

## Effect of Substrate Temperature on the Electrochromic Properties of Nickel Oxide Thin Films by e-Beam Evaporation Method

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(Received 09 July 2013; published online 31 August 2013)

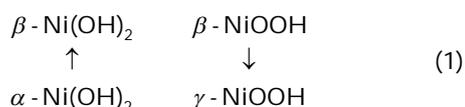
Nickel Oxide (NiO), an anodic coloring material, is used as a counter electrode layer in Electrochromic (EC) devices in combination with Tungsten Oxide (WO<sub>3</sub>) as an EC layer. The NiO thin films were prepared on glass and indium tin oxide coated glass substrates by e-beam evaporation technique at different substrate temperatures ranging from room temperature (27 °C) to 400 °C. The crystallization of the film improves with increase in substrate temperature as inferred from the glancing incident X-ray diffraction measurement. The increase in substrate temperature of the films causes an increase in the transmittance. The electrochromic properties of NiO thin films were investigated in an aqueous alkaline electrolyte (1M KOH) by means of transmittance, cyclic voltammetry (CV), and chronoamperometry (CA) measurements. It is found that films prepared at lower substrate temperature, up to 100 °C, have better EC properties.

Keywords: Nickel oxide, Substrate temperature, Electrochromic

PACS numbers: 78.40.Fy, 78.20.Jq, 61.05.cp, 65.40.gk

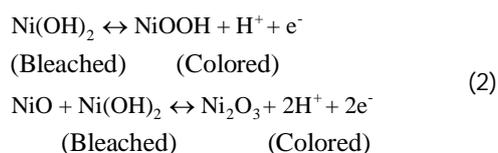
### 1. INTRODUCTION

In most of the thin film electrochromic devices (ECD) Tungsten oxide (WO<sub>3</sub>) thin film have been used as a primary electrochromic (EC) layer due to its high coloration efficiency and good durability [1]. The complementary coloring effect will enhance the optical modulation of ECD by simultaneously changing the color of both EC layers. Nickel oxide (NiO), an anodic EC material, can be used as a complementary to the tungsten oxide electrode in ECD fabrication [2, 3]. In NiO, 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 electrons [4]. The stoichiometric NiO contains only Ni<sup>2+</sup> ions and are transparent in the visible light, while the higher oxidation states produces Ni<sub>2</sub>O<sub>3</sub> and NiOOH compounds, which are strongly absorbing for visible light. Electrochemical properties of nickel oxide based thin films have been mainly investigated in alkaline electrolyte, mostly in aqueous KOH electrolyte. Electrochromism in NiO thin films is complicated. The transformations of nickel hydroxides, and oxyhydroxides into one another upon H<sup>+</sup> or OH<sup>-</sup> exchange is explained by the Bode reaction scheme [5]:

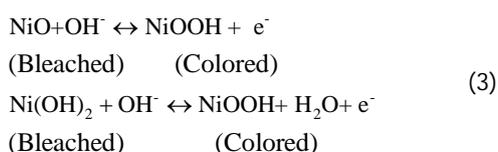


According to the Bode reaction scheme, NiO reacts with hydroxyl ions, and produces  $\alpha$ - and  $\beta$ -phases of

Nickel hydroxides (Ni(OH)<sub>2</sub>). The difference between  $\alpha$ - and  $\beta$ - phase of Ni(OH)<sub>2</sub> is only the quantity of water needed for stabilization; the  $\alpha$ -phase occurs at a low content of water while the  $\beta$ -phase occurs at a high content. These both phases can be further oxidized to the  $\gamma$ - and  $\beta$ - oxy-hydroxides, respectively. Bode reaction scheme restricts the information of the change of valency from 2<sup>+</sup> to 3<sup>+</sup> upon coloration in the case of NiO, thus an extension of this model is put forward to study the changes from NiO to Ni<sub>2</sub>O<sub>3</sub> as shown below [6,7]:



According to these reactions, the extraction of H<sup>+</sup> ion causes a transformation from Ni(OH)<sub>2</sub> to NiOOH, and the extraction of another H<sup>+</sup> is compensated by the creation of a hole on the Ni<sup>2+</sup> in the NiO and in the created Ni<sub>2</sub>O<sub>3</sub>. Alternately, OH<sup>-</sup> groups may contribute some reaction mechanisms for charge extraction/insertion as given in Eqs. 4 [8] or 5 [9]:



The EC properties of the films show that NiO exhibits colorations associated with the extraction of H<sup>+</sup> or

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intercalation of OH<sup>-</sup> for the formation of Ni<sup>3+</sup> color centers. From the theoretical point of view, in NiO, the top of the valance band consists of nickel 3*d* states and it is assumed that the electrochromism in NiO is related to the reversibly extraction and insertion of Ni 3*d* electron. Eqs. (3) and (4) are the generally accepted mechanism for the coloration in NiO materials.

EC NiO thin films have been grown by various physical thin film preparation methods [9, 10, 11]. The stoichiometry, structure, crystalline size, etc. change with different deposition methods and growth conditions; as a result the EC properties and coloration efficiency (CE) vary over a wide range. In the present work, optical and EC properties of e-beam deposited nickel oxide thin films have been studied. The EC behavior, optical modulation, coloration efficiency, and switching time, were investigated in 1M KOH electrolyte by electrochemical characterization.

## 2. EXPERIMENT

NiO thin films were deposited on organically cleaned soda lime and indium tin oxide (ITO) coated glass substrate by e-beam evaporation system (Hindhivac, Model-15F6). NiO powder (Sigma Aldrich, 99.9 %) was used as a source material. The substrate temperature was varied from room temperature (RT), 27 °C to 400 °C using a radiant substrate heater, whose temperature was monitored by using a Cr-Al thermocouple. The thickness of the film, 2500 Å, at the rate of deposition, 4 Å/s, was monitored and controlled by a quartz crystal based thin film deposition controller (Sigma Instruments, SQC 122c). The ITO coated glass substrate has a sheet-resistance of 10 ohms/□ [12]. The crystal structure of the thin film was investigated by a Bruker D8 glancing incident X-ray diffractometer (GIXRD) using monochromatic high-intensity Cu *k*<sub>α</sub> radiation with angle of incidence 0.5° in a 2θ range from 20°-65°. The surface composition of these thin films is determined using X-ray photo-emission spectroscopy (XPS). The XPS measurement is carried out using VSW ESCA instrument, with Al-K<sub>α</sub> (1486.6 eV) X-ray source at a base vacuum of 8.0 × 10<sup>-10</sup> Torr. The optical transmittance was recorded with UV-visible spectrophotometer (Shimadzu UV-2450) in the wavelength range 300-900 nm. The EC properties of NiO thin films were investigated in an aqueous alkaline electrolyte (1M KOH) with the help of two-electrode electrochemical cell, in which the NiO/ITO on glass substrate, acts as the working electrode and a stainless steel plate was used as a counter electrode. Cyclic voltammeteries (CV) of the films were performed in potential between -1.5 V and 1.5 V with different scan rates. For transmittance modulation (Δ*T*) and coloration efficiency measurement a constant current density of 0.2 A/cm<sup>2</sup> was applied for 25 s and the transmittance spectra of the samples for both colored and bleached states were recorded in the wavelength range of 400-1200 nm using the transmittance measurement setup. The electrochromic switching time of NiO thin film was determined by chronoamperometry measurement at potential of ±1.5 V and 0.05 Hz frequency and, concurrently, the transmittance was recorded using a 650 nm laser diode and a Si photo detector.

## 3. RESULT

### 3.1 Structural Properties

The XRD spectra of NiO thin films deposited on glass substrates held at different temperatures are shown in Fig. 1. It is observed that the NiO thin films

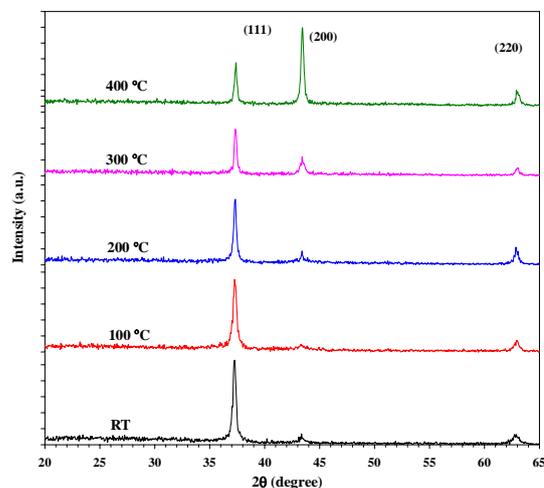


Fig. 1 – The XRD spectra of NiO thin films at different substrate temperatures

deposited from RT to 400 °C are polycrystalline in nature with a cubic structure. The films deposited at RT to 300 °C shows the (111) preferred orientation with (200) and (220) minor orientations. The intensity of the (111) peak decreases while the intensity of the (200) peak increases with the substrate temperature i.e. the (200) preferred orientation improves with the substrate temperature. The intensity of (220) peak increases up to 200 °C and then a decrease in intensity is observed with further increase in substrate's temperature. At 400 °C the preferred orientation changed from (111) to (200) directions. At the higher substrate temperature (400 °C) in NiO thin films the non-stoichiometry decreases and thus the films orientation changes from (111) direction into (200) directions [13]. At the higher substrate's temperature, the deposited atom or molecules have enough kinetic energy to produce a better crystalline film.

### 3.2 Compositional Properties

The compositional characterization of NiO thin films deposited on the glass substrates is determined using the XPS spectra measurements. From survey scan spectra, the Ni 2*p*<sub>3/2</sub> and 2*p*<sub>5/2</sub> peaks were detected at nearly 854 eV and 872 eV, respectively, and the O 1*s* peak was detected at 529.2 eV. Thus, detailed scan spectra were recorded in the range of 840 to 890 eV for Ni 2*p* and 524 to 536 eV for O1*s* peak as shown in Fig. 2.

Fig. 2a shows the Ni 2*p*<sub>3/2</sub> and 2*p*<sub>5/2</sub> peaks, which were located at 854.0 eV and 871.9 eV, respectively, with their respective satellite peaks located at 860.8 eV and 879.5 eV. The satellite peak in NiO is may be caused due to various reasons: the multi-electron excitations, multiple splitting or surface plasmon loss [14]. The as-deposited NiO contained not only Ni<sup>2+</sup> but also

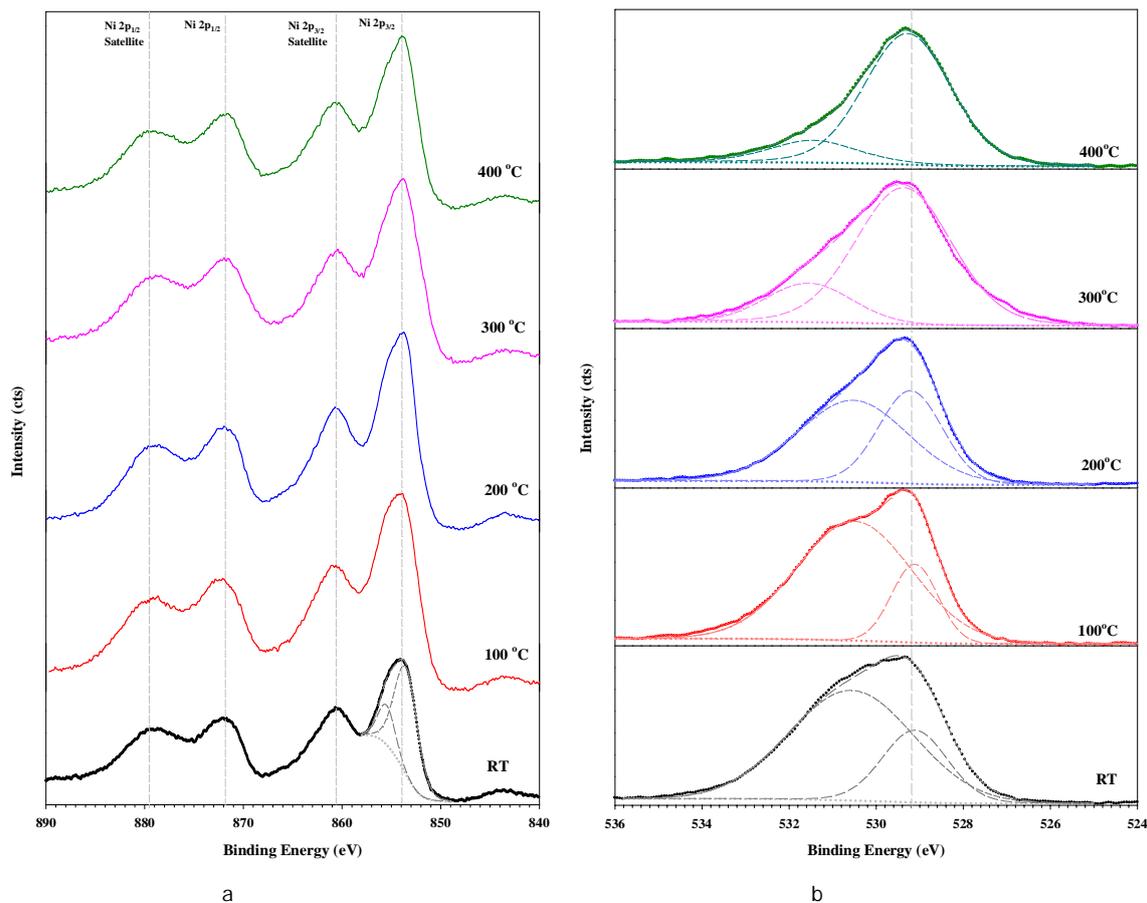


Fig. 2 – The XPS spectra of the (a) Ni 2*p* and (b) O 1*s* for different substrate temperatures

some amount of Ni<sup>3+</sup> ions so the Ni 2*p*<sub>3/2</sub> peak fitted two peaks located at nearly 853.5 eV and 855.5 eV for Ni<sup>2+</sup> and Ni<sup>3+</sup>, respectively. Although the fitted peaks do not give exactly the peak values but analyze which part of the spectra having larger influence. As the substrate's temperature increases, the fraction of Ni<sup>2+</sup> state increases with respect to Ni<sup>3+</sup> in the films due to excess Oxygen. This was also supported by the O 1*s* XPS spectra of the NiO thin film deposited at different substrate temperatures as shown in Fig. 2b. The O 1*s* spectra also got fitted in two peaks, the higher binding energy peak at nearly 529.2 eV is due to the Ni<sup>2+</sup> and the lower binding energy peak is due to the Ni<sup>3+</sup>. The excess Oxygen in the NiO film produces the Ni<sup>2+</sup> vacancies and some of the Ni<sup>2+</sup> ions are oxidized to Ni<sup>3+</sup> ions to keep the overall charge neutral [15].

### 3.3 Optical Properties

The optical transmittance spectra of NiO thin films deposited on glass substrates at different substrate temperatures are presented in Fig. 3. It can be seen that the film prepared at RT, which exhibits a light brown color, has ~ 50 % transmittance. The increase in substrate temperature of the films causes an increase in the transmittance. The lower transmittance is associated with an excess of oxygen in the lattice, which creates Ni<sup>3+</sup> ions and the formation of color centers. This is also supported by our XPS data: an increase in transmittance with substrate temperature

is due to the less defect-scattering (Ni<sup>3+</sup>) and improvement of crystalline microstructure of the films.

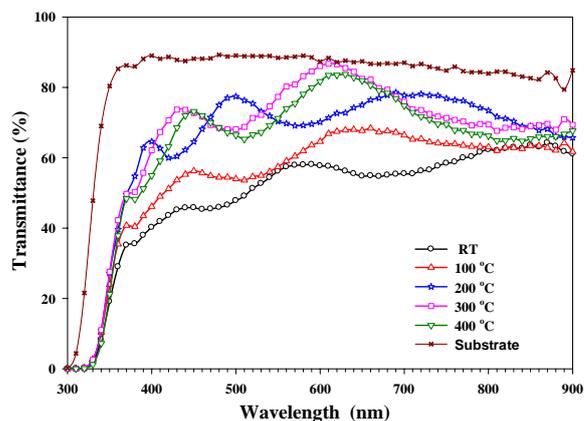


Fig. 3 – The transmittance spectra for NiO thin films deposited at different substrate temperatures

Strong absorption in the UV region is observed at wavelength ~ 325 nm, due to the fundamental absorption edge of NiO.

### 3.4 Electrochromic Properties

The coloration and bleaching in NiO thin film is due to the transition between Ni<sup>2+</sup> and Ni<sup>3+</sup>, which in turn is associated with insertion and de-insertion of OH<sup>-</sup> ions and electrons in the film. To evaluate the EC

behavior of NiO thin films cyclic voltammetry measurements were recorded in 1M KOH electrolyte at different scan rates of 10-50 mV/s as shown in Fig. 4. 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, due to a couple of redox processes taking place in NiO thin film [16]. Usually the redox processes are caused by the transition between NiO,  $\text{Ni}(\text{OH})_2$ ,  $\text{NiOOH}$ , or  $\text{Ni}_2\text{O}_3$ .

From Fig. 4 it is seen that the anodic peak current density ( $j_{pa}$ ) and the cathodic peak current density ( $j_{pc}$ ) increases with the scan rate according to Randles-

Servcik equation, which is further used to estimate the diffusion coefficient of ions in the NiO films.

$$j_p = 2.72 \times 10^5 \times n^3 \times D^{\frac{1}{2}} \times C_0 \times v^{\frac{1}{2}} \quad (6)$$

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  $\text{Acm}^{-2}$ , which is obtained from the CV measurement, and  $n$  is the number of electrons involved in the reaction. The peak current density and the diffusion coefficient at different substrate temperatures for 20 mV/s scan rate are shown in Tabl. 1.

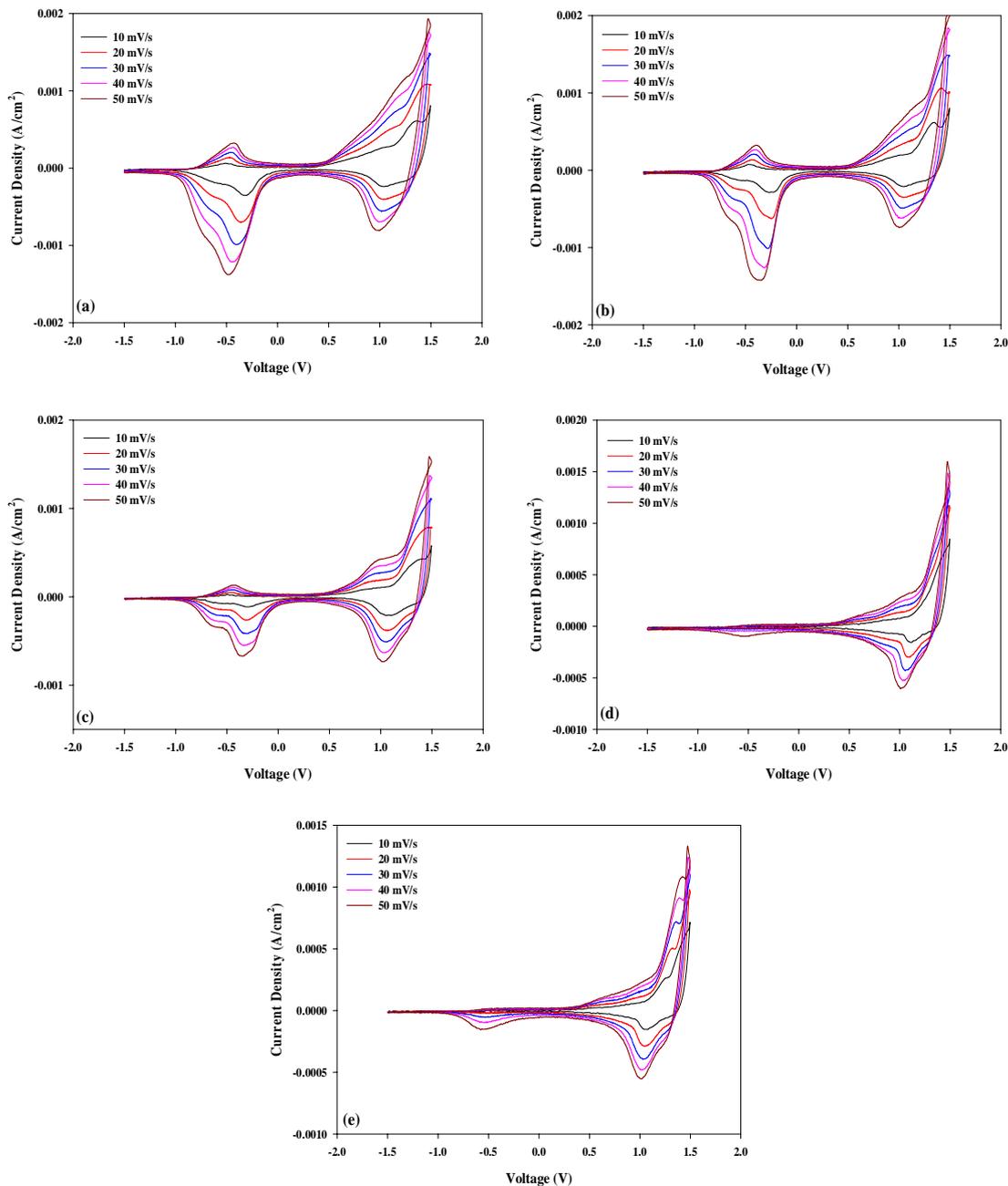


Fig. 4 – Cyclic voltammogram for NiO thin film grown at (a) RT (b) 100 °C (c) 200 °C (d) 300 °C and (e) 400 °C substrate temperature recorded at different scan rates

Table 1 – Electrochemical parameters anodic peak current density ( $j_{pa}$ ), cathodic peak current density ( $j_{pc}$ ), and diffusion coefficients ( $D$ ) of NiO thin films grown at different substrate temperatures in 1M KOH electrolyte at the scan rate 20 mV/s

Substrate Temperature (°C)	Anodic current density $j_{pa}$ (A)	Cathodic current density $j_{pc}$ (A)	Diffusion coefficient $D$ (cm <sup>2</sup> /s)	
			$D$ for $j_{pa}$	$D$ for $j_{pc}$
RT	$7.6846 \times 10^{-4}$	$5.6924 \times 10^{-4}$	$4.0896 \times 10^{-10}$	$2.2440 \times 10^{-10}$
100	$1.2056 \times 10^{-3}$	$6.4165 \times 10^{-4}$	$10.06 \times 10^{-10}$	$2.8512 \times 10^{-10}$
200	$1.0467 \times 10^{-3}$	$5.4237 \times 10^{-4}$	$7.5872 \times 10^{-10}$	$2.0372 \times 10^{-10}$
300	$1.0075 \times 10^{-3}$	$4.9357 \times 10^{-4}$	$7.0295 \times 10^{-10}$	$1.6871 \times 10^{-10}$
400	$9.0072 \times 10^{-4}$	$3.8830 \times 10^{-4}$	$5.6184 \times 10^{-10}$	$1.0442 \times 10^{-10}$

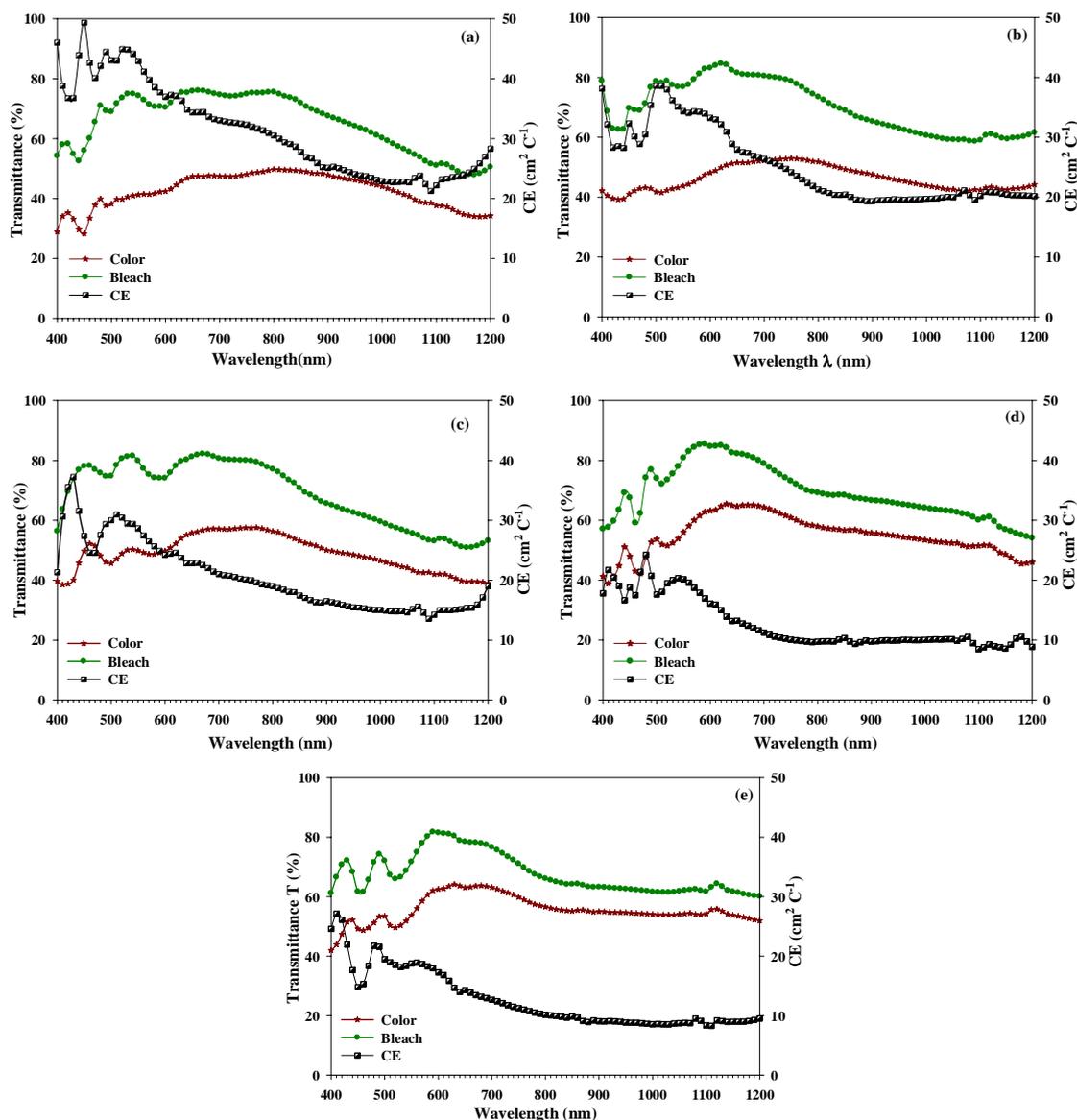


Fig. 5 – The transmittance spectra in the color and bleach state and the ce of nio thin films grown at different (a) RT, (b) 100 °C, (c) 200 °C, (d) 300 °C, and (e) 400 °C substrate temperatures

The current densities at the anodic and cathodic peaks decrease with increase in substrate temperature, i.e., the diffusion of ions in the film decreases. At the higher substrate temperature, the crystallinity of the NiO thin films increases and thus the space between crystallites decrease, which makes it difficult for the ion intercalation or de-intercalation and leads to a decrease in the diffusion coefficient.

In the measurement of transmittance modulation ( $\Delta T$ ) and coloration efficiency, the transmittance spec-

tra of the samples for both colored and bleached states were recorded in the wavelength range of 400-1200 nm at RT. Coloration and bleaching processes were carried out at a constant current density of 0.2 mA/cm<sup>2</sup> applied for 25 s. The coloration efficiency and changes in the optical density, ( $\Delta OD$ ), with the charge density ( $Q$ ) per unit area at certain wavelength ( $\lambda$ ) is shown in the equation below:

$$CE(\lambda) = \frac{\Delta OD(\lambda)}{Q} = \frac{\log(T_b/T_c)}{q/A} \quad (7)$$

where,  $\Delta OD$  is the change in the optical density,  $Q$  is the charge injected per unit electrode area of the thin film, and  $T_b$  and  $T_c$  are the transmittance in the bleached and the colored state, respectively.

Fig. 5 shows the spectral transmittance of the NiO thin films deposited at different substrate temperatures in the colored and bleached states. It is seen that the variation in the colored and the bleached state decreases with increase in substrate temperature. The films deposited at RT and 100 °C substrate temperature show the highest variation in the colored and the bleached states. The transmittance modulation ( $\Delta T$ ) and CE at 650 nm and 1000 nm wavelengths for NiO thin films, grown at different substrate temperatures, are summarized in Table 2 for comparison.

The CE and  $\Delta T$  decreases with increase in substrate temperature for a given wavelength. It is believed that the higher substrate temperature is favorable to the formation of compact crystalline nickel oxide films. The EC process is associated with the double injection

(extraction) of ions and electrons to (and from) the film. At the lower substrate temperature the crystalline size are small and the spacing between the crystals are large enough for ion intercalation. However, with the increase in the substrate temperature the crystalline structure of the sample improves and thus the spacing between crystallites decreases, which is unfavorable for the ion intercalation or de-intercalation [17].

The EC switching time ( $t$ ) of NiO thin film was determined using chronoamperometry measurement with concurrently measuring the transmittance at ~ 650 nm wavelength by applying square wave potential of  $\pm 1.5$  V and frequency 0.05 Hz. Fig. 6 shows the response of optical power and current density with time during pulse potential for the NiO thin films deposited at different substrate temperatures.

The switching time, at 650 nm wavelength, is estimated from Fig. 6, for the NiO thin films grown at different substrate temperatures and presented in Tabl. 3.

The coloration and bleaching process is associated by the ion intercalation / deintercalation and thus the composition of the films. The films grown at 100 °C to 200 °C substrate temperature show low bleaching time,

Table 2 – The transmittance modulation and CE for NiO thin films grown at different substrate temperatures

Substrate temperature, $T_s$ (°C)	Transmittance modulation, $\Delta T$ (%)		Coloration efficiency, CE ( $\text{cm}^2 \text{C}^{-1}$ )	
	$\lambda = 650$ nm	$\lambda = 1000$ nm	$\lambda = 650$ nm	$\lambda = 1000$ nm
RT	29	16	34.5	22.8
100	30	17	27.9	19.7
200	25	13	22.8	15.1
300	18	11	13.2	10.0
400	15	8	14.3	8.6

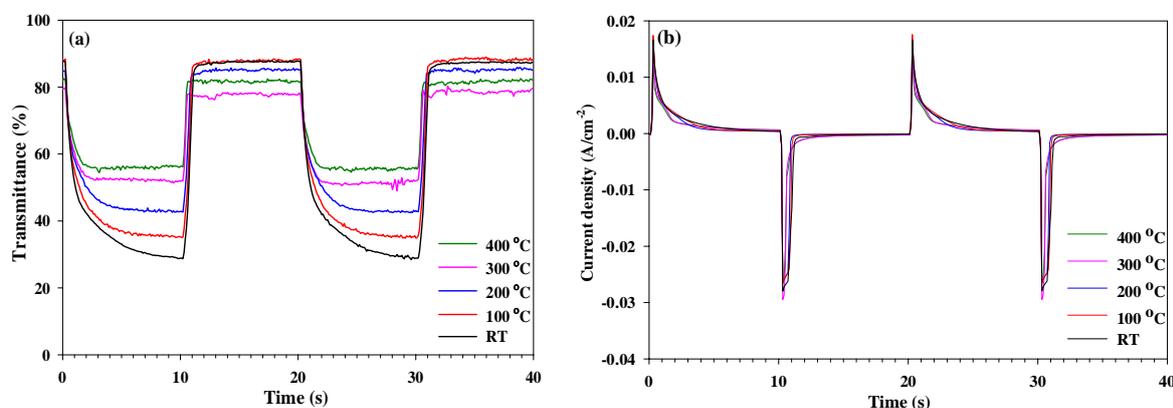


Fig. 6 – The variation in the optical transmittance at 650 nm (a) and the current density for NiO the thin films, grown at different substrate temperature (b), when the electrochemical cell is subjected to a square-wave potential of  $\pm 1.5$  V and frequency 0.05 Hz is applied

Table 3 – Switching time data of NiO thin films for different substrate temperature at 650 nm

Substrate temperature ( $T_s$ ), °C	Bleaching time ( $t_b$ ), s	Coloration time ( $t_c$ ), s
RT	2	10
100	1.5	10
200	1.5	10
300	3	10
400	3	10

1.5 s, and as the substrate temperature increases the bleaching time increases up to 3 s for films grown at 400 °C. The increase in bleaching time due to crystallization or improvement in composition. The coloration switching time is directly affected by several factors such as applied potential, crystal structural, or the time for all the samples is same as ~ 10 s. The response time during the coloring process was higher than that during the bleaching process, due to differences in conductivity between  $\text{Ni(OH)}_2$  and  $\text{NiOOH}$ . The conductivity of  $\text{Ni(OH)}_2$  was lower than that of the  $\text{NiOOH}$ .

Therefore, it would be expected that the coloring process, which involves the transition of  $\text{Ni}(\text{OH})_2$  to  $\text{NiOOH}$ , is slower than the bleaching process, which results in the transition of  $\text{NiOOH}$  to  $\text{Ni}(\text{OH})_2$ .

#### 4. CONCLUSION

$\text{NiO}$  anodic EC thin films are prepared by the e-beam evaporation technique at different substrate temperatures. From the GIXRD measurement, we find that the preferred orientation changes from (111) to (200) direction with increase in substrate temperature. The XPS spectra results show improvement in the composition, which was also confirmed by the optical data i.e. the transmittance of  $\text{NiO}$  thin film increases with substrate temperature. The EC result shows that the films prepared between RT to  $100^\circ\text{C}$  give good electrochromic performance compared to films grown at higher substrate temperatures. In general, the electrochromic characteristics can be related to the

microstructure of the films and one of the key parameter to control the structures of the film is substrate temperature. During the deposition of the  $\text{NiO}$  thin film, when the substrate is heated the particles deposited at the surface of the substrate will have enough kinetic energy to migrate on surface and grow larger grain and compact structure. The space between  $\text{NiO}$  crystallites becomes smaller, which make it more difficult for ions to be injected or extracted from the films. Therefore, a higher substrate temperature ( $> 100^\circ\text{C}$ ) reduces the EC performance of the films.

#### ACKNOWLEDGEMENTS

A part of this work was performed at UGC-DAE Consortium for Scientific Research, Indore, India.

This work was done in joint Ukraine-India scientific-technological project №M/47-2013.

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