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Characterization of Amorphous and Transparent, RF Sputtered V_2O_5 doped WO_3 Thin Films

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Abstract

Thin films of V_2O_5 doped WO_3 were coated using sputtering target by varying RF power between 100 and 250 W and by keeping the source to substrate distance as 60 mm at room temperature. X-ray diffraction studies revealed that the as-deposited films were amorphous. Morphological studies using AFM exhibited uniform growth of films. The optical transmittance was measured over the wavelength range of 300 to 2500 nm. The films showed transmittance in the range of 70 to 90% in the visible region. Optical band gaps were calculated for indirect transitions. FT-IR and electrochromic studies were also carried out.

Keywords: *RF Sputtering; Thin films; Amorphous; Electrochromism; Optical properties.*

Introduction

Transition metal oxides are the widely used inorganic electrochromic (EC) materials owing to the persistent and reversible changes in optical properties by the electrochemical oxidation or reduction process [1]. Tungsten oxide (WO_3) is the most thoroughly investigated and commonly used material for the preparation of EC devices because of its highly stable and fully reversible colouration characteristic. Electrochromic materials can offer optical modulation by the combinational injection and extraction of electrons and ions upon the application of an external voltage or current. The optical absorption in amorphous tungsten oxide films is due to the electron exchange caused between adjacent W^{5+} and W^{6+} ions. The inserted electrons are localized in W^{5+} sites and polarize their neighboring lattice to form small polarons [2]. This small polaron transition mechanism is responsible for the coloration in amorphous films. WO_3 thin films are also photocatalysts (PCs) and find application as a photo-anode in the purification of polluted air, anti-bacterial activity and deodorizing agent [3-6]. By coalescing these EC and PC properties, low maintenance smart glass windows can be realized [7].

Optical, structural and electrochromic properties of metal oxides are alterable with respect to the preparation method, the mixture content and concentration. Several works have been made on WO_3 [8-10], V_2O_5 [11-13] and their mixtures [14-16]. These materials have already demonstrated to be promising for the expansion of the solar energy devices such as counter electrodes for the electrochromic windows and thin film layers for the antireflective filters.

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The bright blue colour of WO_3 films in the reduced state is not favorable for building applications. According to the literatures, proper proportion of V_2O_5 doping can provide the neutral grey coloured films that are suitable for buildings. Moreover, the V_2O_5 doped WO_3 thin films exhibit photocatalytic property as well which helps them to be used in self-cleaning smart window applications [7]. Different chemical and physical deposition techniques like PLD, EB, DC sputtering and sol-gel were used so far to prepare V_2O_5 doped WO_3 thin films. Among these techniques RF magnetron sputtering has the advantage of depositing uniform films on large area substrates. In this present work, V_2O_5 doped WO_3 thin films deposited under different RF powers were studied for their electrochromic applications.

Experimental

V_2O_5 doped WO_3 (98 wt % WO3 and 2 wt % V_2O_5) target having thickness of 5 mm and diameter of 50 mm was prepared from high purity (99.9% Sigma Aldrich) V_2O_5 and WO_3 powders. Thin films were coated using planar magnetron RF sputtering unit (HindHivac, Model-12 MSPT). The base pressure in the chamber was maintained at 2×10^{-6} torr. High purity argon was introduced through mass flow controller. RF power was varied from 100 to 250 W. Thin films were deposited on pre-cleaned glass substrates and fluorine-doped tin oxide (FTO) coated glass substrates with source to substrate distance of 60 mm at room temperature under a constant chamber pressure of 2×10^{-3} mbar. Argon was used as a sputtering gas.

Results and Discussions

(a). Structural and Morphological Studies

The structural identification of the sputtering target and deposited films was carried out using X-ray diffractometer (MPD Diffractometer, PANalytical X'Pert Pro, The Netherlands). X-ray diffraction pattern in Figure 1 showed crystalline peaks and compound formation for the target and it showed amorphous nature of the as-deposited films for all RF powers [7]. For the fabrication of electrochromic devices, WO_3 should be in the amorphous state since it has been reported that crystallographically oriented WO_3 films demonstrated

inferior performance characteristics in electrochromic devices [17]. All films had approximately the same thickness of 1 μm which was measured by Stylus Profilometer.

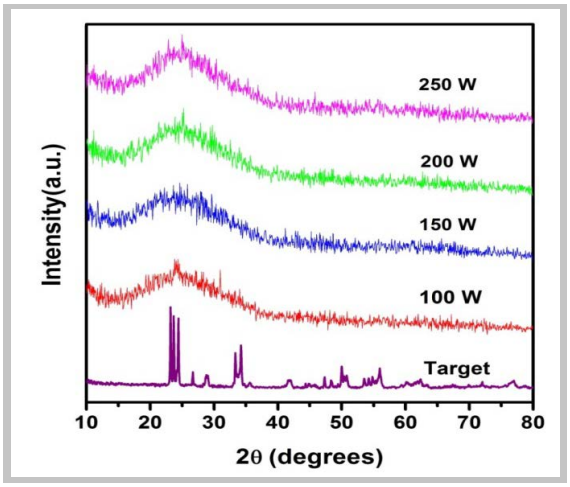

Figure 1. XRD patterns of V_2O_5 doped WO_3 thin films.

(b) Atomic Force Microscopy

Figure 2 shows the 3D AFM micrographs of V_2O_5 doped WO_3 thin films deposited at 250 W RF power. The atomic force microscopy analysis shows a porous free morphology with homogeneity and uniformity on the films surface, which is a characteristic for equal nucleation and growth rates during deposition. The surface morphology of the as-deposited film is related to the thickness and crystallinity which depends on the processing parameters such as substrate temperature, RF power and gas pressure [18]. The as-deposited film surface is free of cracks or holes that result from the optimal deposition and parameters. The sample exhibits large nicely separated conical columnar grains throughout the surface. It shows individual columnar grains sticking out from the surface, with the rather small size forming a smooth and homogenous surface with an average roughness varying as 4.1, 7.4, 9.3 and 9.8 nm. The electrochemical intercalation is a reversible process, making the materials very interesting in applications where the control over the ability of insertion/extraction of an ion in a structure is essential. The electro-physical-chemical properties of intercalation materials are strongly dependent on surface roughness. The surface roughness acts as a gateway to allocate the ions in the network structure of the material [19].

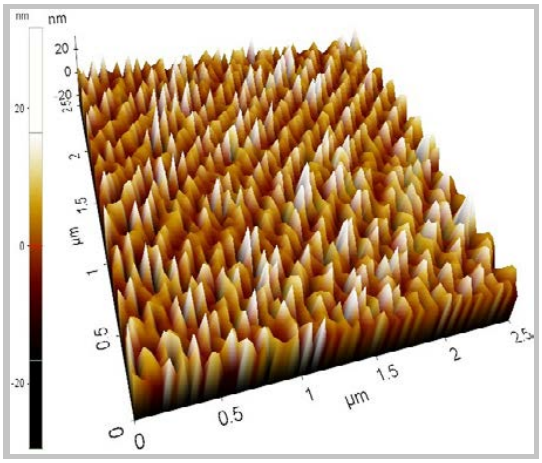

Figure 2. AFM micrograph of V_2O_5 doped WO_3 thin films deposited at 100 W RF power.

(c) Optical Studies

The transmittance spectra of the films carried out in the wavelength range of 300-2500 nm using JASCO UV Vis NIR (Model V-670) spectrophotometer shown in Figure 3 depicts a reduction in transmittance in the visible range with the increase in RF power. This could be due to the large scattering taking place at the defects in the film [20]. The optical band gap calculated using Tauc plot for indirect transition for the doped film decreases as 3.33, 3.09, 2.98 and 2.87 eV with increase in RF power from 100 to 250 W. Gyorgy et al. [21] observed this kind of band gap narrowing for their WO_3 films with the decrease of oxygen pressure, and assigned that behavior to the oxygen deficient sub–stoichiometric WO_{3-y} which may be correlated to the formation of deep localized states in the band gap.

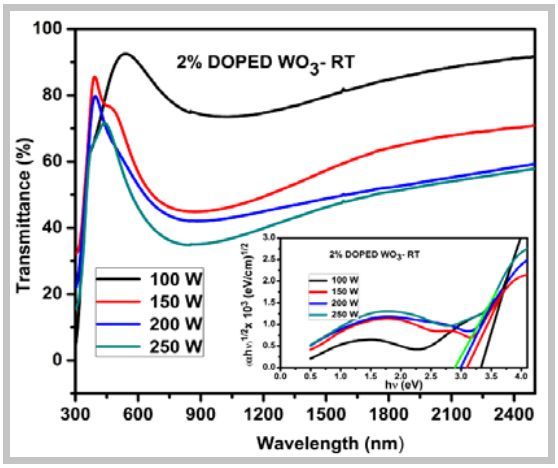

Figure 3: Transmission spectra of films.

FT-IR Study

FT-IR measurements performed in the spectral range of 400-4000 cm^{-1} by Shimadzu FT-IR Spectro-photometer. Figure 4 shows some characteristic bands such as: ν(HOH) and ν(OH) in the region of 3500-2800 cm^{-1}. The low range of spectra shown in the inset of Figure 3 also reveals the presence of less intense peaks of V-O stretching bond at 415 cm^{-1}, V-O-V bending vibrations at 459 cm^{-1}, ν(W-Ointer-W) and ν (W-Ointra-W) at 600-800 cm^{-1}. ν(W=O) around 1000-970 cm^{-1}, δ H_2O around 1660-1550 cm^{-1} and a clear Si-O bond due to Si substrate at 1070 cm^{-1} [22, 23].

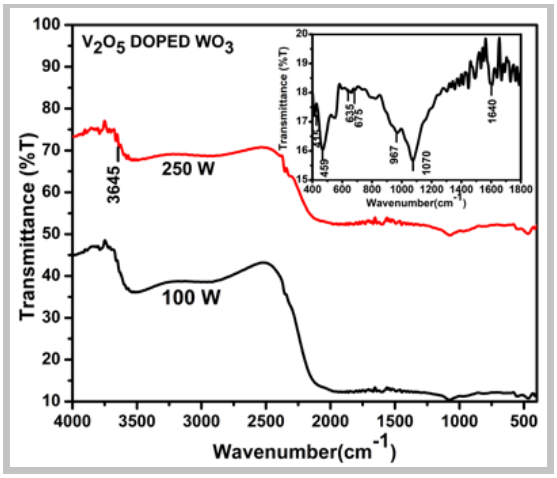

Figure 4: FT-IR spectra of doped films

(d) Electrochromic Studies

The potential was cycled from +1.5 to -1.5 V (versus SCE) at a potential sweep rate of 100 mV/s in 0.1 M ($LiClO_4$ + PC). During the potential sweep, the current resulting from ion intercalation and deintercalation was recorded and the variation is shown in Figure 5. At the cathodic potential (-1.5 V), the film is in the coloured state and at the anodic potential (+1.5 V), it returns to its bleached state. The dark blue coloration (more neutral grey) observed in films indicated the reduction of W^{6+} ionic state to the W^{5+} caused by Li^+ ions intercalation.

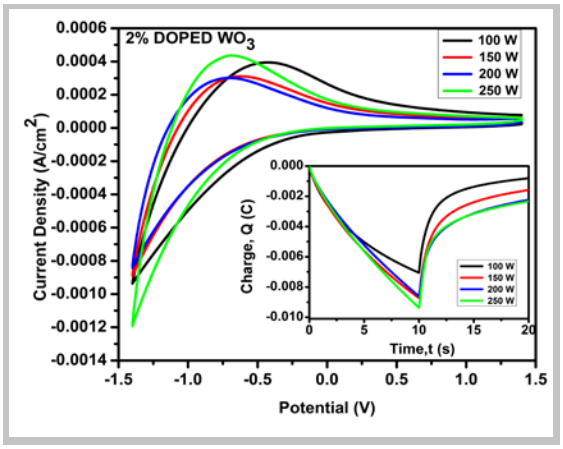

Figure 5: Cyclic Voltammograms and Chronocoulometry (inset) of the films.

During the anodic scan, oxidation of WO_3 (W^{5+} to W^{6+} states takes place with simultaneous deintercalation of Li^{i+} ions and e^- from the film and a transparent (bleached) state is obtained. The CV curves display typical amorphous WO_3 character of similar shape, with different area under the curves. Thus, it is inferred that all the samples undergo reduction–oxidation processes. Moreover, the one maximum and minimum in the redox currents suggested that the films have single intercalation site for Li^+ ion [24]. Ozer and Lampert [25] made similar observations in 0.1 M $LiClO_4$ /PC solution and reported that the shape of the CV curves for films with < 3.5 mol% V_2O_5 were similar to WO_3. Richardson et al., [26] stated that for compositions between 0 % and 10 % vanadium, the CVs resemble those of amorphous, pure tungsten oxide thin films. The observations made in our W-V-O films with 2 at% V_2O_5 agreed well with the literature reports.

The diffusion coefficient D for Li^+ ion intercalation is calculated from Randles – Servick equation [27]. The reversibility of the films is calculated from the ratio of amount of charge deintercalated (Q_{di}) to charge intercalated (Q_i) in the film. From the chronocoulometry and iono-optical studies the reversibility, optical density and coloration efficiency are calculated and tabulated in Table 1. Literatures revealed the presence of several defect states in amorphous WO_3 thin films, including W–O–H and W=O sites, which may act as intercalated ion trapping sites [28]. Since the structural, morphological and optical studies carried out in the present study confirmed such amorphous nature of the films with the presence of W–O–H and W=O sites, the as-deposited films showed good electrochromic performance. Noonuruk et al. in their studies on WO_3 thin films, reported that the sputtering power had considerable influence on the structural properties and electrochromic efficiency [29]. Similarly, in our studies it is observed that the film deposited with 100 W RF power revealed better electrochromic performance among all the as-deposited films.

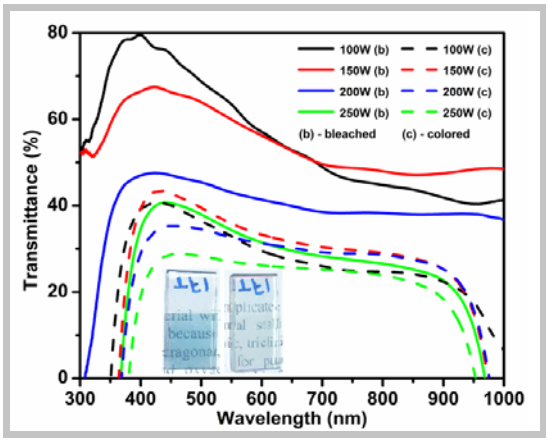

Figure 6: Transmittance spectra recorded at the bleached and colored states for the films at various RF powers.

Conclusion

V_2O_5 doped WO_3 thin films were deposited by RF magnetron sputtering technique at different RF powers. Structural and morphological studies revealed the amorphous homogenous nature of the films. Band gap narrowing was observed from the optical studies. Electrochromic measurements revealed a decrease in the reversibility and coloration efficiency with the increase in RF power. Mixed tungsten-vanadium oxide (WO_3:V_2O_5 – 98:2 %) thin films deposited at 100 RF power unveiled maximum coloration efficiency (75.63 cm^2C^{-1}) suitable for smart window applications to meet out today's energy management.

Table 1: Various electrochromic parameters calculated from CV and CC studies.

RF Power (W)	Anodic peak current i_{pa} (A) x10^{-4}	Diffusion Coefficient D (cm^2/s) x10^{-14}	Q_i (C)	Q_{di} (C)	% Reversibility (Q_{di}/Q_i)	Optical density (ΔOD) = $\ln(T_b/T_c)$	Coloration efficiency = $\Delta OD/Q_i$ (cm^2C^{-1})
100	3.9572	8.5251	0.00705	0.00625	88.65	0.5336	75.63
150	3.1219	5.3043	0.00873	0.00715	81.90	0.6262	71.61
200	3.0381	4.9912	0.00861	0.00637	73.98	0.3921	45.54
250	4.3812	10.379	0.00938	0.00693	73.81	0.3805	40.55

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References

1. CE Patil, NL Tarwal, P.R. Jadhav, P.S. Shinde, H.P. Deshmukh, M.M. Karanjkar, et al. Electrochromic performance of the mixed V_2O_5–WO_3 thin films synthesized by pulsed spray pyrolysis technique. Curr Appl Phys. 2014; 14: 389-395. [Crossref]
2. T. Nanba, M.Ishikawa, Y. Sakai and Y. Miura. Changes in atomic and electronic structures of amorphous WO_3 films due to electrochemical ion insertion. Thin Solid Films. 2003; 445: 175-181. [Crossref]
3. Y.M. Hunge, M.A. Mahadik, A.V. Moholkar and C.H. Bhosale. Photoelectrocatalytic degradation of phthalic acid using spray deposited stratified WO_3/ZnO thin films under sunlight illumination. Appl Surf Sci. 2017; 420: 764-772. [Crossref]
4. Y.M. Hunge. Sunlight assisted photoelectrocatalytic degradation of benzoic acid using stratified WO_3/TiO_2 thin films. Ceramics International. 2017; 43: 10089- 10096. [Crossref]
5. Y. M. Hunge, M. A. Mahadik, R. N. Bulakhe, S. P. Yadav, J.J. Shim, A. V. Moholkar , et al. Oxidative degradation of benzoic acid using spray deposited WO_3/TiO_2 thin films. J Mater Sci: Mater Electron. 2017; 28: 17976-17984. [Crossref]
6. Y.M. Hunge, M.A. Mahadik, A.V. Moholkar and C.H. Bhosale. Photoelectrocatalytic degradation of oxalic acid using WO_3 and stratified WO_3/TiO_2 photocatalysts under sunlight illumination. Ultrason Sonochem. 2017; 35: 233-242. [Crossref]
7. K. Muthu Karuppasamy and A. Subrahmanyam,. Results on the electrochromic and photocatalytic properties of vanadium doped tungsten oxide thin films prepared by reactive dc magnetron sputtering technique . J Phys. D: Appl. Phys. 2008; 41: 035302. [Crossref]
8. V. Madhavin, P. Kondaiah, O.M. Hussain and S. Uthanna. Structural, optical and electrochromic properties of RF magnetron sputtered WO_3 thin films. Phys B. 2014; 454: 141-147. [Crossref]
9. H. Kamal, A. A. Akl and K. Abdel-Hady. Phys B. Influence of proton insertion on the conductivity, structural and optical properties of amorphous and crystalline electrochromic WO_3 films. 2004; 349: 192. [Crossref]
10. M. Bertus, A. Enesca and A. Duta. Influence of spray pyrolysis deposition parameters on the optoelectronic properties of WO_3 thin films. Thin Solid Films. 2012; 20: 4282. [Crossref]
11. W. Yong, H. L. Zhang, H. T. Cao, T. Tian, J. H. Gao, L. Y. Liang, et al. Effect of post-annealing on structural and electrochromic properties of Mo-doped V_2O_5 thin filmsJ. Sol-Gel Sci. Technol., 2016; 77: 604-609. [Crossref]
12. Y. Wei, Zhou, J. Zheng and C. Xu. Improved stability of electrochromic devices using Ti-doped V_2O_5 film Electrochimica Acta. 2015;166: 277-284. [Crossref]
13. D. Vernardou, P. Paterakis, H. Drocos, E. Spanakis, I. M. Povey, M. E. Pemble, et al. A study of the electrochemical performance of vanadium oxide thin films grown by atmospheric pressure chemical vapour deposition. Solar Energy Materials & Solar Cells. 2011; 95:2842-2847. [Crossref]
14. A. Rougier and A. Blyr. Electrochromic properties of vanadium tungsten oxide thin films grown by pulsed laser deposition. Electrochimica Acta. 2001;46: 1945-1950. [Crossref]
15. E. Ozkan and F. Z. Tepehan, Solar energy Materials & Solar Cells. 2001; 68: 256. [Crossref]
16. X. He, J. Li and X. Gao, Sensors and Actuators B. 2005;108: 201. [Crossref]
17. Se-Hee Lee, Hyeonsik M. Cheong, Ji-Guang Zhang, Angelo Mascarenhas, David K. Benson, and Satyen K. Deb, Electrochromic mechanism in a-WO_3−y thin films Appl. Phys. Lett. 1999, 74; 242. [Crossref]
18. Z. Jiang, N. Jiamiao, Z. Xinjian and X. Yuli, Journal of Wuhan University of Tech – Mater Sci. 2011; 26:388-392. [Crossref]
19. V. Bellitto, "Atomic Force Microscopy - Imaging, Measuring and Manipulating Surfaces at the Atomic Scale", In Tech Europe, Chapter 7. 2012;147. [Crossref]
20. Mohit Agarwal, Pankaj Modi and R.O. Dusane. Study of Electrical, Optical and Structural Properties of Al- Doped ZnO Thin Films on PEN Substrates. J. Nano-Electron. Phys. 2013; 5: 02027. [Crossref]
21. E. Gyorgy and A. Perez del Pino. Tunable optical and nano-scale electrical properties of WO_3 and Ag-WO_3 nanocomposite thin films J Mater Sci. 2011; 46: 3560. [Crossref]
22. R. Vijayalakshmi, C. Sanjeeviraja and M. Jayachandran. Structural, electrochromic and FT-IR studies on electrodeposited tungsten trioxide films Curr Appl Phys. 2003; 3:171. [Crossref]
23. G Boduroy, T Ivanoval, M Aleksandrova and K A Gesheval, J Phys.: Conference Series, 356 (2012) 012016. [Crossref]
24. G. J. Fang, K. L. Yao and Z. L. Liu. Fabrication and electrochromic properties of double layer WO_3(V)/V_2O_5(Ti) thin films prepared by pulsed laser ablation technique. Thin Solid Films. 2001; 394:64. [Crossref]
25. N.Ozer and C.M. Lampert, Electrochromic performance of sol-gel deposited WO_3-V_2O_5 films. Thin Solid Films. 1999; 349:205. [Crossref]
26. T. Richardson, K. VonRottkay, J. Slack, F. Machalak and M. Rubin, Proc. Electrochem. Soc., 98 (1999) 26. [Crossref]
27. J.M.O-Rueda de Leon, D. R. Acosta, U. Pal and L.Castaneda. Improving electrochromic behavior of spray pyrolised WO_3 thin solid films by Mo doping Electrochimica Acta. 2011; 56: 2599-2605. [Crossref]
28. S R Bathe and P S Patil. Electrochromic characteristics of pulsed spray pyrolyzed polycrystalline WO_3 thin films. Smart Mater. Struct.2008; 18: 025004. [Crossref]
29. R. Noonuruk, K. Paipitak, M. Horprathum, W. Techitdheera, S. Porntheeraphat, W. Pecharapa, et al. Effect of Sputtering Power on Physical Properties and Electrochromic Performance of Sputtered WO_3 Thin Films Adv Mater Res. 2013; 802: 69. [Crossref]