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## OPTICAL AND ELECTROCHROMIC PROPERTIES OF e-BEAM EVAPORATED NICKEL OXIDE THIN FILM

**K.J. Patel<sup>1</sup>, C.J. Panchal<sup>1</sup>, M.S Desai<sup>1</sup>, P.K. Mehta<sup>2</sup>**

<sup>1</sup> Applied Physics Department, Faculty of Technology & Engineering,  
The M. S. University of Baroda, Vadodara 390001, Gujarat, India  
E-mail: [cjpanchal\\_msu@yahoo.com](mailto:cjpanchal_msu@yahoo.com)

<sup>2</sup> Physics Department, Faculty of Science,  
The M. S. University of Baroda, Vadodara 390002, Gujarat, India

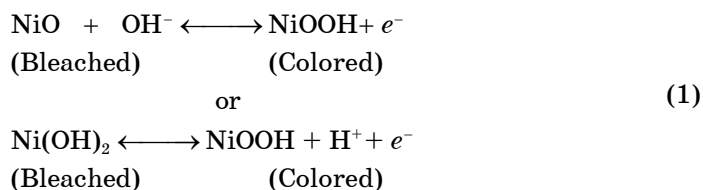
*Nickel oxide (NiO) thin films were deposited by e-beam evaporation on glass and ITO coated glass substrates initially held at room temperature without post-heat treatments. The structural and optical properties were investigated using glancing incident X-ray diffractometer (GIXRD) and spectrophotometer. The electrochromic (EC) behavior of NiO thin film was investigated using electrochemical technique viz. cyclic voltammetry, constant current measurement, and chronoamperometry in 1 M KOH electrolyte. The transmittance modulation and switching time with different operating voltage were also studied.*

**Keywords:** NICKEL OXIDE, THIN FILM, OPTICAL PROPERTIES, ELECTRO-CHROMIC.

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### 1. INTRODUCTION

The electrochromic (EC) materials change their optical properties during electrochemical redox reaction through ion insertion. The EC devices due to their open-circuit memory, and low-power consumption have received a great deal of attention for their potential technological applications such as smart windows, reflectance-adjustable car rearview mirrors, and high-contrast non-emissive information displays [1, 2]. Among the various EC materials, nickel oxide (NiO), an anodic electrochromic material, can be used as a complimentary to the tungsten oxide electrode in EC device application [3, 4], where optical modulation increases due to the simultaneous bleaching and coloring of both electrodes. Electrochromism of NiO thin films is intricate complicated. It is generally accepted that the coloration, transition from a bleached to a colored (brown) state, is related to a charge-transfer process between Ni<sup>3+</sup> and Ni<sup>2+</sup> associated with the deintercalation/intercalation of OH<sup>-</sup> ions or H<sup>+</sup> ions and electron. The commonly accepted reaction mechanisms for charge extraction/insertion are given in Eq. 1 [1].



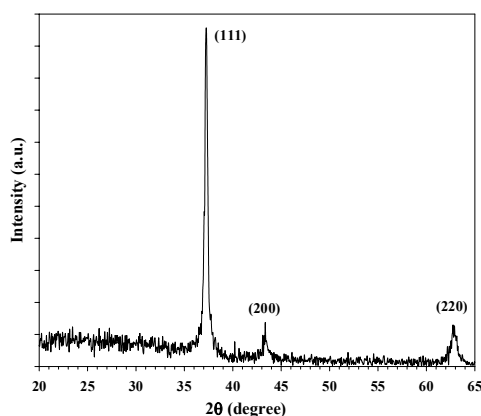
The EC properties of the films show that NiO exhibit coloration associated with the extraction of proton and formation of  $\text{Ni}^{3+}$  color centers. EC NiO thin films have been grown by various physical and chemical thin film preparation methods [1, 5]. In the present work, optical and EC properties of e-beam deposited nickel oxide thin films have been studied. The EC behavior was investigated in 1 M KOH electrolyte by electrochemical characterization. In addition, the effect of the operating voltage on the transmittance modulation and the response time was also measured.

## 2. EXPERIMENTAL

The NiO thin film was deposited by e-beam evaporation technique on glass and indium tin oxide (ITO) coated glass substrates initially held at RT without post-heat treatments. The ITO coated glass substrate has a sheet resistance of 5 Ohms/ $\square$ . The substrates were organically cleaned, rinsed with distilled water, and dried in air. The NiO powder (Sigma Aldrich, 99.9 %) was used as the source material for preparation of thin film. The thickness of the NiO thin films of 2500 Å at 4 Å/s deposition rate was monitored and controlled using quartz crystal based thin film deposition controller (Sigma Instruments, SQC 122c). The crystal structure of the thin film was investigated by a Bruker D8 glancing incident X-ray diffractometer (GIXRD) using monochromatic high-intensity  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15406$  nm) with incident angle of  $0.5^\circ$  in a  $2\theta$  range from  $20$ - $65^\circ$ . The optical transmittance was recorded with UV-visible spectrophotometer (Shimadzu UV-2450) in the wavelength range 300-900 nm in order to find the energy band gap. The EC properties of NiO thin films were investigated in an aqueous alkaline electrolyte (1 M KOH) with the help of two-electrode electrochemical cell, in which the NiO/ITO on glass substrate, acted as the working electrode and a stainless steel plate was used as a counter electrode. Concomitantly, the transmittance spectrum for electrochromic measurement was recorded in the range of 400-1200 nm using the transmittance measurement setup.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Structural analysis



*Fig. 1 – XRD pattern of the NiO thin film*

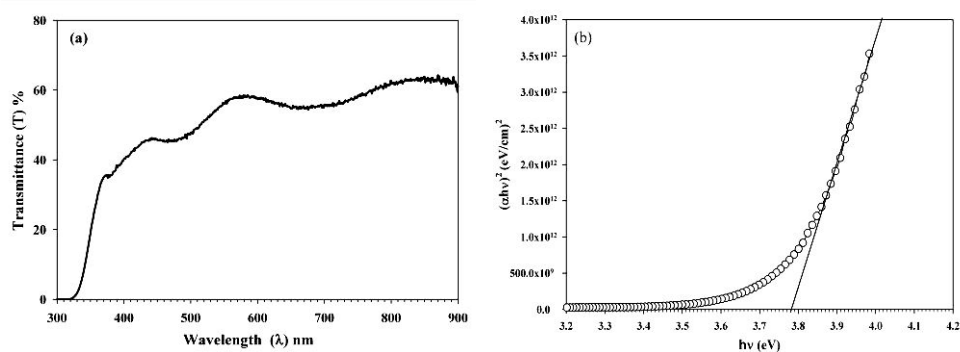
GIXRD pattern of NiO thin films on glass substrate initially held at RT is shown in Fig. 1. The spectrum exhibits three peaks at  $37.3^\circ$ ,  $43.3^\circ$ , and  $62.9^\circ$ , related to (111), (200), and (220) plane, respectively. This XRD pattern indicates that the NiO cubic rock salt structure having strong (111) preferred orientation. The crystallite size ( $D$ ) of the NiO thin films has been calculated by Debye – Scherrer equation [6],

$$D = \frac{0.9\lambda}{B \cos(\theta)} \quad (2)$$

where  $B$  is full-width at half-maximum (FWHM) of the peak,  $\theta$  is the position of the diffraction peak, and  $\lambda$  is the X-ray wavelength ( $1.5406 \text{ \AA}$  for  $\text{CuK}_\alpha$ ). The crystallite size ( $D$ ) in (111) plane has been found to be  $\sim 20 \text{ nm}$ .

### 3.2 Optical analysis

The wavelength dependent transmittance spectra for NiO thin film is shown in the Fig. 2 a. The transmittance spectrum depicts that the NiO thin film presents  $\sim 55 \%$  transmittance, which is due to the defects of non-stoichiometric in compositions. The absorption for wavelength longer than  $400 \text{ nm}$  is associated with an excess of oxygen in the lattice. The excess oxygen gives rise to  $\text{Ni}^{3+}$  ions which created color center in the NiO films and thus the transmittance is decreased [7]. A sharp decrease in transmittance at the fundamental absorption edge near  $320 \text{ nm}$  was observed.



**Fig. 2** – Transmittance spectra (a) and  $(\alpha h\nu)^2$  vs  $h\nu$  plot with band gap energy (b) of NiO thin film

As NiO is a direct band gap semiconductor, the energy band gap ( $E_g$ ) of NiO thin films is obtained by plotting the relation between  $(\alpha h\nu)^2$  and  $h\nu$  as shown in Fig. 3 b. where  $\alpha$  is the absorption coefficient and  $h\nu$  is the photon energy. By extrapolating the straight-line portion of  $(\alpha h\nu)^2$  to the energy axis, the intercept on energy axis gives the value of band gap energy, which is nearly  $3.78 \text{ eV}$ .

### 3.3 Electrochromic analysis

The cyclic voltammetry was performed to exhibit the electrochemical behavior of NiO thin film. The change in optical density,  $\Delta OD$ , was determined for the

NiO thin film in the wavelength range of 400-1200 nm by constant current measurement. The switching time ( $t$ ) measurement was done by chronoamperometry with concurrently measuring the transmittance at  $\sim 650$  nm wavelength.

### 3.3.1 Cyclic voltammetry (CV)

The cyclic voltammetry of NiO thin film was recorded at different scan rates of 10-50 mV/s in the voltage range,  $-1.5$ V to  $+1.5$ V, is shown in Fig. 3.

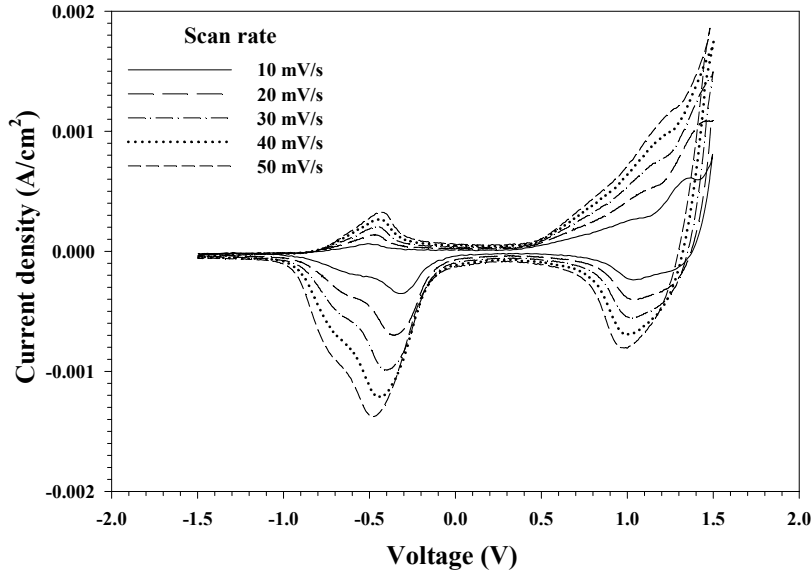


Fig. 3 – Cyclic voltammogram for NiO thin film at different scan rates

During the anodic scan the current density is due to the oxidation of  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$ , which causes colouration of the film, while during the cathodic scan, the increment in current density is due to the reduction of  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$ , which results in bleaching of the thin film. Two different peaks appear in CV, which is related to a couple of redox process is involved in reactions in NiO thin film. From Fig. 3 the anodic peak current density ( $j_{pa}$ ) and the cathodic peak current density ( $j_{pc}$ ) increases with the scan rate, which are further used to estimate the diffusion coefficient using Eq. 3 [8].

$$i_p = 2.72 \times 10^5 \times n^{\frac{3}{2}} \times D^{\frac{1}{2}} \times C_0 \times v^{\frac{1}{2}} \quad (3)$$

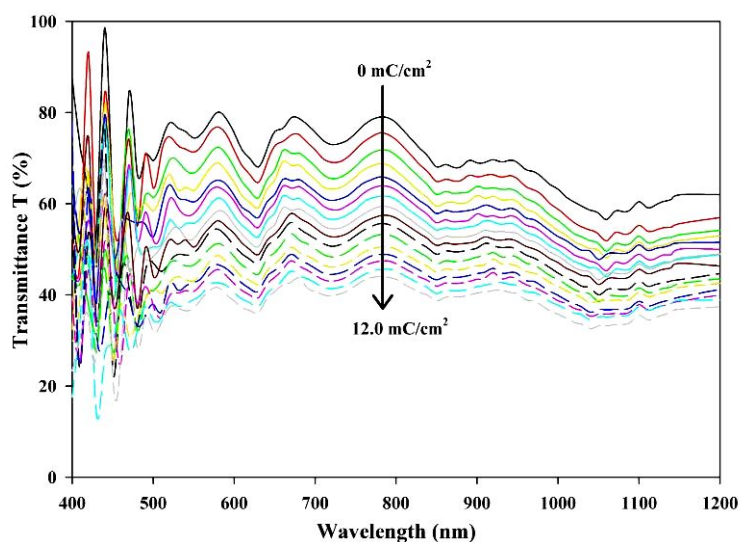
where,  $D$  is the diffusion coefficient in  $\text{cm}^2\text{s}^{-1}$ ,  $C_0$  is the concentration of the active ions in the electrolyte solution in terms of  $\text{mol cm}^{-3}$ ,  $v$  is the potential scan rate mV/s,  $j_p$  is the peak current density in  $\text{A}\cdot\text{cm}^{-2}$ , which is obtained from the CV measurement, and  $n$  is the number of electrons involved in the reaction, assumed to be 1. The estimated value of  $D$  along with the electrochemical parameters  $j_{pc}$ , and  $j_{pa}$ , for different scan rates, are shown in Table 1. We see from the results that the diffusion coefficient is  $\sim 10^{-10} \text{ cm}^2/\text{s}$  for both anodic and cathodic scan of the NiO thin film.

**Table 1** – The electrochemical parameters viz. anodic peak current density ( $j_{pa}$ ), cathodic peak current density ( $j_{pc}$ ), and diffusion coefficients ( $D$ ) of NiO thin film

Scan rate mV/s	Current density (A/cm <sup>2</sup> )		Diffusion coefficients (cm <sup>2</sup> /s)	
	Anodic spike $j_{pc}$	Cathodic peak $j_{pa}$	$D_{jpc}$	$D_{jpa}$
10	$8.05 \times 10^{-4}$	$3.58 \times 10^{-4}$	$8.96 \times 10^{-10}$	$1.78 \times 10^{-10}$
20	$1.09 \times 10^{-3}$	$7.00 \times 10^{-4}$	$8.23 \times 10^{-10}$	$3.39 \times 10^{-10}$
30	$1.47 \times 10^{-3}$	$9.90 \times 10^{-3}$	$9.97 \times 10^{-10}$	$4.52 \times 10^{-10}$
40	$1.72 \times 10^{-3}$	$1.21 \times 10^{-3}$	$10.35 \times 10^{-10}$	$5.10 \times 10^{-10}$
50	$1.85 \times 10^{-3}$	$1.37 \times 10^{-3}$	$9.48 \times 10^{-10}$	$5.26 \times 10^{-10}$

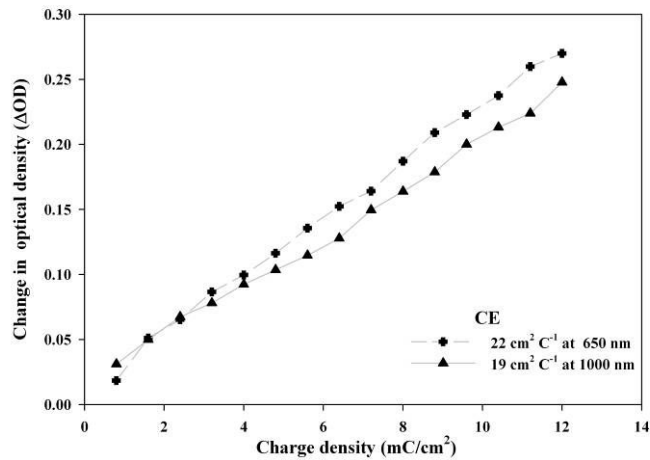
### 3.3.2 Constant current measurement

Electrochemical parameters,  $\Delta OD$  and coloration efficiency (CE), were measured by applying a constant current density of 0.2 mA/cm<sup>2</sup> for the insertion of OH<sup>-</sup> ions in the NiO thin film. Concomitantly the transmittance spectrum for different levels of charge exchange, up to 12 mC/cm<sup>2</sup>, was recorded in the range of 400-1200 nm, as shown in Fig. 4.



**Fig. 4** – Transmittance spectra of NiO thin films for different intercalation level in step of 0.8 mC/cm<sup>2</sup>

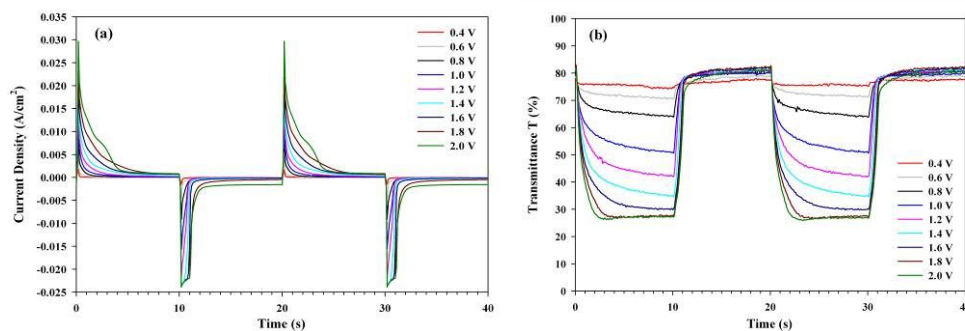
The change in the optical density [ $\Delta OD = \log (T_{bleached}/T_{colored})$ ] with the inserted charge density is shown in Fig. 5. A nearly linear relationship is observed between  $\Delta OD$  and the inserted charge density. This was further used to calculate the value of CE, which is defined as the ratio of the change in optical density of the film in its colored and bleached state at a certain wavelength per unit insertion of charge [ $CE = \Delta OD/Q$ ]. The value of CE at 650 nm and 1000 nm are 22 cm<sup>2</sup> C<sup>-1</sup> and 19 cm<sup>2</sup> C<sup>-1</sup>, respectively.



**Fig. 5** – The change in the optical density with inserted charge density and CE at different wavelengths for NiO thin film

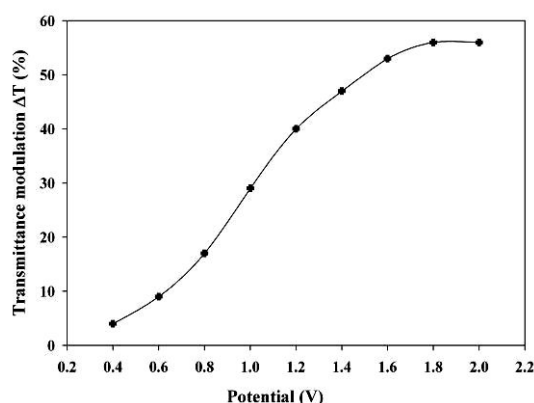
### 3.3.3 Chronoamperometry (CA) measurements

The optical switching time ( $t$ ) was measured by chronoamperometry with concurrently measuring the transmittance at  $\sim 650$  nm wavelength. The transmittance was simultaneously measured by means of a red laser diode ( $\sim 650$  nm) and Si photo detector, the setup was interfaced with PC and automated using Lab VIEW program. A different square-wave potential of  $\pm 0.4$  to  $\pm 2.0$  V, at a frequency of 0.05 Hz, was applied to the EC electrode. The current density and the transmittance at  $\sim 650$  nm with time were recorded and shown in Fig. 5.



**Fig. 5** – The change in the current density (a) and the change in optical density at 650 nm measuring with time (b) for NiO thin film

The transmittance modulation, ( $\Delta T = T_{\text{bleached}} - T_{\text{colored}}$ ) at 650 nm, coloration time ( $t_c$ ) and bleaching time ( $t_b$ ) was estimated from the chronoamperometry data. Fig. 6 shows the transmittance modulation at 650 nm with applied potential.



**Fig. 6** – The transmittance modulation ( $\Delta T$ ) with applied potential at  $\sim 650$  nm for NiO thin film

It is observed from Fig. 5 that the NiO thin film operated at low voltage shows a small transmittance modulation and slower coloration time. The improvement in the response time and  $\Delta T$  is observed with increases in the operating voltage. The maximum  $\Delta T$  (56 %) and fastest switching time ( $\sim 2.5$  s) are found at 2.0 V operating voltage. The switching time during the bleaching process is faster than that of colouring where the back e.m.f. is directed opposite to the applied voltage in the colouring mode and in the same direction as the applied voltage in the bleaching mode. Another factor which contributes to the response difference is the conductivity which can vastly differ between the bleached and colored states [9].

#### 4. CONCLUSION

The XRD spectra reveals that the NiO thin films deposited at RT without post-heat treatments by e-beam evaporation are crystalline in nature with cubic structure. The optical characterization shows that the film has an average 55 % transmittance in the visible region of light and the band gap was found to be about 3.78 eV. The CV measurement in 1M KOH shows that, the diffusion coefficient value for NiO thin films is  $\sim 10^{-10}$  cm<sup>2</sup>/s. The transmittance of the NiO thin film decreases with the increase in intercalation of OH<sup>-</sup> ions in the films. The coloration efficiency was found to be 22 cm<sup>2</sup>C<sup>-1</sup> and 19 cm<sup>2</sup>C<sup>-1</sup> at 650 nm and 1000 nm wavelengths, respectively. The transmittance modulation at  $\sim 650$  nm increases and the coloration time decreases with increase in operating voltage, however, there was no observed effect of the operating voltage on the bleaching time.

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## REFERENCES

1. C.G. Granqvist, *Handbook of Inorganic Electrochromic Materials* (Elsevier: Amsterdam: 2002).
2. X. Zhang, H. Zhang, Q. Li, H. Luo, *IEEE Electr. Device L.* **21**, 215 (2000).
3. J. Zhang, J.P. Tu, X.H. Xia, Y. Qiao, Y. Lu, *Sol. Energ. Mat. Sol. C* **93**, 1840 (2009).
4. A. Subrahmanyam, C.S. Kumar, K.M. Karuppasamy, *Sol. Energ. Mat. Sol. C* **91**, 62 (2007).
5. T. Maruyama, S. Arai, *Sol. Energ. Mat. Sol. C* **30**, 257 (1993).
6. B.D. Cullity, S.R. Stock, *Elements of X-ray Diffraction* (Prentice Hall: New Jersey: 2001).
7. K.M.E. Miedzinska, B.R. Hollebone, J.G. Cook. *J. Phys. Chem. Solids* **49**, 1355 (1988).
8. M.A. Habib, D. Glueck, *Sol. Energ. Mater.* **18**, 127 (1989).
9. S.A. Mahmoud, S.A. Aly, M. Abdel-Rahman, K. Abdel-Hady, *Physica B* **293**, 125 (2000).