

Effects of Thermal Annealing on the Optical Properties of Nickel Oxide Thin Films Prepared by Chemical Bath Deposition Technique.

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ABSTRACT

Nickel oxide thin films have been prepared by chemical bath deposition technique on glass substrates using 3 mls of 1M of NiSO_4 , 4 mls of 1M of KCl_4 , and 1M of Ammonia as the complexing agent. The films were subjected to post-deposition annealing under various temperatures, 100, 150, 200, and 300°C . The thermal treatment of $\text{Ni}(\text{OH})_2$ thin film decomposes to NiO_x .

The films are very prosperous materials with excellent electrochromic properties, firmly adhered to the substrate and resistant to chemicals. The percentage transmittance is very high while the percentage reflectance is low as the wavelength increases. The band gaps obtained under various thermal treatments are between 1.90eV and 4.4eV. The refractive index is between 0.00 and 3.00. The thickness achieved is in the range of 0.12-0.14 μm . These properties of the oxide film supports other important application of NiO film such as preparation of alkaline batteries (as a cathode material) anti-ferromagnetic layers, P -type transparent conducting film.

(Keywords: nickel oxide, electrochromic properties, chemical bath deposition, thin film, thermal annealing, optical properties)

INTRODUCTION

Nickel oxide (NiO_x) film exhibits anode electrochromism (EC) (i.e., they are transparent for visible light in their reduced state and brownish in their oxidized state) [1]. The oxide films are stable, strongly adherent to the substrate, mechanically hard, and resistant to moisture and acids [2].

In recent times, as one of the most expensive anode coloring materials exhibit relatively strong EC properties [1]. Several techniques have been known for NiO_x thin film preparation, such as spray pyrolysis [3], evaporation [4], sputtering [5], cathode electro-deposition method [6], etc. Band gap range of 1.9–4.4 eV has been reported using these techniques. Transparent conductive oxides (TCOs) are unusual materials that are both electrically conductive and visually transparent [7, 8]. Nickel oxide films have large transmittance in the visible region of the electromagnetic spectrum as a consequence of the large band gap.

Owing to its outstanding electrical, optical and electrochemical properties. A variety of applications is known for the electrochromic materials in general. Electrical light-modulation devices, such as: non-emissive large scale displays [9], electrically controlled optical shutters for heat and light modulators for windows, where the switching speed is not a key factor [10], smart windows (photovoltaic powered electrochromic devices) [11], etc. In particular, NiO_x thin films as electrochromic devices have drawn much interest of the material science researchers [12].

Electrochromic devices have also been considered by NASA in hope of replacing the Venetian blind radiators in future satellites [13]. The most important potential commercial application of the electrochromic films would be: glazing of buildings and houses to provide dynamical control of the incoming illumination [10] and thus an energy efficient housing and lifestyle. [12] NiO_x plays an important role in this because of its anode electrochromism.

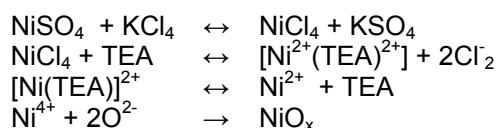
In this paper, we report the successful deposition of thin Nickel oxide films using chemical bath deposition technique and the influence of post deposition thermal annealing on the optical properties of the oxide film.

EXPERIMENTAL DETAILS

The nickel oxide (NiO_x) thin films were prepared using chemical bath deposition technique. The chemical bath system was made up of 3 mls of 1M of NiSO_4 , 4 mls of 1M of KCl_4 , and 1M of triethanolamine (TEA) or Ammonia (NH_3) as complexing agent in 35 mls of prepared PVA (polyvinyl alcohol), 50 ml beakers and 76 mm x 26mm x 1mm glass microscope slides which were used as substrates.

The substrates were degreased in Aqua Regia (3:1 of conc. HCl : HNO_3) solution for 24 hours, washed clean in detergent solution rinsed out in distilled water and allowed to air dry. Solution of the same various concentrations were prepared and used in arriving at the optimum combination and depositing film of nearly the same thickness.

Uniform films were obtained in the process. In each case the substrate was suspended vertically in the reaction bath after stirring the solution properly for homogeneity then allowed to stand in the oven of about $60^\circ\text{C} - 75^\circ\text{C}$ for 3hours. The reaction process is of the form



The films were removed and washed after various periods of deposition and allowed to dry in air.

Even though the thin film samples were deposited at room temperature, some of them were subjected to post deposition annealing between the temperatures of 100°C and 399°C . The optical absorbance/transmittance of the samples were investigated in the spectral range of 200-1000nm (UV-VIS-NIR regions) using Unicam Helios Gamma UV- Visible spectrophotometer

RESULTS AND DISCUSSION

Nickel oxide (NiO_x) thin films were successfully deposited on glass substrate using chemical bath deposition technique. The films are very transparent, firmly adhered to the substrates and resistant to both trioxonitrate (v) acid and hydrochloric acid. Thermal annealing does not affect the physical nature of the films. The range of thickness of the films deposited is $0.12-0.14\mu\text{m}$. Figures 1 and 2 show plots of transmittance and reflectance as functions of wavelength. The graphs show that the properties of the films become more defined with decrease in the annealing temperature. Generally, the films show very high degree of transmittance and very low degree of reflectance in the entire spectral regions.

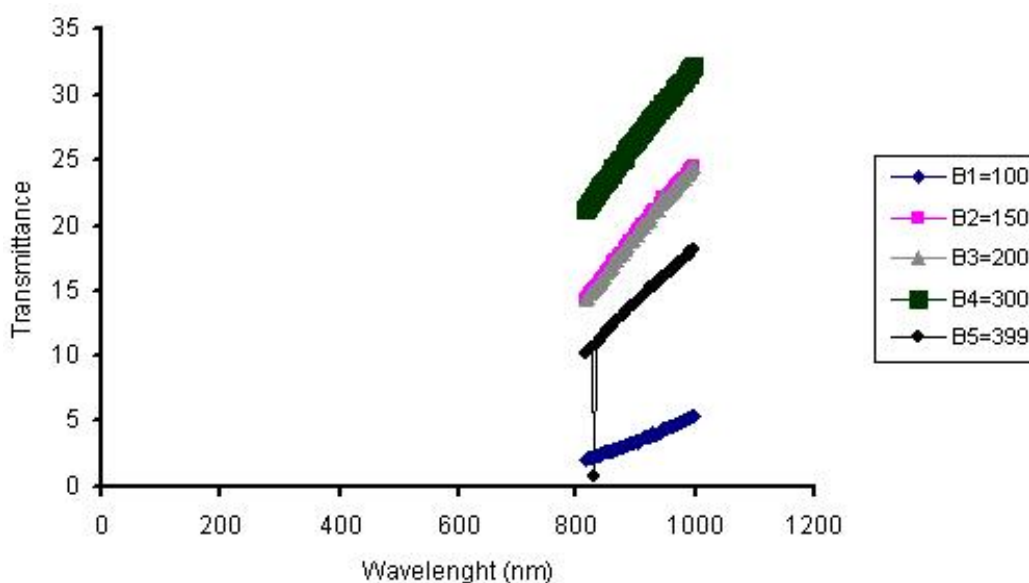


Figure 1: Transmittance Against Wavelength for Nickel Oxide Thin Film at Different Annealing Temperature.

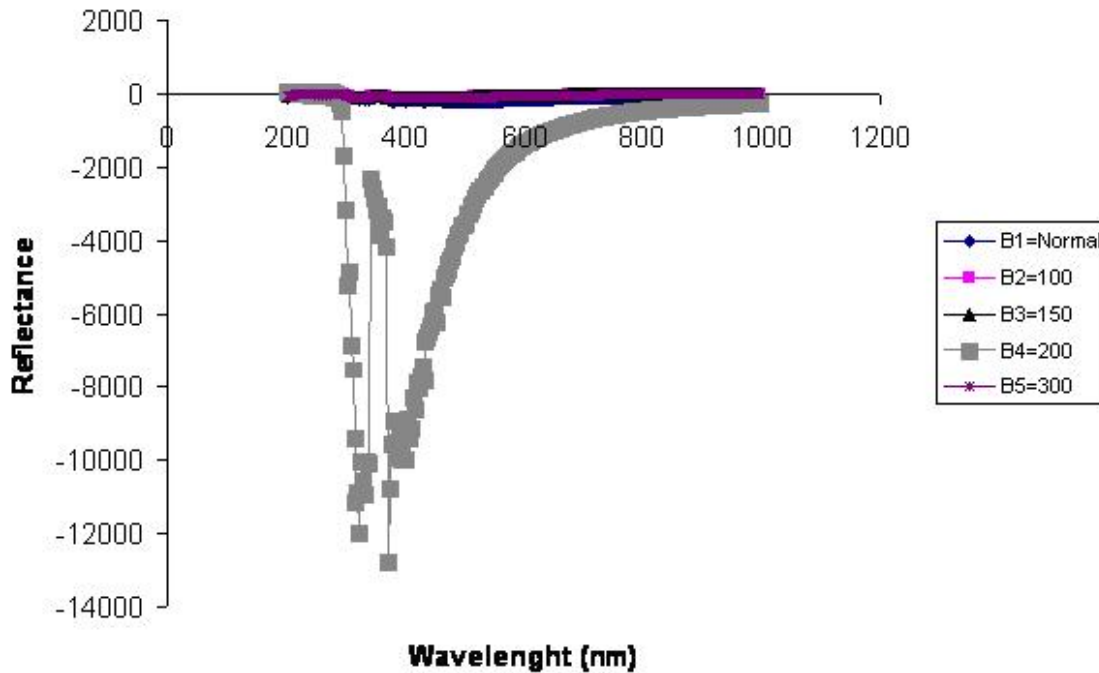


Figure 2: Reflectance Against Wavelength for Nickel Oxide Thin Film at Different Annealing Temperatures.

The films as grown and those annealed at lower temperature (1000 –2000 C) show transmittance in the range of 90% - <100% and reflectance in the range of (-0) -10%. On the other hand, those annealed at higher temperature show depreciation in transmittance and nearly constant on reflectance. The range is now ~60% - 90% and (-0)-10%, respectively. The transmittance rises with increasing wavelength while reflectance decreases with increasing wavelength.

Maximum and minimum values of refractive index, 0.00 and 3.00 respectively were obtained for the NiO_x films. The values decrease with increasing wavelength as shown in Figure 3. The rate of decrease increases with the annealing temperature.

In order to determine the optical band gap of the semiconductor, the following dependence of the absorption coefficient, α on the photon energy equation [8,14,15] is used:

$$(\alpha h\nu) \propto (h\nu - E_g)^n$$

where E_g is the direct transition band gap and $n=1/2$ for direct allowed transition

Figure 4 shows a plot of $(\alpha h\nu)^2$ against the photon energy, $h\nu$. The band gap obtain for various annealing temperature are shown in the table below. The table shows a decreasing band gap with increasing temperature. Even the decreased values of E_g still remain wide.

Various authors in their separate reports had reported band gap ranging from 3.0eV to 4.2eV in agreement with the wide band gap reports.

The optical conductivity is given by [17]

$$\sigma = \frac{\alpha n c}{4\pi}$$

where α is the absorption co-efficient, n the refractive index, c is the velocity of light and σ_0 the optical conductivity.

Plots of optical conductivity as a function of photon energy are shown in Figure 5.

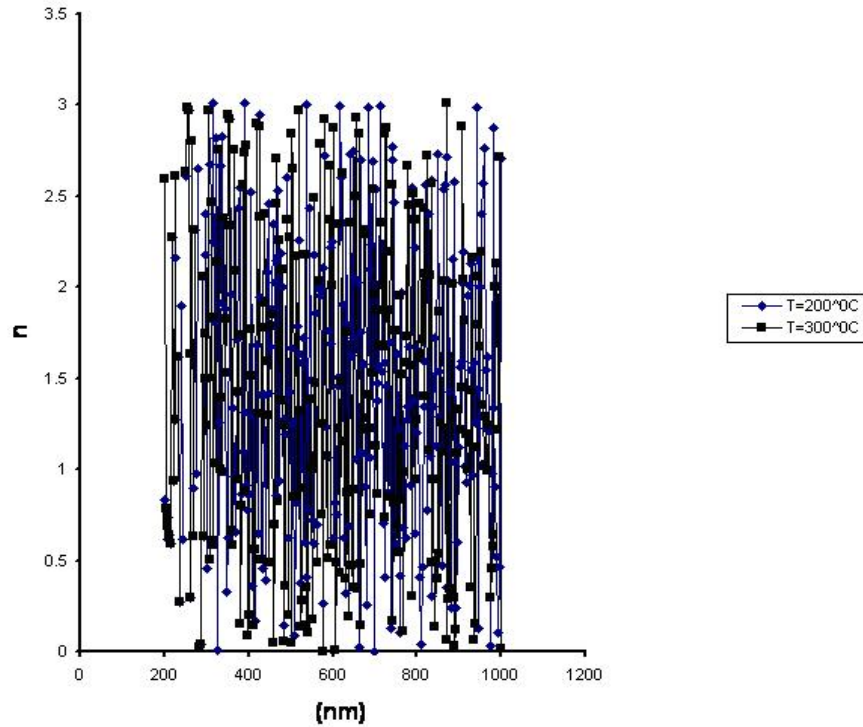


Figure 3: Refractive Index (n) as Function of Wavelength (λ) Under Different Annealing Temperatures.

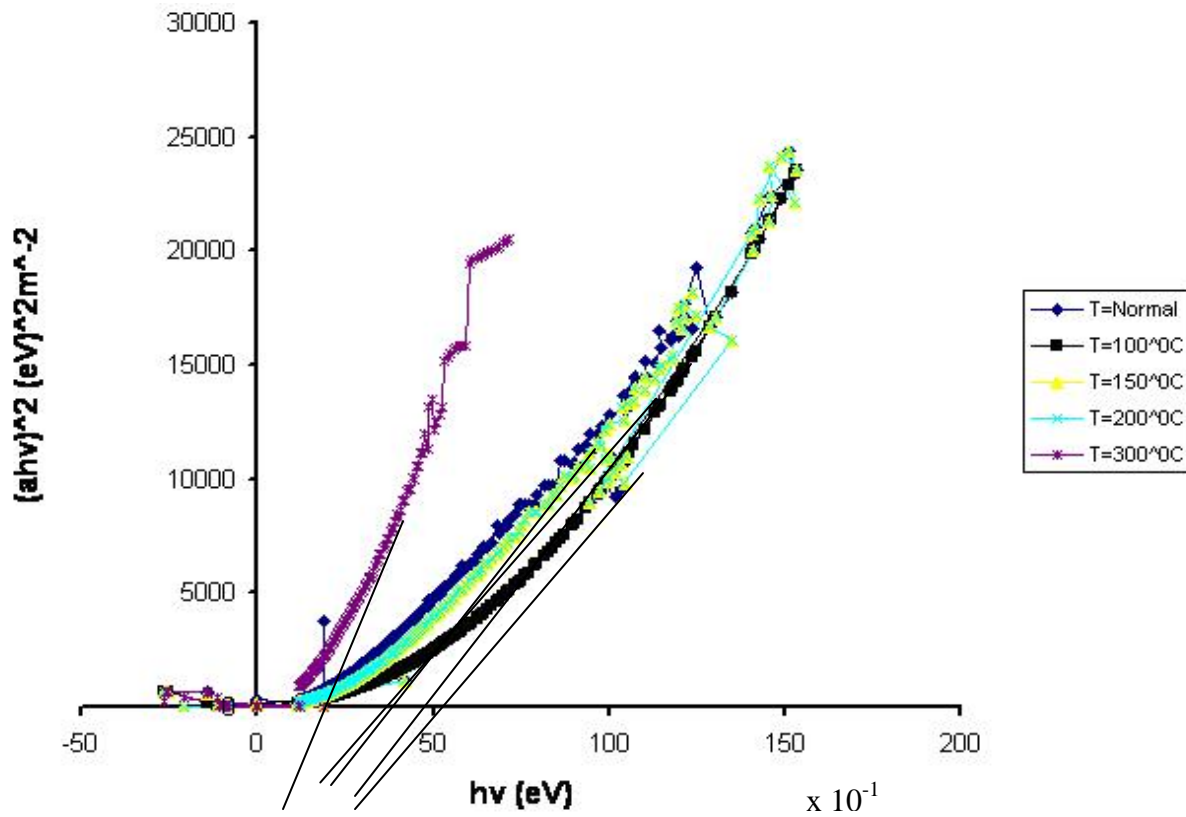


Figure 4: A Plot of $(ahv)^2$ as a Function of Photon Energy ($h\nu$) for NiO_x .

Table 1: Band Gap of NiO_x Under Various Annealing Temperatures.

Sample	Annealing temp	Band Gap (eV)
C ₁	100	4.40
C ₂	150	3.90
C ₃	200	3.00
C ₄	300	2.85
C ₅	399	1.80

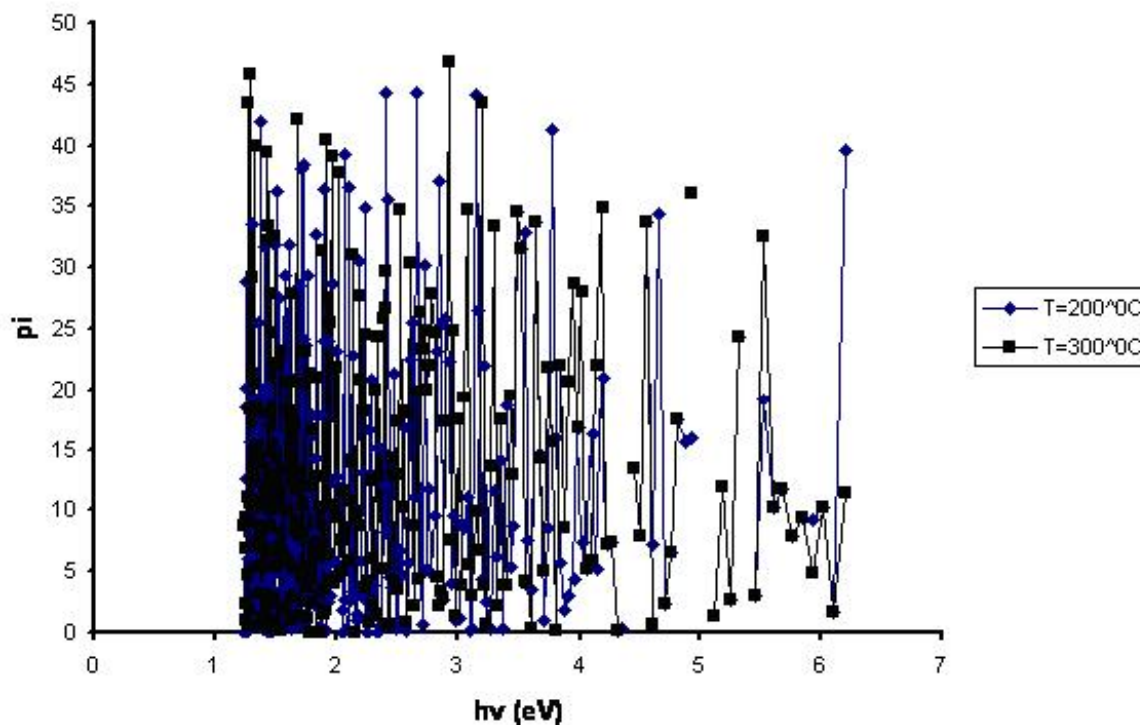


Figure 5: A Plot of Optical Conductivity as a Function of Photon Energy (hν) for NiO_x.

At 200°C, the rate of random increase of σ_0 with increasing photon energy was very steep. However at 300°C, the rate of increase was equally steep but slower. Both maximum values decrease and minimum values increase with increase in photon energy. Minimum and maximum values of 0.00s^{-1} and $4.70 \times 10^{12}\text{s}^{-1}$ respectively are shown the figure.

CONCLUSION

Nickel oxide (NiO_x) thin films have been deposited by chemical bath deposition technique using the method explained above. Post deposition annealing of the films at temperatures 100, 150, 200, 300, and 399°C sharpened the properties of

the films. NiO_x film is a transparent oxide film. It has very high transmittance in all the regions of electromagnetic spectrum. The transmittance increase from UV-NTR regions up to over 90%. The reflectance is generally low.

Band gap of 1.80 – 4.40eV were obtained for the oxide film under various annealing temperatures. The values are in agreement with theoretical values. Values of the refractive index are within the range 0.00 to 3.00.

The outstanding properties of the oxide films show them as good electrochromic materials in general. Electrical light-modulation devices, such as: non-emissive large scale displays, electrically controlled optical shutters for heat and light

modulators for windows, where the switching speed is not a key factor, smart windows (photovoltaic powered electrochromic devices) etc.

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