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Improved electrochromic performance in sprayed WO_3 thin films upon Sb doping

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ABSTRACT

We report for the first time improved electrochromic properties of tungsten oxide (WO_3) nanocrystalline thin films upon Sb doping. The Sb-doped WO_3 films were deposited by cost effective spray pyrolysis technique. The structural and morphological studies of the as-deposited films have been carried out by grazing incidence X-ray diffraction (GIXRD) and field emission scanning electron microscopy (FESEM). XRD analyses reveal polycrystalline monoclinic nature of the as-deposited films. The electrochromic behaviours of the films have been studied in an electrochemical analyzer using a three-electrode electrochemical cell, and 0.01 M H_2SO_4 solution (aqueous) as electrolyte. The charge storage capacity, electrochemical stability and reversibility of the films as well as H^+ ion diffusion coefficient in the films during coloration/decoloration process improve upon Sb doping and are optimal for 20 at% Sb dopant concentration.

1. Introduction

Tungsten oxide (WO_3) now-a-days has become a very promising technological material because of its wide applications in electrochromic window based devices [1–5]. In modern society, the uses of large glass windows or glass panels in residential and commercial buildings are very common all around the globe. But in tropical region like India, the uses of large glass in building help to utilize the natural light but it also unnecessarily warms up the room as glass layer acts as similar to greenhouse effect. Electrochromic glass or smart window is one of the solutions to this problem as it can reduce the need of artificial lighting and air conditioning unit by specifically controlling the transmission of sunlight through these windows, thereby monitoring the indoor temperature and lighting. The most crucial part of any electrochromic device is the electrochromic active layer material and the electrolyte. Although there are various organic and inorganic electrochromic materials, but tungsten trioxide (WO_3) is the most widely studied electrochromic material due to its multifunctional properties along with high coloration efficiency, good reversibility ratio, fast colorization-bleaching speed and long cyclic stability [6–8]. It has a transparent and dark blue state depending on the charge content and electric field applied. Apart from smart windows, WO_3 electrochromic films are also used in modern displays, variable reflectance mirrors and antiglare mirrors [9,10].

The phenomenon of electrochromism was first reported by Deb [11], and since then there has been a significant progress in this area of research interest. But, despite a lot of researches in this field, electrochromic glass is still not widely popular among masses due to major practical challenges such as low-cost deposition of film over a very large area, and high contrast in dark state to colourless state.

In electrochromism, upon applying an electric field, the electrochromic material exhibits a new colour due to electron-transfer or reversible oxidation-reduction (redox) reaction in which it either gains or loses an electron. The reversible redox reaction mechanism is responsible for the change in the optical transmittance or reflectance which, in turn, affects the colour of the material. In WO_3 films, the change in optical transparency is caused by the insertion/deinsertion of alkali ions such as Li^+ or H^+ ions during the coloration/decoloration process. The coloration and bleaching redox reaction in WO_3 thin films can be simplified as [12]:

$$WO_3(\text{colourless}) + xM^+ + xe^- \leftrightarrow M_xWO_3(\text{blue}) \quad (1)$$

where $M^+ = H^+$, Li^+, etc., and x is a quantity termed as insertion coefficient which has value in between 0 and 0.3 [13]. M_xWO_3 is, in general, called as tungsten bronze.

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In crystalline WO_3 films, the electrochromism can be explained by considering the Drude-like free electron absorption model [14]. As the film becomes negatively charged in cathodic state, the electrons and ions from the electrolyte diffuse into the films; and then electrons enter the extended states of conduction band, and the majority of ions are delocalized around the lattice sites, which behave like scattering centers for the intercalated electrons. Due to the scattering of electrons, a high reflectance and a low transmittance state is observed in visible and near infrared regions.

To enhance the electrochromic performance in WO_3 thin films, the easiest and economical way is the introduction of dopants in the host lattice network. Many researchers have used different dopants such as titanium [Ti], molybdenum [Mo], niobium [Nb], lithium [Li], vanadium [V], and nitrogen [N] to increase the electrochromic performance [15–21]. Bathe and Patil [15] have studied the influence of Ti doping on the electrochromic properties of spray pyrolysed WO_3 thin films and found that the cycle stability, charge storage capacity and reversibility of the films are improved upon Ti doping. The influence of Mo doping on the electrochromic behaviour of spray pyrolysed WO_3 thin films has been investigated by O-Rueda de León et al. [16]. They have reported the best electrochromic response in WO_3 films with 6 at% Mo doping, while the electrochemical stability is highest when the Mo doping concentration is about 2 at%. Improved electrochromic behaviour of spray pyrolysed WO_3 thin films by Nb doping has been reported by Bathe and Patil [17]. Effect of post annealing on the electrochromic properties of Nb-doped WO_3 thin films deposited by electron beam method has been investigated by Wang et al. [18]. Efficiency of Li doping on electrochromic WO_3 thin films has been studied by Porqueras and Bertran [19]. The electrochromic and photocatalytic properties of V-doped WO_3 thin films prepared by reactive dc magnetron sputtering technique have been analysed by Karuppasamy and Subrahmanyam [20]. Sun et al. [21] have investigated the electrochromic properties of N-doped WO_3 thin films prepared by reactive DC-pulsed sputtering and found that the film with N content of ~5 at.% exhibits higher optical modulation and coloration efficiency as well as faster Li ion transport kinetics.

As far as we know, the influences of Sb doping on the electrochromic properties of spray-deposited WO_3 thin films have not yet been reported in literature. Therefore, the electrochromic performance of Sb-doped WO_3 thin films have been investigated and reported in this paper.

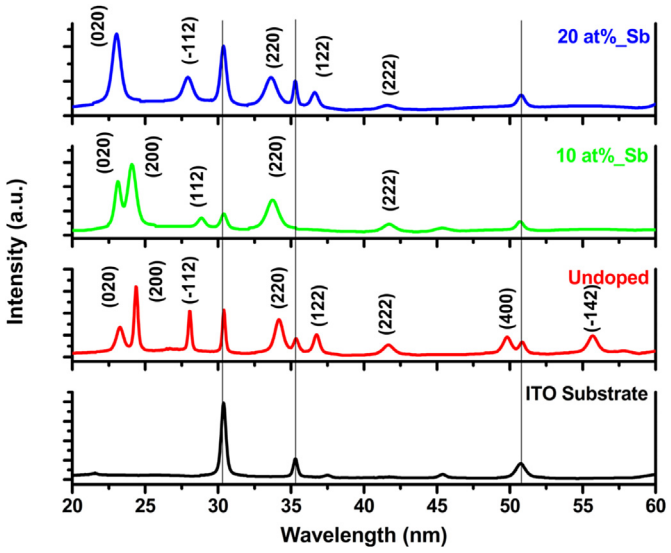

Fig. 1. XRD pattern of the commercial ITO, undoped and Sb doped WO_3 thin films.

2. Experimental details

WO_3 films were deposited on ITO coated glass substrates (Sigma–Aldrich; surface resistivity 10–15 Ω/sq.) using an indigenously assembled spray pyrolysis unit. The spray pyrolysis set-up and the process parameters have been described elsewhere [22]. The atomic percentage of Sb ions used for doping was taken as 0, 10 and 20 at%. The undoped film was prepared using the precursor solution of ammonium tungstate $(NH_4)_2WO_4$ dissolved in hot deionized water (60–65 °C). Sb doping was carried out by the addition of required quantity of antimony trichloride ($SbCl_3$) in the spray solution.

The crystallographic phase of the as-deposited undoped and Sb-doped films has been studied by grazing incidence X-ray diffraction (GIXRD) analyses by varying the diffraction angle from 20° to 70°. A Rigaku X-ray diffraction system with CuKα_1 ($\lambda = 1.5406$ Å) radiation as an X-ray source was used to obtain the XRD patterns of the films. The surface morphology of the films has been examined with JEOL JSM-7600F field emission gun-scanning electron microscopy (FEG-SEM). Electrochromic characterization of the as-deposited films has

Table 1
Structural parameters of the undoped and Sb-doped WO_3 thin films.

WO_3 film	Peak position	d- Spacing Observed (Å)	hkl	Crystallite size (nm)		Lattice strain (%)	a (Å) b (Å) c (Å) β (degree)
Undoped WO_3	23.3	3.821	020	14.08	Average crystallite size: 17.6	0.0122	7.346
	24.4	3.648	200	28.22		0.0058	7.641
	28.1	3.178	−112	34.12		0.0042	7.522
	34.2	2.622	220	12.37		0.0095	96.68
	36.8	2.443	122	17.44		0.0063	
	41.7	2.166	222	9.84		0.0099	
	49.8	1.829	400	13.03		0.0063	
	55.7	1.649	−142	11.70		0.0063	
10 at% Sb	23.1	3.843	020	16.89	Average crystallite size: 12.15	0.0102	7.390
	24.1	3.691	200	12.09		0.0137	7.687
	28.9	3.092	112	14.24		0.0098	7.789
	33.7	2.655	220	8.65		0.0138	92.70
	41.7	2.163	222	8.86		0.0110	
20 at% Sb	23.0	3.859	020	12.06	Average crystallite size: 10.65	0.0144	7.717
	27.9	3.192	−112	10.66		0.0135	7.368
	33.6	2.663	220	8.64		0.0139	7.788
	36.6	2.451	122	14.53		0.0076	92.60
	41.6	2.169	222	7.38		0.0132	