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An investigation on electrochromic properties of $(WO_3)_{1-x}-(Fe_2O_3)_x$ thin films

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Abstract

In this research, the effect of Fe_2O_3 content on the electrochromic properties of WO_3 in thermally evaporated $(WO_3)_{1-x}-(Fe_2O_3)_x$ thin films ($0 \leq x \leq 0.4$) has been studied. The atomic composition of the deposited metal oxides was determined by X-ray photoelectron spectroscopy analysis. The surface morphology of the thin films has been examined by atomic force microscopy. The surface roughness of all the films was measured about 1.3 nm with an average lateral grain size of 30 nm showing a smooth and nanostructured surface. The electrochromic properties of $(WO_3)_{1-x}-(Fe_2O_3)_x$ thin films deposited on ITO/glass substrate were studied in a $LiClO_4$+PC electrolyte by using ultraviolet–visible spectrophotometry. It was shown that increasing the Fe_2O_3 content leads to reduction of the optical density (ΔOD) of the colored films and also leads to increasing the optimum coloring voltage from 4 to 6 V in which ΔOD shows its maximum values, in our experimental conditions. Furthermore, by using this procedure, it is possible to make an electrochromical filter which behaves similar to the colored WO_3 film in the visible region, while it can be nearly transparent for near-infrared wavelengths, in contrast of the pure colored WO_3 film.

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1. Introduction

The electrochromic materials are known as certain materials which can change their optical properties in response to the application of an electric current or potential. This property has been used to produce adjustable electrochromic devices to transmit optical energy selectively [1–3]. Electrochromic devices have potential applications in energy efficient smart windows [4,5], anti-glare mirrors [6], non-emissive displays [7], and recently, hybrid organic/inorganic memory devices [8]. Among the electrochromic materials, tungsten oxide is the most important inorganic matter for electrochromic applications [1,2].

In several works, efforts have been made to change electrochromic properties of WO_3 by mixing it with other metal oxides such as: Ta_2O_5 [9], TiO_2 [10], MoO_3 [11], and V_2O_5 [12]. Another metal oxide that could probably modify the properties of WO_3 is Fe_2O_3. This is because, pure Fe_2O_3 has excellent properties similar to WO_3 [13,14] due to its many valence states which can be easily changed by either heat treatment or potential cycling. Therefore, combination of WO_3 and Fe_2O_3 may result in new electrochromic properties. To the best of our knowledge, the electrochromic properties of combined $(WO_3)_{1-x}-(Fe_2O_3)_x$ thin films has been not reported in the literature, yet.

In this work, we have investigated the effect of Fe_2O_3 content on the electrochromic property of the thermally evaporated $(WO_3)_{1-x}-(Fe_2O_3)_x$ thin films. For each combination, an optimum coloring voltage has been determined. In addition, surface roughness and chemical composition of the deposited films have been studied by AFM and XPS, respectively.

2. Experimental details

Thin films of $(WO_3)_{1-x}-(Fe_2O_3)_x$ with $x=0$, 0.05, 0.3, and 0.4 were deposited on microscope slide glass and indium tin oxide (ITO)-coated glass ($R_s \sim 100\ \Omega/\square$) using thermal evaporation method with a base pressure of $\sim 4 \times 10^{-3}$ Pa. Thickness of the deposited films was considered about 200±50 nm measured by the stylus and optical techniques. More details about the other deposition parameters of the films are recently reported elsewhere [15].

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X-ray photoelectron spectroscopy (XPS) with Al K_α anode was employed to study the atomic composition of the thin films. All binding energy values were determined by calibration the C(1s) line to 285.0 eV. Surface topography of the films was investigated by atomic force microscopy (AFM) at the nanoscale in air with a silicon tip of 10 nm radius in contact method.

To study the electrochromic properties of the thin films, they were deposited on the ITO/glass substrate. Each of the $(WO_3)_{1-x}-(Fe_2O_3)_x$ films, as a working electrode, was electrochemically cycled in a 1 M $LiClO_4$+propylene carbonate (PC) electrolyte in a glass test vessel, along with a bare ITO film as the counter electrode. The optical transmittance of the thin films was studied by an ultraviolet–visible spectrophotometer, in the two separately experiments. In the first one, transmittance was measured as a function of time at a constant wavelength of 500 nm at different coloring voltages, and correspondingly, at negative voltages applied for bleaching the films. In addition, during the electrochromic process, magnitude of the current passing between the two electrodes was recorded. In the second one, the transmittance was measured by the spectrophotometer in a range of 300–1100 nm wavelength for the films colored after a constant time (90 s) at the different coloring voltages.

3. Results and discussion

To understand the surface stoichiometry of the samples, $(WO_3)_{1-x}-(Fe_2O_3)_x$ thin films were studied by XPS analysis. Fig. 1 shows XPS survey scans of the films at the different amounts of x. It can be seen that only tungsten, iron and oxygen peaks with a small amount of surface carbon and no other surface impurities exist on the surface of this type of films. The atomic ratio of oxygen, tungsten and iron on the surface was obtained from O(1s), W(4f) and Fe($2p_{3/2}$) XPS peaks, as a function of x. It was observed that as the iron concentration increased on the surface, the tungsten concentration decreased, while the oxygen concentration on the surface remains at a constant value of about 80 at.%. This behavior can be related to the tendency of the Fe_2O_3 doped films for adsorbing more water. From W(4f) peak, it was determined that all of tungsten is in W^{6+} state. In addition

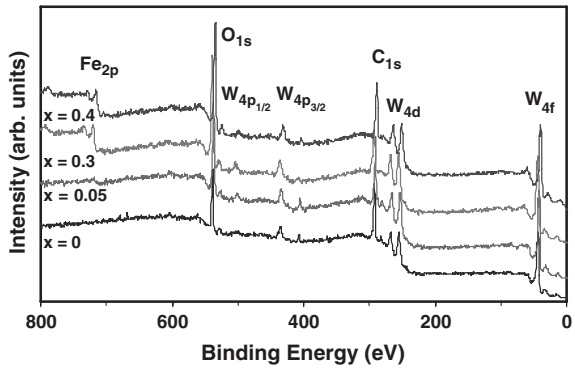

Fig. 1. XPS survey spectra of the $(WO_3)_{1-x}-(Fe_2O_3)_x$ thin films with $0 \le x \le 0.4$.

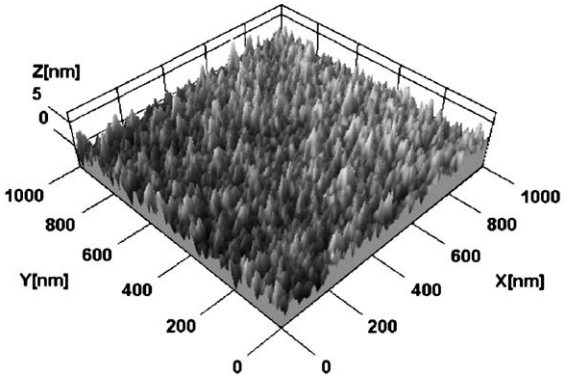

Fig. 2. AFM surface morphology of the $(WO_3)_{0.6}-(Fe_2O_3)_{0.4}$ thin film.

deconvolution of Fe($2p_{3/2}$) peak showed that more than 70% of iron is in Fe^{3+} state. Therefore, XPS results showed that WO_3 and Fe_2O_3 in the films is nearly stoichiometric and no metallic state of W and Fe was observed.

The surface topography of the $(WO_3)_{1-x}-(Fe_2O_3)_x$ films has been studied by AFM images analysis. Fig. 2 shows the AFM images of the deposited $(WO_3)_{0.6}-(Fe_2O_3)_{0.4}$ film in a scale of 1 μm × 1 μm presenting a smooth surface with an amorphous structure. The other AFM images of the different x's indicated similar surface morphologies which are not shown here. The topographic parameters of all x's obtained by analyzing their AFM images have been listed in Table 1. In fact, using statistical analysis the roughness measurement of the films showed that all the surface exhibit the same values about 1.3 nm for the root mean square (RMS) of surface roughness. Moreover, a similar behavior was observed for the measured average lateral grain size on the surface. However, roughness of a surface can also be expressed by using fractal dimension. Our AFM analysis showed that by increasing x, the fractal dimension is decreased. This means as Fe_2O_3 content increased, the surface roughness of the films decreased.

The coloration–bleaching kinetics and the optical modulation of the $(WO_3)_{1-x}-(Fe_2O_3)_x$ films were also investigated. It performed by putting the ITO and the $(WO_3)_{1-x}-(Fe_2O_3)_x$ thin films as electrodes in the prepared electrolyte, and then applying different coloring voltages to them. Fig. 3a illustrates the optical transmission variation of the WO_3 films as a function of time at the constant wavelength (500 nm) and at the various applied coloring voltages. By applying the voltages to the electrodes at $t = 10$ s, and after 2-s delay, the transmittance of the WO_3 films continuously decreased and they were colored. By changing the polarity, the transmittance of the films was increased and they were bleached with a rate faster than the coloration process. The coloration and bleaching processes of WO_3 films are associated with the intercalation

Table 1
The topographic parameters of the $(WO_3)_{1-x}-(Fe_2O_3)_x$ films obtained by AFM analysis

Surface parameter	$x=0$	$x=0.05$	$x=0.3$	$x=0.4$
RMS roughness (nm)	1.29	1.23	1.29	1.27
Mean grain size (nm)	34	33	32	32
Fractal dimension	2.39	2.35	2.30	2.27