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## **Electrochromic Nickel Oxide Thin Films for Solar Light Modulation**

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### **Abstract**

Nickel oxide (NiO<sub>x</sub>) thin films were prepared by three different deposition techniques: electrochemical (EC) deposition, low vacuum evaporation (LVE), and chemical bath deposition (CBD). Those films were deposited onto fluorine doped tin oxide (FTO) coated glass substrates. Electrochromic behavior of the films was examined in an electrochromic device (ECD) constructed by using NiO<sub>x</sub> films as working electrodes, together with the FTO coated glass as a counter electrode in alkaline environment (0.1 M NaOH aqueous solution). The films exhibited anodic electrochromism, changing color from transparent to dark brown. Visible transmittance spectra of the nickel oxide thin films in bleached and colored states were recorded in-situ. Absorption coefficients spectra were calculated using the transmittance spectra. The output integral of the spectral intensity and the integral of the spectral modulation were calculated by taking the solar irradiance spectrum AM 1.5 for a normal illumination on a nickel oxide – based ECD, and the absorption coefficients spectra of the nickel oxide films in their bleached and colored states.

**Keywords:** Electrochromism; Nickel oxide; Thin films; Solar light modulation.

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## **1. Introduction**

The industrial and technological development in the twentieth century caused the increase in emissions and heat, thus increased the temperature of the Earth's climate. Global warming due to the increase of carbon dioxide emission was one of the major problems that appeared and threatened our environment in many aspects. The increase in temperature of the Earth's climate led to a negative impact on energy consumption. There is no doubt that one of the biggest challenges of the present century throughout the world is environment protection. In order to protect our environment, we have to reduce our energy consumption. Buildings, consuming more than one third of the overall energy worldwide, have more impact on environment than industry and transportation. This is the reason why, the energy consumption reduction in the buildings is a big challenge for every country in the world, especially countries with large climate and temperature variations.

Over the last years buildings design has been oriented toward the energy usage, the protection of the environment and the occupants' comfort [1]. On the other hand, modern urban architecture involves the construction of large buildings with a big percentage of glazed areas. Glass is ubiquitous in buildings because of the positive impact that natural daylight and the connection with outdoors have on people's health and well-being. Despite these desirable benefits, windows are also the greatest cause of thermal and visual discomfort in buildings. Since glazing constitutes one of the less energy efficient components of the building envelope, the window choice has a huge impact on the reduction of building energy consumption. The control of incident solar radiation through the windows is a key element for the achievement of indoor comfort and more generally of greater energy efficiency in buildings.

The increasing attention to issues of visual comfort and energy efficiency that characterized the architecture of the twenty first century led to the development of innovative dynamic glazing technologies, aimed not only at reducing heat loss, but also at controlling incoming solar radiation, in order to maximize the solar gain in winter and minimize it in summer, as well as ensuring the best natural lightening conditions with no glare [2]. Among these technologies is electrochromic glazing (smart windows), that manage solar radiation flux entering buildings by controlling the glazing opacity [3]. In this manner, smart windows offer increased thermal and visual comfort, daylight control and energy savings without loss of view. With an electrochromic glazing, architects can for the first time design larger areas of glass into the building envelope to capitalize on the beneficial aspects of the sun while at the same time minimizing its negative effects [4].

Special materials with electrochromic properties play crucial role in smart windows. The term electrochromic describes materials that can change their color between colored and transparent states, or between two colored states, by applying a small voltage. The classification of the electrochromic materials is related to the potential at which the coloration process occurs. Materials with anodic coloration exhibit coloration at positive potential, i.e. they darken upon charge extraction (oxidation). Cathodic materials, on the other hand, exhibit coloration at negative potential, i.e. they darken upon charge insertion (reduction). When thin films of such materials are integrated in devices, it becomes possible to vary the parameters of transmission, absorption and reflection of solar radiation between widely separated extremes [5-7]. A standard electrochromic design consists of a substrate coated with transparent conductor, an electrochromic coating, an electrolyte and a counter electrode. A

voltage applied between the transparent conductors causes the ions from the electrolyte to be injected into the electrochromic film (cathodic material), or extracted from the electrochromic film into the electrolyte (anodic material). At the same time the electrons are injected into the electrochromic film from the transparent conductor (cathodic material), or extracted from the electrochromic film into the transparent conductor (anodic material). The electrons are needed to preserve charge neutrality. Reversing the voltage polarity brings back the original properties [8].

The electrochromic material is optically active material in the electrochromic device. It is deposited in a form of thin film on the top of the transparent conductor. Electrochromism is known to exist in many types of materials, both organic and inorganic. Among them, transition metal oxides have attractive technological importance for electrochromic applications because they show considerable variations in stoichiometry, and can be quite easily deposited in a form of thin film, which is appropriate for device manufacturing.

Nickel oxide is very promising as an active electrochromic material. It is among least expensive materials and can be easily fabricated. Upon applying a small voltage, the transparent nickel oxide transforms into a dark brown nickel oxide, otherwise known as a bleached and colored state respectively. It is generally accepted that the cause of this coloration is due to the oxidation of Ni(II) to Ni(III) in alkaline media, which means that nickel oxide is anodic electrochromic material [9, 10]. Electrochromic NiO<sub>x</sub> films have been previously prepared by a variety of different techniques including electrodeposition [10], chemical vapor deposition [11], sol-gel [12], sputtering [13], spray pyrolysis [14], etc. The electrochromic properties of NiO<sub>x</sub> thin films strongly depend on their structural, morphological and compositional characteristics [5], which, in turn, depend directly on the deposition technique and deposition conditions. The aim of this work is to investigate the possibilities for solar light modulation using nickel oxide thin film, prepared by three different techniques. Our intention was to obtain films with thickness of about 100nm.

## **2. Materials and methods**

Techniques employed for preparation of the nickel oxide thin films were: electrochemical (EC) deposition, low vacuum evaporation (LVE), and chemical bath deposition (CBD). The films were deposited onto fluorine doped tin oxide (FTO) coated glass substrates with transparency of about 80% for visible light, and sheet resistance of about 10 – 20 Ω/□. Before the deposition, the substrates were degreased by ultrasonic treatment in acetone and ethanol in turn, and then rinsed in deionized water and dried in air.

### ***2.1. Electrochemical deposition***

Electrochemical deposition was performed in a 0.01 M ammonia complex solution of NiSO<sub>4</sub>. The conducting substrates used for deposition were FTO coated glass substrates, and a nickel foil was employed as a counter electrode [15]. The films were deposited at room temperature using a current density of 1 mA/cm<sup>2</sup> for 20 min. Deposited films were rinsed with distilled water, dried, and then heat treated at 200<sup>0</sup> C in the air, for 20 min.

### ***2.2. Low vacuum evaporation***

Nickel oxide films were deposited on the substrates by thermal evaporation of pure Ni/metal from a tungsten boat [16]. During the evaporation, the substrate temperature changed from room temperature up to values of about 100<sup>0</sup> C. The evaporation pressure was 0.2 Pa and the deposition rate was 3 nm/s.

### **2.3. Chemical bath deposition**

The chemical bath deposition was carried out in an aqueous solution containing 1 g Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and 3 g carbamide in 80 ml deionized water [17]. FTO coated glass substrates were immersed into the solution which temperature was adjusted and kept at 95<sup>0</sup> C. After 15 min, the substrates with deposited films were taken out, rinsed with distilledwater and dried in air.

### **2.4. Characterization**

For practical electrochromic investigations, an electrochromic device was constructed [16-18]. It consisted of a home built glass cuvette with a 0.1 M NaOH aqueous solution as an electrolyte, in which two electrodes were immersed. The working electrode represented the nickel oxide thin film onto FTO coated glass substrate, whereas counter electrode was a blank FTO coated glass substrate. The distance between the electrodes was about 1.5 cm, and the volume of the electrolyte was 20 ml. The active surface area of the electrodes was approximately 6 cm<sup>2</sup>. In order to determine optical properties of the obtained films spectro-electrochemical techniques were used. The visible transmittance spectra were recorded in-situ using Varian CARY 50 Scan UV-Visible spectrophotometer, in the wavelength range from 300 to 800 nm in both, the completely bleached and colored states of the films. The measurement of the relative transparency spectra was done by accuracy of 0.001 or 0.1%, while the accuracy of the light wavelength was 0.1 nm. The bleaching and the coloring of the films were performed with applied voltages of -2 V and +2 V respectively. A transparent glass cuvette with two clean FTO coated glass substrates, filled with electrolyte, was measured as 100 % background.

From the transmittance data ( $T$ ), and the film thickness ( $t$ ), the absorption coefficients spectra, in the bleached and colored states of the films, were calculated using the equation:

$$\alpha(\lambda) = \frac{1}{t} \ln \frac{1}{T(\lambda)} \quad (1)$$

The spectral intensity of the transmitted (modulated) solar irradiance through the films was calculated by the equation:

$$I(\lambda) = I_0(\lambda) e^{-\alpha(\lambda)t} \quad (2)$$

where  $I_0(\lambda)$  is the spectral intensity of the incident irradiation. The AM 1.5 solar irradiance spectrum [19] was used as reference. The AM 1.5 spectra represents terrestrial solar spectral irradiance on a receiving surface defined in the standards as an inclined plane at a 37<sup>0</sup> tilt toward the equator, facing the sun. These distributions of power (Watts per square meter per nanometer of bandwidth) as a function of wavelength provide a single

common reference for evaluating spectrally selective materials.

The calculated output spectral intensities within the visible region, transmitted across the nickel oxide thin films in their bleached and colored states, were numerically integrated. The relative change of the integrated intensity (the visible transmitted intensity and the light modulation) can be calculated [20] by the equation:

$$M = \frac{I_{tb} - I_{tc}}{I_{tb}} \quad (3)$$

where  $I_{tb}$  and  $I_{tc}$  are integrated transmitted intensities of the films in their bleached and colored states respectively, and  $M$  is the integrated intensity modulation of the solar illumination.

### 3. Results and discussion

Nickel oxide thin films prepared by all three techniques employed in this work, revealed electrochromic behavior changing color from transparent to dark brown [21]. They could be repeatedly colored and bleached with alternative application of positive and negative potential respectively, versus counter electrode.

Electrochemically deposited films were heat treated at 200<sup>o</sup> C in the air for 20 min. After the heat treatment, the films became completely transparent and they had to be activated by a few color-bleach cycles in NaOH aqueous solution to obtain complete coloration. This necessity of activation may be due to loss of adsorbed water [22] since the films become NiO which need to be activated, i.e. to be turned into nickel hydroxide. After the activation, the films exhibited electrochromic behavior.

Low vacuum evaporated films were deposited in partly colored state. By single application of cathodic bias in the NaOH aqueous solution, the films became completely transparent and revealed electrochromic behavior.

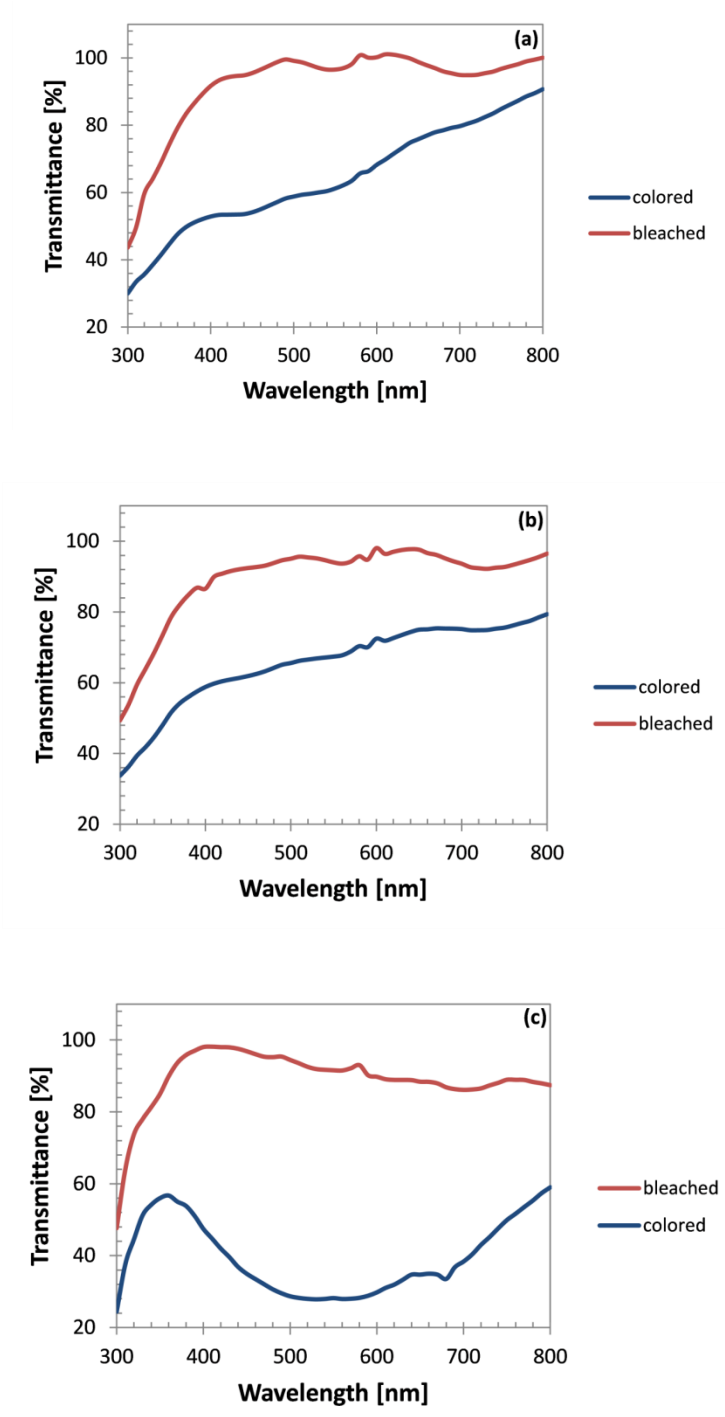
The films prepared by chemical bath deposition were obtained in completely transparent state and didn't need any activation.

The x-ray diffraction (XRD) patterns of the NiO<sub>x</sub> films showed amorphous structure for the EC and LVE prepared films [15- 17]. On the other hand, the films prepared by CBD had crystal structure.

The transmission spectra in the wavelength range from 300 to 800 nm, for the EC (a), LVE (b) and CBD (c) prepared films in their bleached and colored states are presented in Fig. 1. As can be seen, the maximum transmittance change (of about 31% for LVE, 42% for EC, and 66% for CBD prepared films) between bleached and colored states occurs at 490 nm.

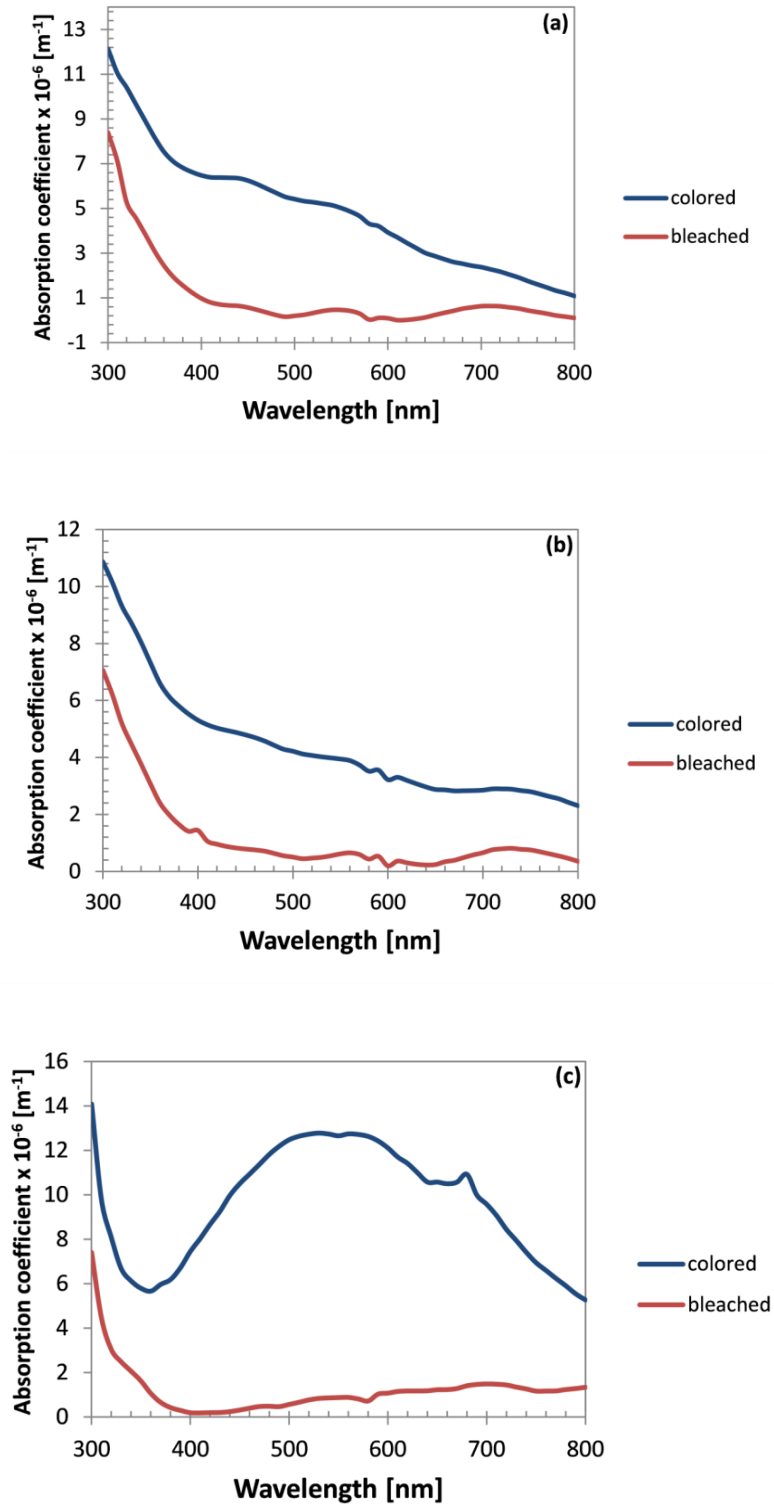
Figure 2 shows absorption coefficient spectra calculated from the equation (1) for the EC (a), LVE (b) and CBD (c) prepared films in their bleached and colored states. These spectra were taken as input parameters together with the AM 1.5 irradiance solar spectrum. The output intensities transmitted across the nickel oxide thin films, in the bleached and colored states, were calculated and presented in Fig. 3. The results of the numerical

integration for the spectral intensity within the visible region (300 – 800 nm), and the integrated intensity modulation of the solar illumination  $M$  in the same wavelength region are presented in the Table 1.



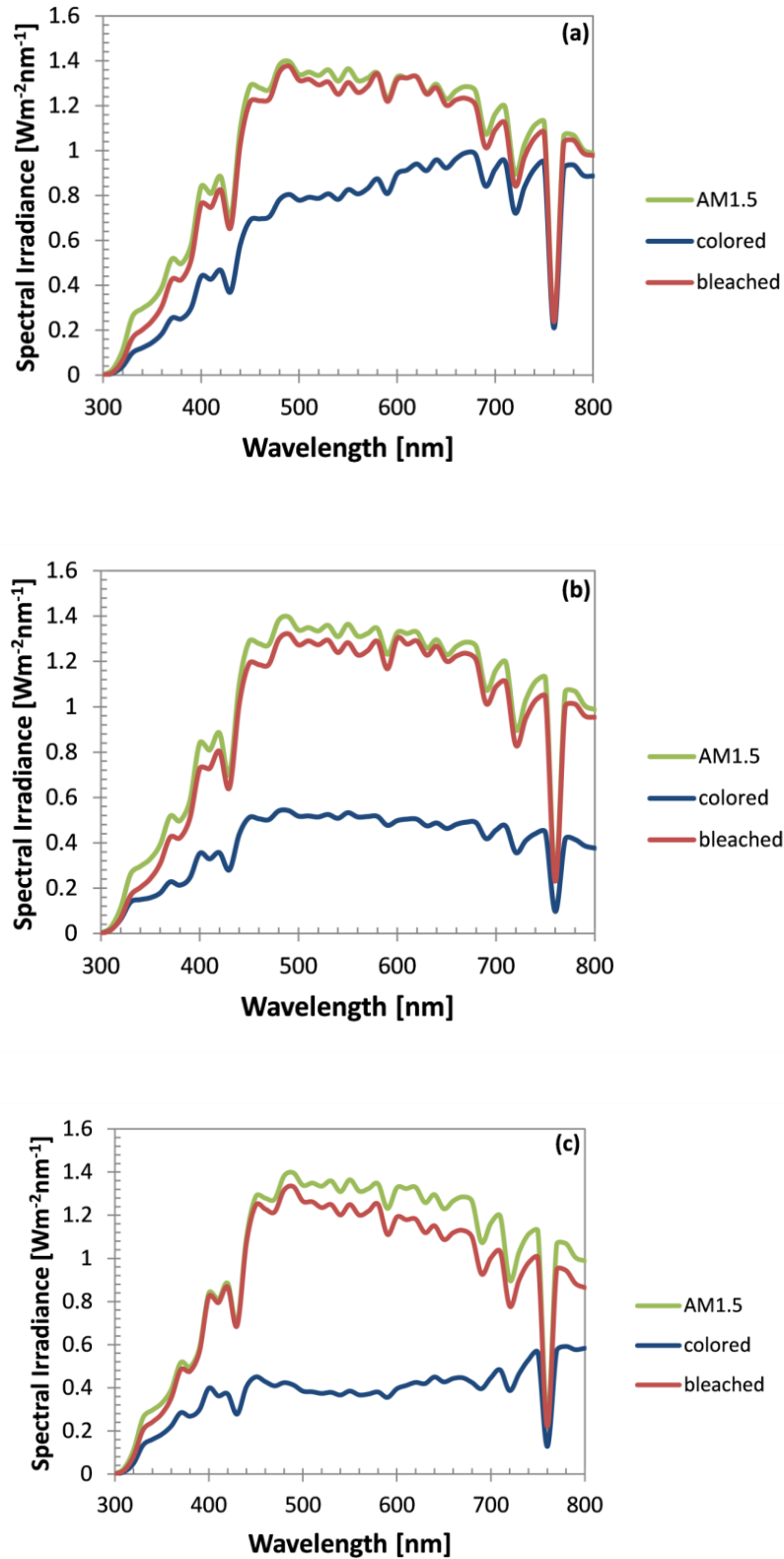
**Figure 1:** In-situ visible transmittance spectra of nickel oxide thin films prepared by: (a) electrochemical deposition, (b) low vacuum evaporation, and (c) chemical bath deposition techniques,

in their bleached and colored states



**Figure 2:** Absorption coefficient spectra of the 100 nm thick colored and bleached  $\text{NiO}_x$  films prepared by:

(a) electrochemical deposition, (b) low vacuum evaporation, and (c) chemical bath deposition techniques



**Figure 3:** Spectral intensity of the transmitted AM 1.5 solar irradiance spectrum through the  $\text{NiO}_x$  films prepared by: (a) electrochemical deposition, (b) low vacuum evaporation, and (c) chemical bath deposition techniques, in their colored and bleached states



**Table 1:** Numerical Integral of the transmitted intensity from 300 to 800 nm through the NiO<sub>x</sub> films prepared by different techniques in their bleached and colored states, and integrated intensity modulation of solar radiation calculated by the equation (3)

Technique	$I_{tb}$ (W/m <sup>2</sup> )	$I_{tc}$ (W/m <sup>2</sup> )	$M$ (%)
EC	485.12	339.45	30
LVE	474.98	199.72	58
CBD	462.82	188.57	59

As can be seen from the Table 1, NiO<sub>x</sub> thin films prepared by different techniques, in the same conditions, revealed different integrated intensity modulation of solar radiation in the visible range. The integrated intensity modulation of the solar illumination of about 60 % obtained with the films prepared by low vacuum evaporation and chemical bath deposition is a considerable value, which gives opportunity for implementation of these films in electrochromic devices such as the “smart windows”. On the other hand, the value of the integrated intensity modulation of the solar illumination obtained with the film prepared by electrochemical deposition was about twice lower. This result could be ascribed to lower optical transmittance difference in the red region (Fig. 1a). Another reason could be lower coloration efficiency of the EC prepared films (18.7 cm<sup>2</sup> C<sup>-1</sup>) compared to films prepared with LVE (32.4 cm<sup>2</sup> C<sup>-1</sup>), and CBD (40.6 cm<sup>2</sup> C<sup>-1</sup>) method.

#### 4. Conclusions

Nickel oxide thin films investigated in this work were deposited onto FTO coated glass substrates by three different techniques: electrochemical deposition, low vacuum evaporation, and chemical bath deposition. All obtained films exhibited electrochromism, changing color from transparent to dark brown, and can be used for solar light modulation. Maximum transmittance change of about 31%, 42%, and 66% was obtained at 490 nm for LVE, EC, and CBD prepared films respectively. The maximum light intensity modulation ability of the films, as the AM 1.5 spectrum is taken for an input, was calculated to be about 30% for EC deposited films, while the maximum light intensity modulation abilities of the films prepared by LVE and CBD technique were calculated to be about 58% and 59% respectively. These considerable values make NiO<sub>x</sub> thin films suitable for application in electrochromic devices.

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