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Structural, electrical and optical properties of TiO_2 doped WO_3 thin films

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Abstract

TiO_2 doped WO_3 thin films were deposited onto glass substrates and fluorine doped tin oxide (FTO) coated conducting glass substrates, maintained at 500 °C by pyrolytic decomposition of adequate precursor solution. Equimolar ammonium tungstate ($(NH_4)_2WO_4$) and titanyl acetyl acetonate (TiAcAc) solutions were mixed together at pH 9 in volume proportions and used as a precursor solution for the deposition of TiO_2 doped WO_3 thin films. Doping concentrations were varied between 4 and 38%. The effect of TiO_2 doping concentration on structural, electrical and optical properties of TiO_2 doped WO_3 thin films were studied. Values of room temperature electrical resistivity, thermoelectric power and band gap energy (E_g) were estimated. The films with 38% TiO_2 doping in WO_3 exhibited lowest resistivity, n-type electrical conductivity and improved electrochromic performance among all the samples. The values of thermoelectric power (TEP) were in the range of 23–56 μV/K and the direct band gap energy varied between 2.72 and 2.86 eV.

Keywords: Spray pyrolysis technique; TiO_2 doped WO_3 thin films; Optical; Electrical and structural properties; Electrochromism

1. Introduction

The transition metal oxides form a group of predominantly ionic solids, which exhibit a wide range of optical and electrical properties. Tungsten oxide is the most widely investigated material [1–3]. There has been great interest in the study of TiO_2 doped WO_3 thin films due to their possible applications in large area display devices [4] and smart windows [5]. Several groups have studied electrochromic properties of TiO_2 doped WO_3 thin films [6–9].

Our interest is in the study of electrochromic (EC) performance of TiO_2 doped WO_3 thin films. The aim of this study is to improve the electrochromic

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performance of WO_3 thin films in general and EC reversibility in particular by doping it with TiO_2. In this investigation, we have employed solution thermolysis technique for the preparation of WO_3 thin films with various doping concentrations of TiO_2, and studied their structural, electrical, optical, and electrochromic properties. The WO_3 thin film deposition with TiO_2 doping was carried out with a postulation that the resultant film retains some amount of water content as TiO_2 is hydrophilic [10], which is conducive to get better EC effect.

2. Experimental

The fluorine doped tin oxide (FTO) conducting coatings were prepared by using pentahydrated stannic chloride ($SnCl_4{\cdot}5H_2O$) (purity 98%) and ammonium fluoride (NH_4F) (purity 95%) as precursor salts. The solution was prepared in double distilled water and sprayed through a specially designed glass nozzle onto ultrasonically cleaned glass substrates. The deposition parameters like solution concentration, spray rate, nozzle to substrate distance (NSD), carrier gas flow rate, etc. were kept constant at optimized values. The FTO coated conducting glass substrates, with 90–95% transparency and sheet resistance 10–15 $\Omega\,cm^{-2}$, were prepared. These FTO coated conducting glass substrates were further used for deposition of TiO_2 doped WO_3 thin films. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of titanyl acetyl acetonate was carried out using TA instrument (USA) SDT 2960 (simultaneous DSC-TGA).

For the deposition of TiO_2 doped WO_3 thin films by solution thermolysis technique, the precursor solution was prepared by dissolving WO_3 powder and titanyl acetyl acetonate (TiAcAc) ($C_{10}H_{14}O_5Ti$) powder in hot ammonia and methanol respectively. The homogeneous solution of ammonium tungstate and titanyl acetyl acetonate solution were prepared at 90 °C and room temperature respectively. The undergoing chemical reactions are given in Eqs. (1) and (2)

$$WO_3 + 2NH_3 \xrightarrow{90\,^\circ C} (NH_4)_2WO_4 \quad (1)$$

$$TiC_{10}H_{14}O_5 + CH_3OH \xrightarrow{\text{Room temp.}} TiO_2 + 11CO\uparrow + 9H_2O\uparrow \quad (2)$$

These two solutions were mixed together in different volume proportions ranging from 4 to 38% (in the volume ratio 1:24, 3:22, 5:20, and 7:18, to vary the doping concentration of TiO_2 in WO_3). In this study, the maximum TiO_2 doping concentration was limited to 38%, as beyond this value inhomogeneous solution forms and precipitate dominates. For undoped WO_3, thin films ammonium tungstate ($(NH_4)_2WO_4$) solution was sprayed without adding titanyl acetyl acetonate (TiAcAc) precursor. The pH of the solution was adjusted to 9. The precursor solution was then sprayed onto the preheated glass and FTO coated conducting glass substrates. The TG and DT curves were consulted in selection of the deposition temperature. The substrate temperature was kept constant at 450 ± 5 °C, and continuously monitored by chromel–allumel thermocouple fixed to the hot plate. The pyrolytic decomposition of the precursor solutions onto preheated substrate results in the formation of TiO_2 doped WO_3 thin films and pristine WO_3 thin films, respectively.

The samples were transparent, uniform and well adherent to the substrates. The samples prepared using the doping concentrations, viz. 4, 14, 25, and 38% are denoted by WT1, WT2, WT3, and WT4, respectively. The undoped WO_3 sample was denoted by WT0.

The structural properties were studied by using Philips PW 3710 X-ray diffractometer (XRD) with Cr Kα radiation of wavelength 2.2897 Å. The film thickness was measured using Talystep method. The measured thickness of all the samples is given in

Table 1
Effect of doping concentration on properties of TiO_2 doped WO_3 thin films prepared by spray pyrolysis technique at 500 °C

Sample	Film thickness (μm)	Thermo electric power (μV/K)	Band gap energy, E_g (eV)	Resistivity × 10^4 (Ω cm)	Activation energy (eV)
WT1	1.246	55.27	2.72	2.31	0.019
WT2	1.289	26.74	2.78	2.07	0.018
WT3	1.556	23.55	2.84	1.05	0.016
WT4	1.820	23.38	2.86	0.60	0.007