Synthesis and Characteristics of Electrochromic Glass with Multi-Layer Configuration Based on glass/ITO/WO₃/ZrO₂/NiO/ITO/glass

In the present work, three transition metal oxides; tungsten trioxide (WO₃), zirconium dioxide (ZrO₂) and nickel oxide (NiO) were prepared as thin films. Spray pyrolysis and magnetron sputtering techniques were employed to deposit these thin films on indium-doped tin oxide (ITO) coated glass substrates. The prepared samples were characterized by x-ray diffraction, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and UV-visible spectroscopy. The smart window (device) with the configuration: glass/ITO/WO₃/ZrO₂/NiO/ITO/glass was fabricated and characterized by UV-visible spectroscopy. This device was tested by applying ±5 V and high optical transmittance modulation at about 30.93% was observed.

Keywords: Electrochromic material; Smart window; Thin films; Metal oxides

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1. Introduction

Electrochromism is defined as a reversible change in the color and optical properties of chromic material caused by applying an electric field [1]. These changes are due to an oxidation-reduction process [2]. Electrochromic devices (ECD) have great impact on the scientific and commercial applications due to their optical properties, such as controllable transmission, absorption, and/or reflectance [3]. The ECD structure may have five layers (transparent conducting oxide layer/ion-storage layer/solid electrolyte/electrochromic layer/transparent conducting oxide layer) composed on one substrate or may be positioned between two substrates in the laminate configuration [4], as illustrated in Fig. (1).

![Fig. (1) Scheme diagram of the electrochromic device (ECD) structure](image)

The ECD has two sides: one side is a tungsten oxide layer, which represents an ion-conducting layer and colored cathodically [5] and another side is a nickel oxide layer, which represents an ion-storage layer and colored anodically [6]. In the ECD structure, both layers are colored and bleached with each other, thus the optical modulation increases. Zirconium oxide (ZrO₂) thin film is used as a solid electrolyte “proton (H⁺) conducting” and an indium tin oxide (ITO) is used as a transparent conducting electrode [7]. During the EC coloration and bleaching processes, the following electrochemical reactions occur in WO₃ and NiO layers [8]:

\[
\text{WO}_3\text{(trans.)} + x\text{M}^+ + xe^- \leftrightarrow \text{MxWO}_3\text{(blue)}
\]

\[
\text{NiOOH (black-brown)} + \text{H}^+ + e^- \leftrightarrow \text{Ni(OH)}_2\text{(trans.)}
\]

Various techniques, such as thermal evaporation, electron beam evaporation, anodic oxidation, chemical vapor deposition, atomic layer epitaxy, spray pyrolysis, sol-gel, and magnetron sputtering, have been adopted for the deposition of the different thin film layers for the ECD structures [9-13].

In the present study, WO₃ and ZrO₂ were prepared using the spray pyrolysis technique while NiO was prepared using reactive magnetron sputtering technique. All prepared thin films are characterized for their structural and optical properties. A smart window (device) with the configuration “glass/ITO/WO₃/ZrO₂/NiO/ITO/glass” was fabricated and tested.

2. Experimental Part

Tungsten oxide thin films were prepared using a homemade spray pyrolysis system consisting of a spray nozzle, heater, thermocouple, spray controller unit, and air compressor. The precursor solution consists of tungsten metal powder (purity 99.9%) and hydrogen peroxide 30%, and the concentration of the solution was 0.1M. After 4 hours, the tungsten was completely melted then, the solution was heated by a hot plate at 100°C for 80 min until its color was changed. After that, it was left to cool for 1 hour at room temperature. Then, it was diluted by adding ethanol with 1:4 volume ratio followed by stirring for 2 days at room temperature. The final result was a pale yellow solution. The precursor solution was sprayed through the nozzle on a hot
ITO glass substrate at temperature of 200°C at spray rate of 1 mL/min and deposition time of 40 min.

Zirconium oxide thin films were also prepared by the spray pyrolysis system. The precursor solution consists of zirconium tetra chlorate (ZrCl₄) (purity 99.9%) dissolved in 38mL of distilled water and 2mL of absolute ethanol (for low surface tension and viscosity), and the concentration of the solution was 0.05M. The precursor solution was sprayed through the nozzle on a hot ITO glass substrate at temperature of 250°C with spray rate of 0.4mL/min and deposition time of 90 min.

A closed-field unbalanced d.c reactive magnetron sputtering system was used to deposit nickel oxide thin films. A pure nickel (99.9%) sheet of 0.3mm thickness and 80mm diameter was maintained on the cathode as the target to be sputtered while the ITO-coated glass substrates were placed on the anode. The plasma column was produced by glow discharge of argon gas at pressure of 0.5mbar, discharge current of 40mA, discharge voltage of 290V and vacuum pressure of 0.09mbar. The mixing ration of oxygen and argon gases was optimized to be 50:50 with a deposition time of 4 hours.

The NiO and ZrO₂ thin films were sequentially deposited on the ITO-coated substrates. The H⁺ ions were injected into the NiO film via the ZrO₂/NiO/ITO film structure by cycling it electrochemically in 0.1M KOH electrolyte. After removing the film from the KOH electrolyte, it was washed with distilled water to get rid of KOH and dried using dry air. The WO₃ thin film was deposited on another ITO-coated substrate. Finally, the two substrates were collected to produce a sandwich-type electrochromic device, as illustrated in Fig. (2).

The FTIR spectrum of the prepared WO₃ thin film sample is illustrated in Fig. (4a). The structural characteristics of forming WO₃ can be observed through the broad absorption band from 400 to 1000 cm⁻¹ that involves a peak at 584.39 cm⁻¹, which is due to O=W=O stretching modes and the peaks at 769.54 and 819.69 cm⁻¹ are due to W-O=W stretching modes, while the peak at 983 cm⁻¹ is due to W-O stretching vibration mode. The broadband is centered at 3434.98 cm⁻¹ and assigned to the O-H stretching vibration modes. The observed peaks at 1674.10 and 1614.31 cm⁻¹ are assigned to the W-OH bending vibration modes [19]. The peaks seen at 1083.92, 1467.73, 1512.09 and 1544.88 cm⁻¹ are due to the COO group in the reaction between H₂O and C₃H₆OH [11].

The FTIR spectrum of one of the prepared NiO film sample is illustrated in Fig. (4b). The structural characteristics of NiO can be observed through the broad absorption band from 400 to 500 cm⁻¹ that involves the peaks at around 430.1, 445.53, and 474.46 cm⁻¹ which are due to Ni-O stretching vibrations [20,21]. The broadband indicates the nanocrystalline nature of such oxides. The broadband centered at 3444.63 cm⁻¹ is assigned to the O-H stretching vibration. The observed peak at 1639.38 cm⁻¹ is assigned to the H-O-H bending vibration mode [22,23]. These peaks indicate the presence of water molecules in the prepared sample due to the humidity in room environment.

3. Results and Discussion

The XRD pattern of WO₃ thin film prepared using spray pyrolysis technique at deposition temperature of 200°C is illustrated in Fig. (3a). There are three characteristic peaks at 34.4°, 62.8°, and 72.49°. These peaks are corresponding to the crystal planes (220), (340) and (440), respectively, which are matched with the standard (ICDDPDF No.96-101-0619) [14,15] and indicate the triclinic phase, which was confirmed by determining the positions and the relative intensities of the diffraction peaks and was compared with the ICDPDF card. The crystalline phase of WO₃ was proved as the most efficient in the smart window [16] due to the preparation conditions of WO₃ which are appropriate in the fabrication of smart windows.

The crystallinity of the prepared NiO thin film is illustrated in Fig. (3b). There are more than three characteristic peaks at 37.27°, 43.31°, 62.86°, 75.75°, and 79.25°. These peaks are corresponding to (111), (220), (202), (311) and (222), respectively, which are matched with the standard (ICPDSD, No.73-1519) [17]. From the analysis of positions and relative intensities of the diffracted peaks, the presence of a polycrystalline cubic structure of NiO was confirmed. The XRD pattern shows that no other distinct diffraction peaks belong to pure Ni atoms were detected, as shown in Fig. (3b).

The XRD pattern of ZrO₂ thin film is illustrated in Fig. (3c). In this figure, there are no patterns arising from the crystalline phases and this confirms that the ZrO₂ has an amorphous phase at temperature of 250°C. This behavior is attributed to the low temperature of the glass substrate. While the hump that appeared in the figure is due to the glass substrate. In ECD, ZrO₂ is considered as one of the best electrolytes. In all-solid-state smart windows, amorphous phase is preferred because the grain boundaries in the polycrystalline or crystalline phase will increase the current leakage and this lead to reduce device efficiency [18].
broad absorption bands from 400 to 800 cm\(^{-1}\). These bands are located at 426.24, 443.6 and 493.74 cm\(^{-1}\) related to the stretching vibrations of Zr–O [24], while the bands located at 526.53, 667.32, 711.68 and 769.54 cm\(^{-1}\) are related to the characteristic vibrations of ZrO\(_2\) [25]. The broadband centered at 3431.13 cm\(^{-1}\) is assigned to the O-H stretching vibration. The peak observed at 1627.81 cm\(^{-1}\) is assigned to the H-O-H bending vibration mode [26]. These peaks indicate the presence of water molecules in the prepared sample due to the humidity in room environment.

The FTIR spectrum of the prepared ZrO\(_2\) thin film is illustrated in Fig. (4c). The structural characteristics of ZrO\(_2\) can be observed through the broad absorption bands from 400 to 800 cm\(^{-1}\). These bands are located at 426.24, 443.6 and 493.74 cm\(^{-1}\) related to the stretching vibrations of Zr–O [24], while the bands located at 526.53, 667.32, 711.68 and 769.54 cm\(^{-1}\) are related to the characteristic vibrations of ZrO\(_2\) [25]. The broadband centered at 3431.13 cm\(^{-1}\) is assigned to the O-H stretching vibration. The peak observed at 1627.81 cm\(^{-1}\) is assigned to the H-O-H bending vibration mode [26]. These peaks indicate the presence of water molecules in the prepared sample due to the humidity in room environment.

The SEM images of thin films prepared in this work are illustrated in Fig. (5). The average particle size of the WO\(_3\) is about 47nm (Fig. 5a). The evaporation rate increases by increasing temperature which leads to make some solution droplets in nano-size and dried before deposited on the substrate. By decreasing the droplet size, the particle size decreases.

The SEM image of NiO thin film illustrated in Fig. (5b) shows the formation of large particles, which is attributed to the accumulation of NiO molecules due to the short distance they traverse.
from the cathode to the anode (2cm), where they are deposited. The average particle size of NiO is about 29nm. Such nanoparticle size can be desired as an electrochromic material.

Figure (5) SEM images of thin films prepared in this work (a) WO$_3$, (b) NiO, and (c) ZrO$_2$

The average particle size of ZrO$_2$ thin film shown in Fig. (5c) is about 29nm. There are some cracks that can be seen in the film and they are due to the fast drying caused by the high temperature of the substrate.

The formation of nanostructures in the prepared layers – as confirmed by SEM results – is desired for ECD because the light scattering is inversely proportional to the average particle size and thus the loss of light is reduced. Accordingly, the rate of light trap within the structure of the ECD is drastically increased, which means that the performance of ECD is consequently enhanced.

Figure (6) displays the transmission and absorption spectra of the prepared thin films in the UV and visible regions. The transmittance of WO$_3$ thin film reaches to 88.5% in the range of 576-700nm (visible region), as shown in Fig. (6a). This transmittance is very desired for the electrochromic devices. The absorption spectrum of WO$_3$ thin film shows an absorption edge around 318nm, as shown in Fig (6b). By plotting $(\alpha h\nu)^2$ versus photon energy $(h\nu)$, the energy band gap of the WO$_3$ sample was determined to be 2.85 eV, as illustrated in Fig. (7a).

The transmission spectrum of NiO thin film in Fig. (6a) reaches to 95.3% in the range of 570-
700nm. Such high transmittance can make such films applicable in the electrochromic applications. An exponential behavior of absorbance of NiO thin film is shown in Fig. (6b). This behavior is typical for many semiconductors and can be attributed to the internal electric fields within the crystal and deformation of lattice due to the strain caused by imperfection and inelastic scattering of charge carriers by phonons. The value of optical band gap of NiO is about 3.5 eV, which corresponds to a UV absorption edge, as illustrated in Fig. (7b).

As shown in Fig. (6a), the transmittance of the ZrO$_2$ thin film reaches 50.7% in the spectral range of 647-700nm. An exponential behavior of absorbance is clearly observed and the absorption edge is seen around 317 nm. Therefore, the energy band gap of ZrO$_2$ thin film is about 3.32 eV, as illustrated in Fig. (7c).

Figure (8) presents the optical transmission spectra of the multi-layer electrochromic device (glass/ITO/WO$_3$/ZrO$_2$/NiO/ITO/glass) in the visible region (400-700nm). At 459nm, the transmittance in colored state $T_c$ (applied voltage was +5V) is 53.74% and the transmittance in bleached state $T_b$ (applied voltage was -5V) is 84.67%. Therefore, the optical transmittance modulation ($\Delta T = T_b - T_c$) is 30.93%.

4. Conclusions
In concluding remarks, a multi-layer ECD structure containing three overlaid layers of tungsten oxide, zirconium oxide and nickel oxide between two ITO-coated glass substrates can be successfully prepared by spray pyrolysis and magnetron sputtering techniques. The optical transmittance measurements show that the prepared multi-layer ECD structure exhibits a transmittance difference reaching to 30.93%. Such characteristics encourage using this structure efficiently in electrochromic devices and their applications.

References


