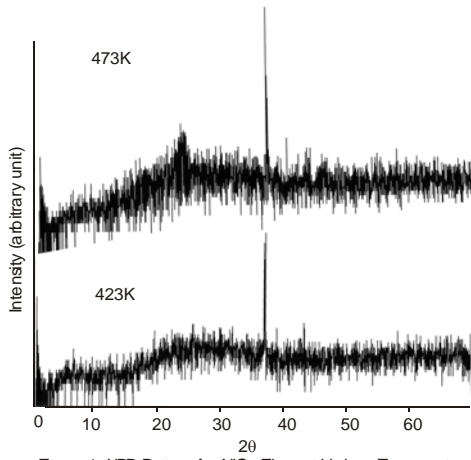
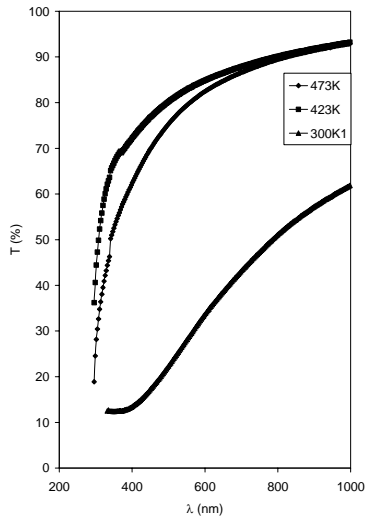**Figure 1.** XRD pattern for NiOx film sat various temperatures.

Figure 2. Transmittance (T) as function of wavelength (λ) for NiOx thin film under various treatments.
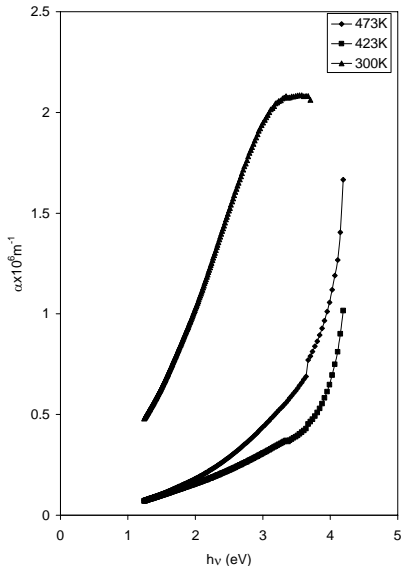

Figure 3. Plots of α as a function of photon energy (hν) for NiOx thin film at various treatments.

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 an uncoated glass slide as reference.

Results and discussion

The XRD pattern and the values related to peaks are shown in figure 1. As-deposited NiOx 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 $2\theta = 37.12^{o}$ with the preferential orientation of the films being (111).

For film annealed to 473K there are 2 obvious peaks which are at $2\theta=24^{o}$ and 37.12^{o} while for film annealed to 423K there is only 1 peak at $2\theta=37.12^{o}$, although there are other peaks, which are within the noise level. 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 $2\theta=19.2$, while the lowest diffraction located at $2\theta = 11.0$ corresponds to α-phase $Ni(OH)_2$ [22]. Diffraction peaks at $2\theta=19.2^{o}$, 33.62^{o}, 38.93^{o} and 57.77^{o} are values reported for β-$Ni(OH)_2$ [23]. The diffraction peaks arising from NiO appear at $2\theta= 36.98^{o}$, 37.17^{o} and 43.34^{o}, which are values reported for cubic NiO [22, 24-25]. These indicates that at 150 and 200°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 [23].

The transmission spectra of NiO_x film prepared at 300K and annealed to 423K and 473K with different thickness is displayed in Figure 2.from the transmission spectra it is observed that 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 transmission spectra showed that the films annealed to 423K and 473K have transmittances greater 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% [8]. 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
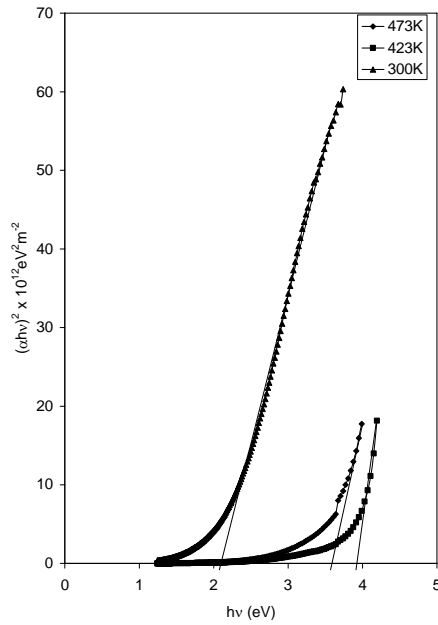
Figure 4. Plots of $((\alpha h\nu)^n$ as a function of photon energy (hν) for NiOx thin film at various treatments.
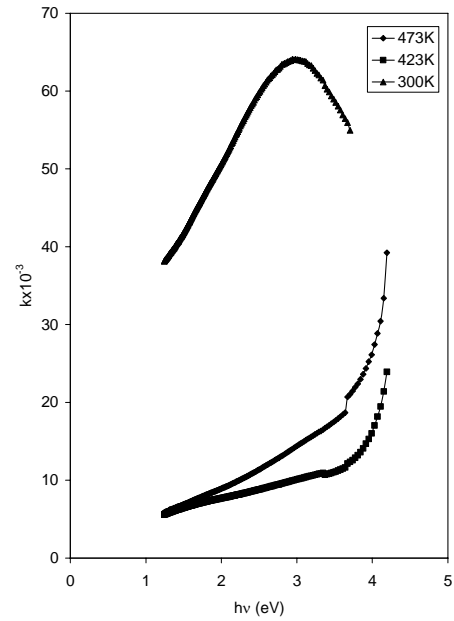

Figure 5. Extinction (k) as function of photon energy (hν) for NiOx thin film under various treatments.

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.

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 [7] which were prepared by sputtering technique.

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.

In high absorption region, the form of absorption coefficient with photon energy was given in a more general term [12, 26]: For direct transitions

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

and for indirect transitions

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

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 hν is extrapolated to α = 0 the intercept gives the transition band gaps.

The plots of α against hν are shown in Figure 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 [27]. The plots for location of the direct transition band gaps are shown Figure 4. The direct band gap values range between 2.10 and 3.90eV. 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 for films deposited by a combination of the electrochemical and sol-gel deposition methods of NiO_x thin films on SnO_2:F coated glass substrates, which were reported as suitable for use as electrochromic films [9] and thin films deposited by chemical bath deposition and by spray pyrolysis [11] .

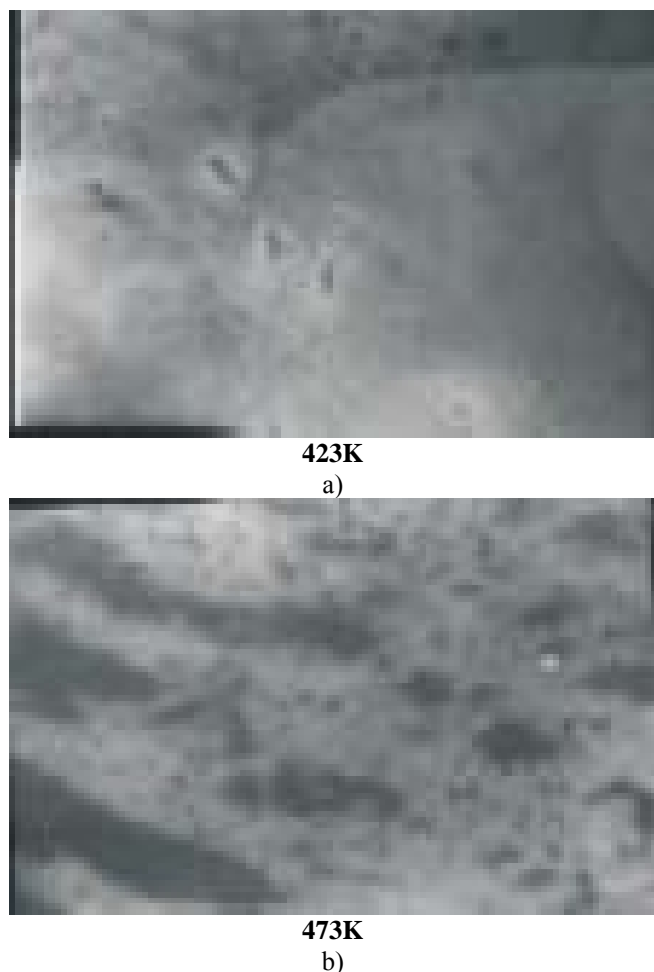There is a relationship between k and α given by [12, 28-31].

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

Figure 6a-b shows the optical micrograph of NiO_x thin film deposited and annealed at different temperatures. The optical micrographs (magnification 100x) 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.

423K

a)

473K

b)

Figure 6a – b. Optical Micrograph of NiOx thin film annealed (a) at 423K and (b) at 473K.

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

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 hv are displayed in Figure 5. 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	$t(\mu m)$
473K	0.112	89	0.707	3.90	0.061
423K	0.104	90	0.655	3.60	0.062
300K	0.676	51	4.278	2.10	0.346

Conclusion

Thin films of NiO_x 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 3.90eV. The films therefore have potential applications for poultry protection and warming coatings, solar control and antireflection coatings.

References

[1] A. Kuzmin, J. Purans, and A.Rodionov, J. Phys: Condens. Mater. **9**, 6979 (1997)

[2] G.W. Briggs, Electrochemistry, Specialist Periodical Reports, the Chemical society London. **4**, 33 (1974).

[3] M. Fantini and A. Gorenstein Solar Energy Materials, **16** 487 (1987)

[4] D. Mutschall, S.A. Berger, and E. Obermeier, Proc. of 6th international meeting on chemical sensors, Gaithersburg, 28 (1996)

[5] M.K. Carpenter, R.S. Conell, and D.A. Corrigan, Solar Energy Material. **16** 333 (1987).

[6] P.C. Yu, G. Nazri and C.M. Lampert, Solar Energy Materials. **16**, 1 (1987)

[7] J.S.E.M. Svensson and C.G. Granqvist, Solar Energy Materials **16**, 19 (1987)

[8] A.E Jiménez-González, J.G. Cambray, and A.A.R Gutiérrez., Surface Engineering. **16**, 77 (2000).

[9] A.E. Jiménez-González and J.G. Cambray, Surface Engineering. **16**, 73 (2000).

[10] W. Brückner, R. Kaltofen, J. Thomas, M. Hecker, M. Uhlemann, S. Oswald, D. Elefant, and C. M. Schneider, Journal of Applied Physics. **94**, 4853 (2003).

[11] L. Berkat, L. Cattin, A. Reguig, M. Regragui and J.C. BernedeMater. Chem. and Phys. **89**,11 (2005).

[12] J.I. Pankove, Optical processes in semiconductors, Prentice-Hall, New York (1971).

[13] F.I. Ezema and C.E.Okeke, Nig. Journal of Physics, **14**, 48 (2002).

[14] F.I. Ezema and C.E Okeke, Academic Open Internet Journal www.acadjournal.com **9**, (2003).

9

[15] F.I. Ezema and C.E Okeke, Greenwich Journal of Science and Technology. **3**, 90 (2003).

[16] F.I. Ezema, Journal of university of science and Technology. **23**, 32 (2003).

[17] F.I. Ezema and P.U. Asogwa, Pacific Journal of Science and Technology. **5**, 33 (2004).

[18] F.I. Ezema, Journal of the University of Chemical Technology and Metallurgy. **39**, 225 (2004).

[19] F.I. Ezema., Academic Open Internet Journal, http://www.acadjournal.com/2004/v11/part2/p1/index.htm

[20] M. Theye, In Optical Properties of Thin Films, (Edited by K.L. Chopra and L.K. Malhota), thin film technology and Applications, Tata McGraw-Hill, New Delhi, (1985).

[21] G.F. Liptrot, Modern inorganic chemistry, English language Book Society/Unwin Hyman, London p386-388 (1989).

[22] J Park, K. Ahn, Y. Nah and H. Shim Y. Sung, J. Sol-Gel Sci. and Tech. **31**, 323 (2004)

[23] X. Liu, G. Qiu, Z.Wang and X. Li, Nanotechnology. **16**, 1400, (2005)

[24] S. Kim, K. Park, J. Yum, and Y. Sung, Solar Energy Materials & Solar Cells, 0, 000–000 (2005)ARTICLE IN PRESS

[25] F. Atay, S. Kose, V. Bilgin, and I. Akyuz, Turk. J. Phys. **27**, 285 (2003)

[26] I.M.Tsidilkovsk, Band structure of semiconductors, Pergamon Press, Oxford (1982).

[27] M. F. Kotkata, H.T.El-Shair, M.A. Afifi and M.M.A. Azizi, J. Phys. D: Appl. Phys. **27**, 623 (1994).

[28] I.C. Ndukwe, Sol. Ener. Mater. Sol. Cells. **40**, 123 (1996).

[29] J.I. Gittleman, E.K. Sichel, and Y. Arie, Sol. Ener. Mater. **1,** 93 (1979)

[30] M. Janai, D.D. Alfred, D.C. Booth and B.O. Seraphin, Sol. Ener. Mater. **1**, 11 (1979).

[31] K.L. Chopra, Thin Film Phenomena, McGraw Hill Book Company USA, p.729, 1983.