



Structural and optical properties of tungsten doped TiO₂ thin films fabricated by spray pyrolysis technique

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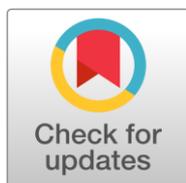
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Abstract: The pure and tungsten doped titanium oxide W_xTi_{1-x}O₂ (x=0, 0.1) thin films have been successfully deposited on the glass substrate at 400 °C using spray pyrolysis technique. The structural properties of the prepared films were characterized by X-Ray Diffraction (XRD). From the XRD spectrum, the sample shows the amorphous structure. Their surface morphology was probed using Scanning Electron Microscopy (SEM) and the mechanical properties, topography and surface roughness of the grown films was investigated by Atomic Force Microscopy (AFM). The functional group and optical characteristic of prepared films were analyzed by Fourier Transform Infra-Red (FT-IR) spectroscopy and UV-Vis-double beam spectrometer. The optical energy gap was determined by transmittance measurement.

Keywords: Thin films, Spray Pyrolysis, Titanium Oxides, Optical properties, FTIR.

1. Introduction

In the last several decades, many transition metal oxides have been exploited in many challenging fields of information science, nano biotechnology, and microelectronics, computer science, energy, transportation, safety engineering, military technologies, optoelectronic, electrochromic devices etc. Materials capable of persisting and reversible change in color under a reversible electrochemical process are known as

electrochromic materials, which have been widely used for the fabrication of optical modulation devices. Among these devices antiglare car rear view mirrors are already commercially available, solar control windows (smart windows) currently drives intensive developments.

Tungsten trioxide has been employed in the production of electrochromic windows, or smart windows. These windows are electrically

switchable glass that changes light transmission properties with an applied voltage. This allows the user to tint their windows, changing the amount of heat or light passing through [1]. In this junction, tungsten oxide is the most extensively studied electrochromic material due to its outstanding electrochromic (EC) properties [2-8]. However, for practical electrochromic device still improvement in its EC properties, viz. electrochromic reversibility, stability, etc. is required.

TiO₂ is an attractive material with excellent photoresponsive properties. It exhibits EC properties which make it suitable for variable reflection mirrors, dazzle-free mirrors in automobiles, variable sun protection system usually called 'smart window' (variable transmittance) and surfaces with a tunable emittance of thermal control of satellites. It has been recognized as a significant chromic material that can be colored through electro, photo, gas, laser and thermochromism processes. Electrochromic (EC) materials have the potential to act as emissivity modulators. Some researchers have attempted to improve the colouration performance of WO₃ thin-films by doping TiO₂. The addition of adequate dopant of WO₃ into TiO₂, modifies its structure, leading to the better EC performance. Several studies have been made on the tungsten doped TiO₂ thin films. The WO₃ loses its amorphous structure at about 400°C and becomes crystalline. The crystalline structure is not conducive for electrochromic properties. The addition of tungsten into TiO₂ preserves the amorphous structure even at relatively high temperature (450°C) and as TiO₂ is hydrophilic it adsorbs water from the air [9]. This small amount of water adsorbed, accelerates the H⁺ ion insertion/removal in to or from the tungsten doped TiO₂ thin films [10]. Tungsten doped TiO₂ thin films have been reported which are produced through different methods such as chemical vapour deposition [11], electro-deposition [12], sol-gel process [13], sputtering [14] and spray pyrolysis [15]. The chemical

spray pyrolysis is a simple method, to deposit thin films and only in few works the formation composition of chemical spray pyrolysis deposited TiO₂ films from acetyl-acetone stabilized Ti-alkoxide precursors have been studied [16,17].

In this paper we have reported that the effect of doping of W_xTi_{1-x}O₂ with x= 0 to 1.0 M thin films prepared by spray pyrolysis technique and its structural, surface morphology, vibrational and optical properties are systematically studied.

2. Experimental Procedure

The precursor solution contained titanium (IV) Isopropoxide (C₁₂H₂₈O₄Ti) (TTIP), Sodium tungstate hydrated (Na₂WO₄·2H₂O), acetylacetone (CH₃COCH₂COCH₃) (AcAc) and Isopropyl Alcohol (IPA) at TTIP: AcAc molar ratio of 1:2. The solution was atomized by a spray system using compressed air as a carrier gas onto a cleaned glass substrate. This precursor solution was sprayed in fine droplets using air as a carrier gas, the spray rate was fixed at 3ml min⁻¹, and the distance between the nozzle and the substrate at 25cm, the solution sprayed was 30ml. Micro glass slides were used as substrates in the present work, and substrate cleaning plays an important role in the deposition of thin films. The glass slides rinsed in acetone and dried in the open air before use. This process is to ensure a clean surface, which is necessary for the formation of nucleation centres, required for film deposition [18].

TiO₂ thin films were prepared on this glass substrate with the different molarities of Tungsten like 0M (Pure), 0.02M, 0.04M, 0.06M, 0.08 and 0.1 M. For each deposition 30 ml of solution was sprayed onto glass substrates kept at 400 °C. The schematic representation of the experimental procedure is shown in Fig. 1.

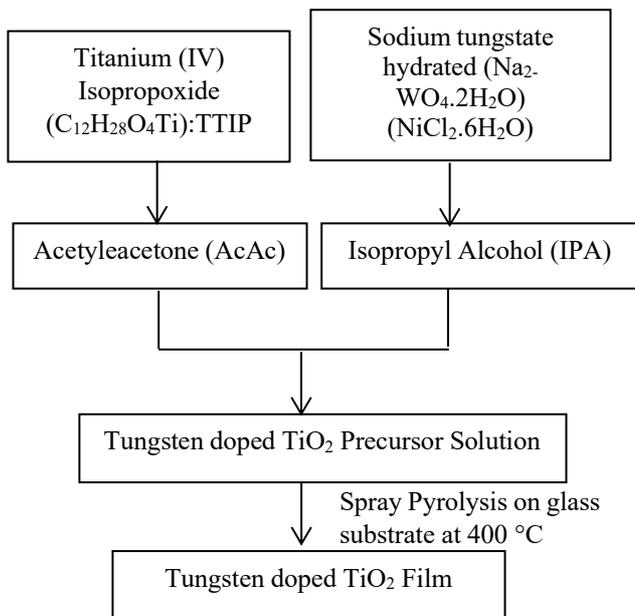


Figure.1. Flowchart of preparation of Tungsten doped TiO₂ films

The structural property of the prepared films are analyzed through X-ray diffraction (XRD) studies. XRD patterns of prepared films were recorded by a RigakuUltima III X-ray diffractometer using the W-K α radiation ($\lambda = 1.5406 \text{ \AA}$). The thickness of the as-deposited samples was measured using the film-matrix thickness measuring instrument. The surface morphology, homogeneity, and grain size of the deposited films were studied by SEM, model JSM35CFJEOL, Optical absorption measurements were carried out by using a Lambda 35 UV-vis-NIR spectrophotometer. Fourier Transform Infrared (FT-IR) spectroscopy was performed to identify the local structure of the particles using Bruker Make (alpha) spectrometer at room temperature.

3. Results and Discussion

3.1 Structural studies

The films are smooth, highly uniform, and showed good adhesion to the substrate. They also showed long term stability with respect to their optical and electrochemical properties. X-ray diffraction pattern for 0.1M of Tungsten (W) doped TiO₂ thin films deposited on glass substrate. There are several

interesting features contained within the XRD data. Figure (b) shows the XRD pattern for tungsten doped TiO₂ thin films with the substrate temperature of 400 °C and annealed at 600°C respectively. The noticeable improvements are not observed upon annealing the film for 1 hr at 600°C. Figure (a) shows the XRD pattern for tungsten doped TiO₂ thin film deposited on a glass substrate. The broadened diffraction peak around $2\theta = 23^\circ$ is mainly attributed to the amorphous nature of the films. The thermally activated transformation from an amorphous to anatase phase is depended on experimental parameters.

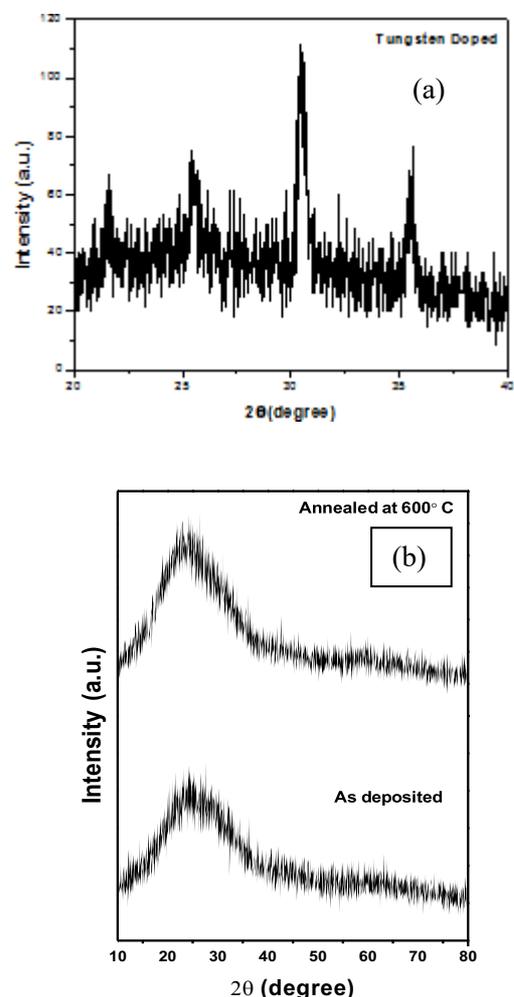


Figure.2 XRD patterns of (a) Tungsten doped TiO₂ thin films (b) Pure TiO₂ thin films

The small peaks appearing in this diffraction angle range (21.5° , 23.7° and 26.5°) originated from the argillaceous compound

that holds the specimen to be measured to the sample holder of the X-ray apparatus. Since tungsten and Ti have comparable ionic radii ($W^{4+}=0.60\text{\AA}$ and $Ti^{6+}=0.62\text{\AA}$), substitutional doping is presumed.

Moreover, the incorporation of tungsten to Nb_2O_5 has caused the resulting films to be amorphous [18]. The observed structure is in agreement with the reported value. Hence, tungsten doping is projected to be favorable for the electrochromic property.

The substitution of tungsten at TiO_2 film was further confirmed by Energy Dispersive Spectroscopy (EDS) technique and the results are shown in Figure.3. The peaks related to titanium and other elements can be clearly observed. Based on these results, it can be

deemed that tungsten doped TiO_2 films with 0.1M have occurred at TiO_2 films.

3.2 Surface Morphological Studies

Figure 4 (a) and (b) show SEM images of the surface morphology of Pure and Tungsten (W) doped TiO_2 films. The grain size of the films became smaller. Images show that deposited film is compact. The surface morphology of tungsten doped TiO_2 film is slightly different than pure TiO_2 thin films. It can be explained that the different morphologies of the films might be related to the lattice structure and defects generated during deposition governed the chemical adsorption, subsequent nucleation and growth.

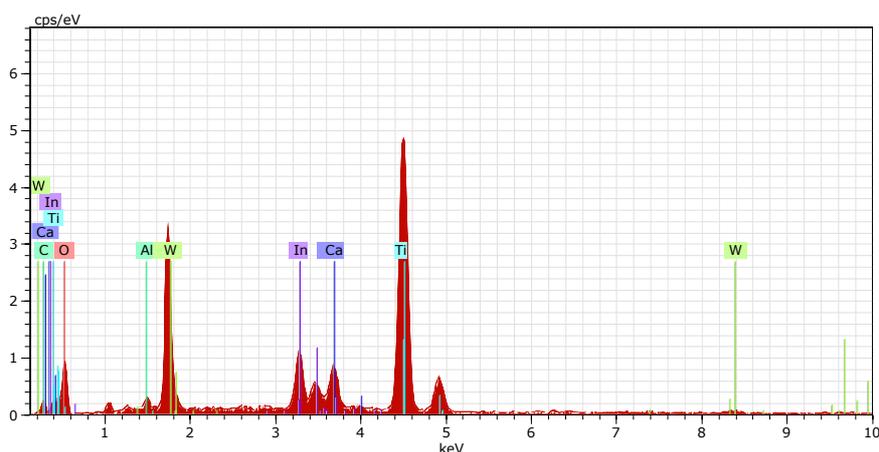


Figure 3 EDS spectrum of Tungsten doped TiO_2 thin films

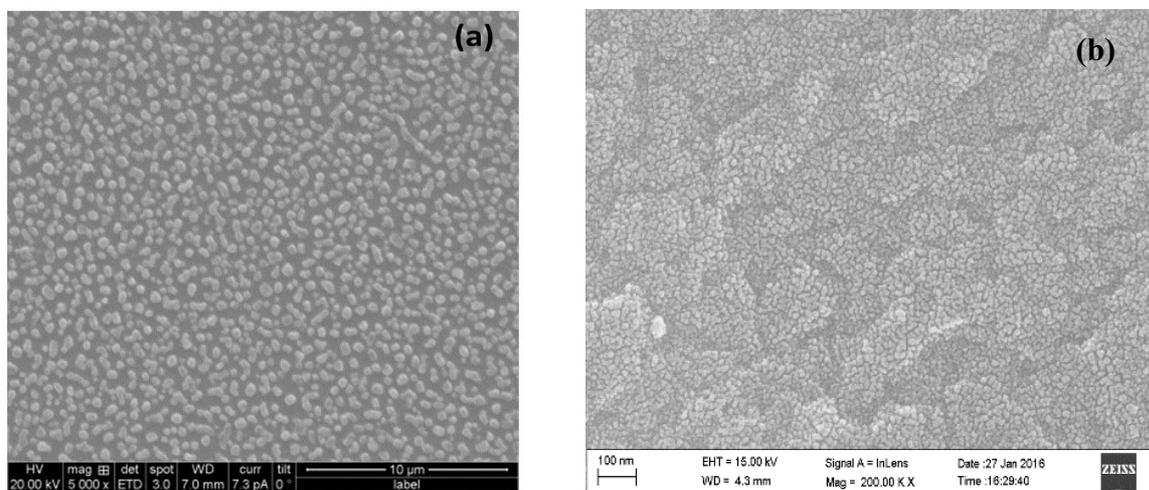


Figure 4 SEM micrographs of (a) Pure TiO_2 thin films (b) Tungsten doped TiO_2 thin films

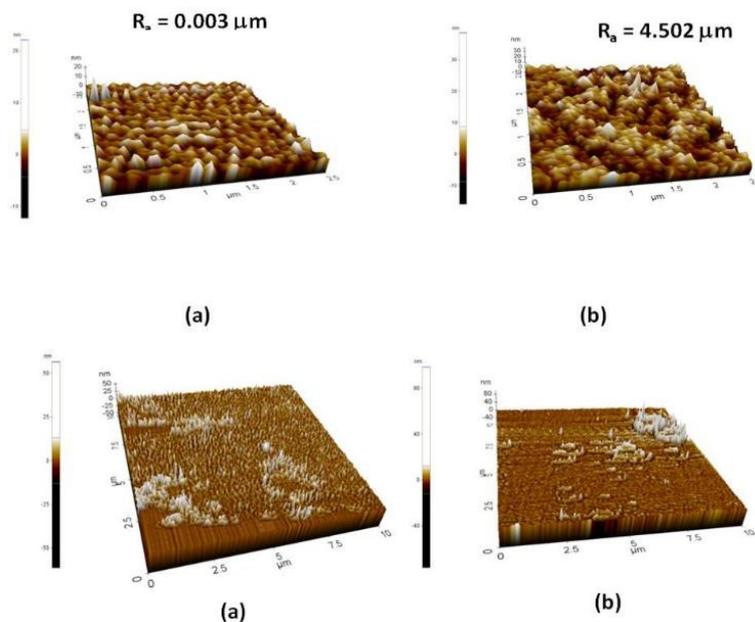


Figure. 5 AFM images (a) Pure TiO₂ (b) Tungsten doped TiO₂

3.3 Atomic Force Microscope (AFM) studies

The three-dimensional (3D) Atomic Force Microscopy (AFM) images of the tungsten doped TiO₂ thin film deposited on the glass substrate are shown in Figure 5. It represents a three-dimensional image of the glass substrate, as-deposited pure TiO₂ and tungsten doped TiO₂ on glass substrate recorded over an area of 2.5 μm × 2.5 μm. It can be clearly seen that all the films are dense and homogeneously grown without any cracks. It is evident from the AFM picture that as the tungsten doped, the crystal grains tend to grow laterally, which is appropriate for the formation of high-quality thin films. The growth mode transition is considered due to the increases of strain in the grains with doping. The height distribution showed that with adding the dopant the grains became reduced in corresponding Z scale. The grains in all the films exhibit granular structure with the surface root mean square roughness values varied. The increase in roughness with doping is mainly attributed to the increase in grain size. Figure 5 (b) shows the presence of hills on the top of the surface of the samples which are recorded over an area of 10 μm × 10

μm of the glass substrate, as-deposited Pure TiO₂ and tungsten doped TiO₂ on a glass substrate. The grain sizes of the tungsten doped TiO₂ thin films increases is in very good influence the electrochromic properties.

3.4 FTIR Studies

substrate with the substrate temperature 400 °C. The IR modes and corresponding bonds for the present films were identified. The presence of Ti-O-Ti and Ti-O polymeric chains was clearly evident from the bands at 471 and 789 cm⁻¹. Also, the vibration of the Ti-O-O band was identified from the band at 693 cm⁻¹. Moreover, the bands at 1009, 1122, and 1138 cm⁻¹ were ascribed to stretching of Ti-O-C while LO mode of amorphous TiO₂ appeared at 874 cm⁻¹.

The broadband from 2000 to 3600 cm⁻¹ associated with the stretching vibration modes of hydroxyl groups, began to broaden after the addition of water appeared at 1635 cm⁻¹. The bands appeared at 1288 and 1368 cm⁻¹ are the vibration mode of C-O-O group. The doublet in 1441 and 1538 cm⁻¹ designated the symmetric and asymmetric stretching vibration of the

carboxylic group coordinated to Ti as a bidentate ligand.

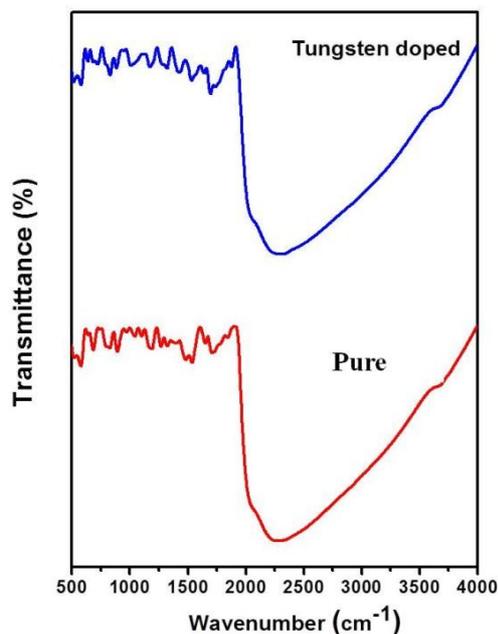


Figure 6 FTIR spectra of Pure and W doped TiO₂ thin films

3.5 Optical Studies

The optical transmission spectra of TiO₂ films are measured in the wavelength range 350-900 nm at room temperature. The nature of transition involved in oxide semiconductors can be determined on the basis of the dependence of absorption coefficient (α) of the material on incident photon energy ($h\nu$). The energy band gap of the film is evaluated from the relation

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where A is a proportionality constant and E_g is the direct transition band gap. The optical absorption coefficient is of the order of 10^4 cm^{-1} [19, 20].

Figure 7 shows the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for all the samples. Since there is not sharp absorption edge, band gap energy of the films is obtained from the intersection of extrapolation of the linear region (higher photon energy region) to zero absorption coefficient, i.e. at $\alpha = 0$ and the horizontal baseline [21]. The band gap energy

of TiO₂ increases from 3.36 to 3.54 eV with tungsten doping concentration. The change in the band gap energy can be explained in terms of Burstein-Moss band gap widening [22]. According to the Burstein-Moss effect, the increase in the Fermi level in the conduction band leads to the band gap energy broadening with increasing carrier concentration.

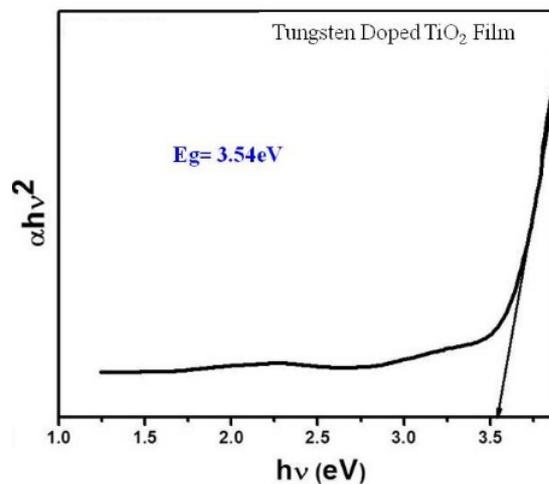
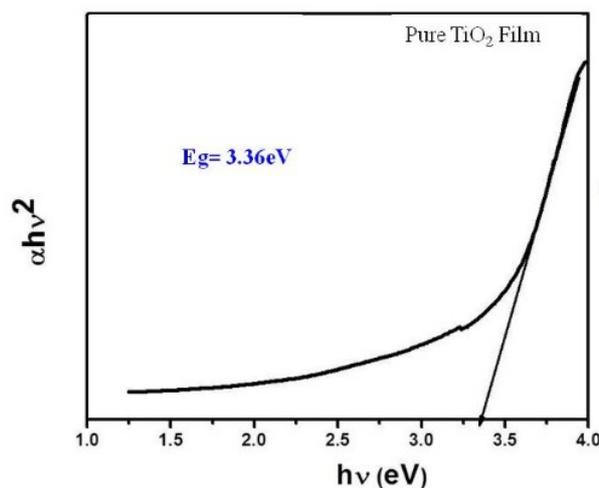


Figure 7 UV spectra of Pure and W doped TiO₂ films

4. Conclusion

The Tungsten doped TiO₂ thin films are successfully deposited on a glass substrate using a spray pyrolysis deposition technique. The structure of TiO₂ having the amorphous state. The layered interconnected thread-like network is converted into an amorphous structure at higher Tungsten concentration. It was seen that Tungsten doping could lead to

significant morphological changes in TiO₂ films. The functional groups are analyzed through FTIR studies. The UV visible study showed that the band gaps are varied with the doping concentration of tungsten.

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