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Electrical, optical and electrochromic properties of Ti:WO_3 thin films deposited by the pulsed chemical spray technique

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ABSTRACT

Ti:WO_3 thin films were deposited by the pulsed spray pyrolysis technique on FTO/glass substrates using WCl_6 and $TiCl_3$ precursors in the sprayed solution. The effect of titanium concentration in the solutions on structural, electrical, optical properties and on the electrochromic behavior of Ti:WO_3 films been studied using physical and electrochemical techniques. The films are polycrystalline and the crystallographic microstructure remains constant for all films studied in this work. Modifications in structural surface details, electrical conductivity and in band gap values are observed as the Ti concentration is increased. During electrochromic response it has been observed that the color-bleaching kinetics, coloration efficiency, and chemical stability of electrochromic Ti:WO_3 films are closely related to titanium doping concentration. While a nominal 2.0 at.% titanium doping produces best electrochromic response in Ti:WO_3 films, the electrochemical stability is highest when the nominal concentration of titanium is about 6.0 at.%. The improved electrochromic behavior of the Ti:WO_3 films can be explained from the improved H^+ ion diffusion coefficient in the films during coloration and bleaching processes.

1. Introduction

The electrochromic behavior of pure and metallic doped tungsten trioxide [WO_3] thin films has been studied extensively for the last 30 years due to their potential applications in display devices [1–5], rear view windows and "smart windows". The electrochromism is the process of changing transmittance and/or reflectance caused by an externally applied voltage, which is believed to occur through a reversible electron and cation intercalation and for the case of WO_3 is expressed as:

$$WO_3(\text{transparent}) + nM^+ + ne^- \Leftrightarrow M_nWO_3(\text{blue}). \quad (1)$$

While the rate of ion intercalation or coloration under applied electric field is controlled by the charge transfer at the WO_3–electrolyte interface [6,7], the bleaching is controlled by the diffusion of H^+ ions in the WO_3 structure. Therefore, the coloration kinetics of Ti:WO_3 thin films depends largely on their carrier concentration and mobility of the inserted ions, which indirectly depend on the texture, crystalline state, defect structures and impurity contents of the thin films [8,9].

A large variety of deposition techniques like thermal evaporation [10], sputtering [11], chemical vapor deposition [12], solution thermolysis [13], electrochemical [14], and spray pyrolysis [15–18] have been utilized to obtain WO_3 thin films with different morphologies, crystalline state and compositions. To enhance the electrochromic efficiency through transitions between two kinds of metal sites, efforts have also been made to fabricate thin films of selective mixed oxide semiconductors, based on their electrochromic performance [19–21]. The electrochromic efficiency of WO_3 thin films can also be modified by doping with suitable metal ions with higher electronegativity or lower oxidizing capability than tungsten ions. Doping of such material in an electrochromic host lattice is expected to benefit the coloration efficiency and durability of the host, extending the switching potential range and enhancing the reaction kinetics. Though several elements like titanium, nickel, iron, vanadium and molybdenum have been tried to incorporate into WO_3 thin film matrix [21–28], considerable improvement of its electrochromic behavior has only been observed for Ti doping [29,30].

2. Experimental details

2.1. Fabrication of Ti:WO_3 thin solid films

The pulsed spray pyrolysis technique was used to fabricate Ti:WO_3 thin films, which were deposited on FTO(F:SnO_2)/glass substrates utilizing a home-made device [23,24]. The titanium doped tungsten trioxide (Ti:WO_3) thin films were obtained from a starting solution prepared using [WCl_6] (Sigma-Aldrich, 99.9%,) as a precursor dissolved in dimethylformamide ([$HCON(CH_3)_2$], Baker, 99.9%) dissolved with a molar concentration of 0.15 M. Titanium(III) Chloride ([$TiCl_3$], Alfa Aesar 99.999%) was used as the dopant source. The nominal content of Ti in the starting solutions was 0, 2, and 6 at.% by adding different amounts of Titanium(III) Chloride into the precursor solution. The final pH of the precursor solutions remained between 4 and 5. It is

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worth to mention that also 8 and 10 at.% Ti concentrations were used during the complete set of Ti:WO_3 thin film synthesis but the results set for these samples are not reported in this work because their corresponding electrochromic response was incomplete and unstable, presenting for both cases, a very poor bleaching phenomena.

The soda lime glass substrates (2.54 cm × 2.54 cm) were ultrasonically cleaned with trichloroethylene ([C_2HCl_3], Baker), acetone ([CH_3COCH_3], Baker), and methyl alcohol ([CH_3OH], Baker) sequentially, and dried under nitrogen flow. The substrates were then placed on a fused tin bath, maintained at 500 °C (±0.5 °C). The precursor solution was then sprayed over FTO/glass substrates at the rate of 12 mL min^{-1} using filtered atmospheric air as carrier gas (8 L min^{-1}). The deposition was carried out for about 7.5 min.

2.2. Characterization of Ti:WO_3 thin films

The thicknesses of the deposited thin films were obtained with a Profilometer Tencor, model P15 (resolution = 0.15 nm) and varied between 480 and 520 nm. The electrical surface properties were obtained with a MMR (Micro-Miniature Refrigerator) Technologies equipment in the van der Pauw configuration. Optical transmittance (T) spectra of the films were recorded through an Agilent HP 8453 UV–visible spectrometer, using a FTO/glass substrate as reference. Cu Ka_1 ($\lambda = 1.5406$ Å) radiation in an AXS D8 advanced X-ray diffractometer operating in the Bragg–Brentano geometry was used for recording the X-ray diffraction (XRD) patterns of the samples. A LV JEOL 5600 Scanning Electron Microscope (SEM) operated at 30 kV and equipped with a Noran EDS analytical system was used for morphological and compositional evaluation of the Ti:WO_3 films. A JEOL FEG 2010-F Transmission Electron Microscope operated at 200 kV was used for recording the Bright Field (BF) and High Resolution Electron Microscopy (HREM) micrographs of the samples. The Ti:WO_3 films were carefully stripped out from glass support following standard procedures and were mounted on 200 mesh copper grids covered with holey carbon films. Electrochromic behavior of the Ti:WO_3 thin films was studied with a Potentiostat/Galvanostat (GillAC system) using a three electrode electrochemical cell, using 0.001 M sulfuric acid ([H_2SO_4], Baker) solution (aqueous) as electrolyte. Platinum wires were used as pseudo reference and counter electrodes.

3. Results and discussion

3.1. Structural properties

X-ray diffraction patterns of Ti:WO_3 thin films deposited on FTO/glass substrate are shown in Fig. 1. The diffraction patterns revealed several peaks related to WO_3 apart from the peaks arising from the FTO on the substrate. There appeared no diffraction peaks related to titanium or titanium oxides in the Ti:WO_3 thin films. The intensity of the diffraction peaks associated to WO_3 increased with the increase of Ti concentration up to 2.0 at.% (nominal). However, for 6.0 at.% Ti, the intensity of the diffraction peaks decreased. All the diffraction peaks could be indexed (Fig. 1) to the monoclinic phase of WO_3 (JCPDS card # 05-0363). The sharp diffraction peak at about $2\theta = 23.14°$ ($d = 3.84$ Å) for all the samples indicates a preferred orientation of the crystallites along the c-axis.

Average crystallite size of the thin films was estimated using the (200) peak of their XRD patterns using the Debye–Scherrer formula [31]:

$$D = \frac{0.9\,\lambda}{B\cos\theta} \tag{2}$$

where D is the crystallite size, λ is the wavelength of the incident radiation (Cu K_α line), θ is the Bragg angle and B is the Full Width at Half Maximum of the diffraction peak measured in radians [32]. Estimated crystallite size values for Ti:WO_3 thin films are listed in Table 1. As can be seen, the crystallite size increases from 9.3 (±0.6) nm to 14.9 (±0.6) nm as the doping concentration in the solution increases from 0.0 to 10 at.%.

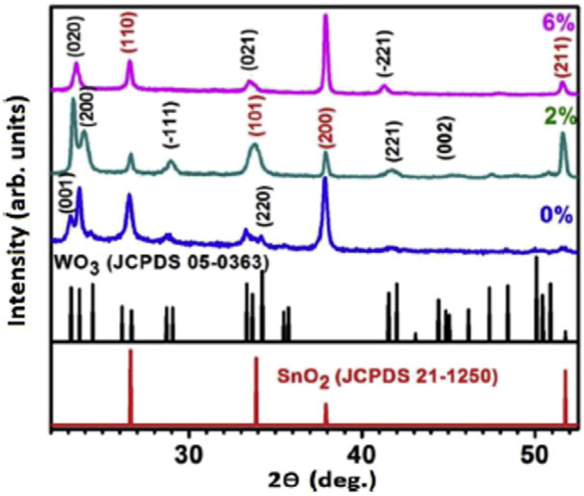

Fig. 1. XRD patterns of Ti:WO_3 thin films deposited over FTO coated glass substrates at 500 °C. The standard peak positions of WO_3 (JCPDS # 05-0363) and SnO_2 (JCPDS # 21-1250) are given at the bottom.

3.2. Scanning Electron Microscopy (SEM) studies

In Fig. 2a–c a series of typical SEM images of the surface of Ti:WO_3 thin films with (a) 0.0 at.%, (b) 2.0 at.% and (c) 6.0 at.% nominal Ti content thin films are displayed. The formation of films with nanometric particles with sizes running from 80 to 350 nm is appreciated in the micrographs. The grain sizes increased and the surfaces look denser and more compact with well faceted grains. Increasing in grain sizes with Ti concentration can be observed.

All the films look regular, dense and compact without voids or intergrain spacing. Most of the particles in the samples are well faceted crystallites which can be appreciated more clearly in Fig. 2c. On incorporating Ti at nominal 2.0 and 6.0 at.% concentrations, the films surface are populated with bigger Ti:WO_3 crystallites than for WO_3 films. It becomes clear that the amount of Ti in the starting solution affects the grain growth and hence the morphology of the film surface, which is expected to have an influence on the electrical and optical properties of the films. It has been reported that increasing Ti concentrations on WO_3 influences the ion insertion which in turn improves its electrochromic properties [33].

Energy Dispersive Spectroscopy (EDS) analysis was carried out during SEM observations and the incorporation of Ti was for all the cases lower than 1 at.% but increases with the Ti concentration in the starting solution (Table 1).

3.3. Transmission Electron Microscopic studies

High resolution electron microscopy (studies were carried out in order to detect the nanocrystalline nature of Ti:WO_3 films and secondary tungsten and titanium oxide nanophases. Fig. 3a and b corresponds to typical HREM micrographs of samples prepared with 0, 2 and 6 Ti at.%

Table 1
EDS composition and average crystallite size values in Ti:WO_3 films doped with different Ti concentrations.

Nominal Ti (at.%)	Crystallite size (nm) ± 0.5	EDS (at.%) W	EDS (at.%) O	EDS (at.%) Ti
0	09.3	23.5	76.5	0.0
2	07.5	19.2	80.4	0.4
6	12.2	21.7	77.7	0.6
10	14.9	19.2	79.9	0.9