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Effect of RF Power on the Structuraland Optical characterization of (WO3)0.90(V2O5)0.10 Thin Films

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Abstract : Tungsten oxide is one of the salient n-type semiconducting oxide materials having wide band gap energy (2.6–3.6 eV). Tungsten oxide thin films can be modified by doping V2O5 to achieve neutral coloring. In this present work V2O5 doped tungsten oxide thin films are prepared on glass substrates using RF magnetron sputtering by varying the sputtering parameters such as RF power(100, 150, 200 and 250 W) and substrate temperatures (RT and 300°C) with a constant chamber pressure of 10^{-3} mbar with a target of diameter 50 mm and thickness of 5mm. Thin films of (WO3)1-x(V2O5)x, were coated on glass substrates. The effect of RF power on the structural and optical properties of films was investigated by X-ray diffraction (XRD), AFM, Micro Raman, Photoluminescence and UV-Visible spectrophotometry. The X-ray diffraction analysis indicates a highly amorphous structure for all the films. The atomic force microscopy analysis shows a porous free morphology with homogeneity and uniformity on the films surface. Raman studies revealed no significant peaks corresponding to the compounds of vanadium due to doping. Room temperature photoluminescence characterizations revealed the presence of strong emissions in the near UV (375 nm) and blue (418 nm) regions when excited at 275 nm. The UV-visible transmittance spectra showed decrease in transmittance with the increase of RF power and the influence of RF power on the optical band gaps are calculated.

Key Words: RF sputtering, Thin films, Photoluminescence, Optical properties.

Introduction

Over a period of years, tungsten oxide (WO₃) has been widely studied because of its attracting physical and chemical properties. Tungsten oxide provides wide range of applications such as electrochromic smart windows, infrared switching devices, photo-catalysis, writing-reading and erasing optical devices and gas sensors[1]. WO₃ is probably the most widely studied electrochromic material, especially in an amorphous state. The literature survey of WO₃ based materials reveals that its electrochromism and photocatalytic properties are closely related with the composition, morphology, particle dimension, porosity and optical characteristics of WO₃ films and powders[2]. Two or three different composite systems WO₃ films th a t synergistically interact can be combined to provide an improvement in the desired functionality of WO₃ films[3]. It has been proved that addition of small amount of another oxide to WO₃ can change its (i) structural properties than promoting or

inhibiting the cluster growth during deposition and (ii) electrical conductivity due to exchange of electrons between the dopant and the host. High efficiency in photocatalytic property can be achieved by optimizing the semiconducting band gap. Advantages of WO3 films are its high coloration efficiency, reasonable stability and comparatively low cost. Due to the prominent reversible field aided ion intercalation property of WO3, ions such

as Li^+ , H^+ , Na^+ and K^+ can be easily incorporated into the host WO3 lattice. This incorporation results in suitable changes of its electronic and optical properties. These properties can be effectively used in electrochromic devices[4]. For smart window application that is based on the electrochromic property of WO3 thin films, a neutral gray is more suitable than the bright blue color of WO3 films in the reduced state[5]. Vanadium pentoxide (V2O5) on the other hand has both electrochromic and photocatalytic properties and their proper mixture composition would exhibit a more neutral color than the simple WO3 films[6]. V2O5 mixed WO3 films are more neutral in color than pure WO3 films[7].

Among the various thin film deposition techniques, RF magnetron sputtering has been used for deposition of uniform films on larger area substrates. The aim of this present work is to study the influence of doping of 10% V2O5 with WO3 in modifying the structural and optical properties of the pure WO3 thin films prepared by RF magnetron sputtering process and analyze its use for electrochromic applications.

Materials and Methods

Target preparation:

(WO3)0.90(V2O5)0.10 targets was prepared from high purity 99.9% (Sigma Aldrich) WO3 and V2O5 powders. The powders were mixed well in a ball milling machine (FRITSCH,Pulverisette-6) for 15 hours. The mixture prepared at different mixing times (i.e., 6, 11 and 15 hours) was analyzed using X-ray diffractometer (MPD Diffractometer, PANalytical, X'PertPro, Netherlands) with CuK α radiation in the 2 θ range from 10 to 80° to verify the homogeneity of the mixture. Finally, the mixture was pressed in to sputtering target having a diameter of 50 mm and thickness of 5 mm. The target was sintered at 700 °C for 8 hours in a vacuum atmospheric furnace to get a homogenized ceramic target.

Experimental Analysis:

Thin films were coated on pre-cleaned microscopic glass substrates using planar magnetron RF sputtering unit (Hind Hivac, Model-12 MSPT). The depositions were carried out for various RF powers such as 100, 150, 200 and 250 W at RT and 300 °C. The substrate was kept at a distance of 6 cm from the target. Argon

gas was used as the sputtering gas. The chamber was properly cleaned and the pressure was maintained at 10

³mbar. The argon gas flow and the impedance matching network were adjusted for maintaining this pressure and keeping zero reflection power to the RF magnetron respectively.

The films were X-ray analyzed to identify their crystal structure. The topography of the films were analyzed with the AFM (Model: XE70, Park Systems -S. Korea). The Raman spectrum was recorded in the range of 200 to 1200 cm⁻¹ using STR Raman spectrometer system (SEKI TECHNOTRON Corporation, Tokyo) with 514.5 nm line of an argon gas laser at a power level of 100 mW. Photoluminescence (PL) spectra were recorded using Varian Cary Eclipse Fluorescence Spectrophotometer with Xe flash lamp as the source of excitation. The transmittance spectra of the films were analyzed in the wave length range of 300–2500 nm using JASCO V-670 UV-Vis-NIR spectrophotometer.

Results and Discussion

Structural studies:

Figure 1 shows the X-ray Diffractogram patterns of (WO3)0.90(V2O5)0.10 powder analyzed for various time intervals of ball milling i.e.,6, 11 and 15 hours. Presence of peak around 20.23° corresponding to V2O5 in addition to the usual peaks of WO3 was observed.

It is also observed that the peak of V2O5 diminished as the time of grinding period was increased. The X-ray diffraction pattern of the mixed powder indicated the presence of monoclinic WO3 (JCPDS #830950). Then the powder was pressed with 20 kg/cm² pressure into sputtering target having thicknesses of 5 mm and diameter of 50mm. After sintering, even this peak at 20.315° vanished and a thorough homogeneity of the as-prepared target was obtained. The as-deposited films using (WO3)0.90(V2O5)0.10 target were amorphous for various RF powers at RT and 300 °C as substrate temperature.



Figure 1. XRD patterns of (WO3)0.90(V2O5)0.10 powder

Morphological studies

The surface topography of an area of $2.5X2.5 \ \mu\text{m}^2$ of the films was studied using AFM. Figure 2 (a, b) shows the 3D AFM micrographs of (WO3)0.90(V2O5)0.10 thin films deposited at 250 W-RT and at the substrate temperature of 300°C. The atomic force microscopy analysis showed a porous free morphology with homogeneity and uniformity on the films surface, characteristic for equal nucleation and growth rates during deposition. The film surface exhibited no apparent cracking. The room temperature deposited film exhibited large nicely separated conical columnar growth combined with large needle like grains throughout the surface with coalescence of some columnar grains at few places. At low temperatures (RT), as the thermal energy does not provide enough mobility to the sputtered species, as they condense on the substrate surface, they may remain stuck to the regions where they impinge[8]. It showed an average particle size of 7-8 nm and rms roughness of~9.9 nm. As the species mobility on the surface increases, the film deposited at 300 °C showed a fine, rather uniform micro structure distribution with an average particle size of 6-7 nm and rms roughness of~8.4 nm. The decrease in surface roughness of the deposited films with higher substrate temperature is due to the growth of grains with favorable orientation dictated by surface and grain boundary diffusivity, ad-atom mobility, film thickness and induced thermal stress[9].



Figure 2. AFM images of the films deposited with 250 W RF power at (a) RT and (b) 300°C as substrate temperature.

Raman Studies:

Raman spectroscopy can be used for the phase analysis of $(WO_3)_{0.90}(V_2O_5)_{0.10}$ thin films. Not only the identification of different oxide phases but also the detection of H₂O molecules is possible with aid of this technique. Raman bands of transition metal oxide in the range 950–1050 cm⁻¹ were attributed to asymmetric stretching mode (v_s) of short terminal M=O bonds. The bands in the range750–950cm⁻¹ were assigned to either the anti-symmetric stretching bonds (v_{as}) of M-O-M, or the symmetric stretching bonds (v_s) of –O-M-O-[10]. Figure 3 (a, b) depicted the Raman spectrum of V₂O₅ doped WO₃ films deposited at various RF powers at room temperature and at the substrate temperature of 300 °C. According to the literature two characteristic bands were associated with WO₃. The first band (200-500cm⁻¹) was attributed to the O-W-O bending modes and the second band was associated with the stretching modes. These bands exhibited weak peaks, the features of films having an amorphous nature[12]. In Figure 3(a) with 100 W and 150 W RF power, the Raman spectrum of V₂O₅ doped WO₃ showed one broadband in the low frequency region. The high frequency region has one distinct band at 960 cm⁻¹ and a less intense band at 807 cm⁻¹. No typical peaks of crystalline WO₃ had been recorded. For 200 W RF power, a peak around 270 cm⁻¹ appeared in the low frequency region and the other two peaks in the high frequency region became prominent.



Figure 3. Raman spectra of the films prepared at (a) RT and (b) 300° C as substrate temperature.

The two peaks at 950 cm⁻¹ and 807 cm⁻¹ were associated to the vibrations of the $W^{6+}=O$ and $W^{6+}-O$ bonds respectively[5]. These peaks were usually assigned to the stretching frequency modes of bridging oxygen W=O and O-W-O respectively[12]. Amorphous and nano-structured WO3 films were usually composed of O-W-O mode, similar to the WO6 octahedral structure of the bulk crystal with terminal W=O on their boundaries[13]. The peak at 950 cm⁻¹ is contributed to the W⁶⁺=O stretching mode of terminal oxygen atoms on the surface of the cluster and micro-void structures in the film. Since this double bond is stronger than the W⁶⁺-O single bond, its vibration frequency is expected to be higher than that of the bond. There is no peak corresponding to this in the Raman spectrum of crystalline WO3, because a crystal does not have double bond[5]. The W=O terminal stretching belongs to the W–O bonds at the free surface of internal grains and is due to the absorbed water molecules which can be frequently observed in sputtered or evaporated films at lower temperature[10].

As the RF power was increased to 250 W, the broad band in the high frequency region started to split into three distinct peaks at 697 cm⁻¹, 807cm⁻¹and 950cm⁻¹. The peak at 950 cm⁻¹ assigned to the stretching mode of terminal W^{6+} =O bond was shifted to the high frequency (~974cm⁻¹). It was inferred that the vanadium substitution at W^{6+} site might have a stronger interaction with the terminal oxygen atoms[14]. This shift was associated with the shortening of O-W-O bonds[15] corresponding to the slightly smaller cell parameters of V2O5 doped WO3 film when compared to the pure WO3 film[16]. No peaks were found corresponding to the stretching modes of V3–O (520cm⁻¹), V2–O (650cm⁻¹) and V⁵⁺= O (1027cm⁻¹) [14]. The films deposited at 300 °C substrate temperature (Fig. 3(b)) almost showed the same kind of Raman spectrum except with the difference of peak intensity.

Photoluminescence Studies:

Figure 4(a,b) indicated the PL spectrum in the range of 275 to 525 nm for the (WO3) $0.90(V_2O5)0.10$ films deposited at different RF powers at RT and at a substrate temperature of 300 °C. As the excitation energy (275 nm/4.52 eV) used is higher than the band gap energy (3.11-2.64 eV), it is easy for an electron in the valence

band to be directly excited to the conduction band (more likely to be excited to the localized levels within the forbidden gap) [17]. The spectrum revealed PL emissions near UV and visible (blue and blue green) regions with several shoulder peaks. As WO3 was an indirect bandgap semiconductor, its thin films did not show strong luminescence[18]. The UV luminescence band can be ascribed to the strong near–band–edge (NBE) emission due to the free–electron recombination in the films and visible light emission by transitions of excited optical centers in the deep levels. The presence of impurities in the films is normally responsible for the deep level emission. The near ultraviolet emission at 375 nm giving an energy band gap of 3.3 eV was nearer to the reported values of either 361 nm or 390 nm[19]. Similar PL peak had been detected for thermally evaporated W18O49 nanowires and they assigned the strong luminescence to the quantum effect[21]. The blue emission at 418 nm and blue green emission at 488 nm were also close to the reported results[21]. These emission peaks could be attributed to band-band transition and localized state induced by the presence of oxygen vacancies or defects[18]. The PL intensity of these films decreased as the RF power was increased. The variation in the intensities of the peaks with respect to the RF power was due to the excessive WO3 species that functioned as recombination centers rather than charge transports of the charge carriers[22].



Figure 4. PL spectra of the films prepared at (a) RT and (b) 300° C as substrate temperature

UV Studies:

Figure 5(a) shows the optical transmittance of the (WO3)0.90(V2O5)0.10 thin films. It showed a decrease in transmittance when the RF power was increased. Decrease in transmittance was visibly seen in the thin films ranging from colorless to the opted color progressively (Brown for 10% V2O5 doped WO3) while the RF power was increased[7]. The interference fringes in transmittance spectra indicated that the films were smooth with little scatter. The transmission spectra of the films showed a relatively sharp absorption edge near 300 nm. A strong absorption normally would occur due to the electronic band transitions of carriers[23]. The band gap energy (Eg) of the films was determined from the Tauc plot using the relationship as given in Eq.(1).

$$\alpha hv = A(hv - Eg)^{\eta}$$

(1)

where hv is the incident photon energy, A is a constant, α is the absorption coefficient and η is an exponent.



Figure 5. (a,b) Transmittance spectra and Tauc plot of the films deposited at RT.

Figure 5(b) shows the extrapolation of the straight line portion of the curve along the photon energy to estimate the optical energy band gap. The optical band gap calculated using Tauc plot for indirect transition for the films deposited at RT decreases as 2.97, 2.88, 2.75 and 2.64 eV with increase in RF power from 100 to 250 W. This kind of band gap narrowing was observed by Gyorgy et al., (2011) for their WO3 films with the decrease of oxygen pressure, and assigned that behavior to the oxygen deficient sub–stoichiometric WO3-y which may be correlated to the formation of deep localized states in the band gap[24]. Films deposited at 300 °C substrate temperature also showed this kind of decrement in their band gaps for indirect transition (3.11–2.97 eV).

Conclusion

Thin films of $(WO_3)_{0.90}(V_2O_5)_{0.10}$ deposited by RF sputtering on glass substrates were amorphous. Raman studies revealed the existence of no secondary peaks of Vanadium due to V₂O₅ doping. V₂O₅ does not appear as a separate dispersed compound or as a catalyst on the surface. The doped V₂O₅ is completely incorporated into the host WO₃ matrix. The optical emissions (PL) can be assigned to the localized states of the oxygen vacancies and surface states. Influence of RF power on transparency of the films was also studied. Energy band gap narrowing was observed for (WO₃)_{0.90}(V₂O₅)_{0.10} thin films.

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References

- 1. Song X C, Yang E, Liu Z S,Chen H F, Wang Y, Preparation and photocatalytic activity of Mo doped WO3 nano wires, J. Nano Part Res., 2010, 12,2813-2819.
- 2. Bica E, Tungsten tri oxide unconventional materials with special optical and electrical properties, Thesis submitted in the faculty of Chemistry and Chemical Engineering, University Cluj-Napoca, Romania, 2011.
- 3. Charles W. Dunnill, Sacha Noimark, Ivan P. Parkin, Silver loaded WO_{3-x}/TiO₂ composite multifunctional thin films, Thin Solid Films, 2012, 520,5516-5520.
- 4. Xilian Sun, Zhimin Liu, Hangtao Cao, Electrochromic properties of N-doped tungsten oxide thin films prepared by reactive DC-pulsed sputtering, Thin Solid Films, 2011, 519, 3032-3036.
- 5. Guo Jia Fang, Kai-Lun Yao, Zu-Li Liu, Fabrication and electrochromic properties of double layer WO₃(V)/V₂O₅(Ti) thin films prepared by pulsed laser ablation technique, Thin Solid Films, 2001, 394,64-71.
- 6. Ranjbar M, Mahdavi S M, Irajizad A, Pulsed laser deposition of W-V-O composite films: Preparation, Characterization and gasochromic studies, Solar Energy Materials and Solar Cells, 2008, 92,878-883.
- 7. Richardson T J, Rottkay K V, Slack J, Michalak F and Rubin M, Tungsten-vanadium oxide sputtered films for electrochromic devices, Proc. Electrochem. Soc., 1999, 98,26.
- 8. Felicia S. Manciu, Young Yun, William G. Durrer, James Howard, Ute Schmidt, Chintalapalle V. Ramana, Comparative microscopic and spectroscopic analysis of temperature-dependent growth of WO3 and W0.95Ti0.05O3 thin films, J. Mater. Sci.,2012, 47,6593–6600
- 9. Derbali L, Ezzaouia H, Efficiency improvement of multi crystalline silicon solar cells after surface and grain boundaries passivation using vanadium oxide, Material Science and Engineering B, 2012, 177, 1003-1008
- 10. Diaz-Reyes. J, Dorantes-Garcia. V, Perez-Benitez. A, Balderas-Lopez. J. A., Obtaining of films of tungsten oxide (WO3) by resistive heating of tungsten filament, Superficiesy Vacio, 2008, 21,12-17.
- 11. Tuquabo Tesfamichael, Andrea Ponzoni, Mohammed Ahsan, Guido Faglia, Thin film deposition and characterization of pure and Iron doped electron beam evaporated Tungsten oxide for gas sensors, Thin Solid Films, 2012, 518, 4791-4797.
- Legore L Jetal., Defects and morphology of tungsten trioxide thin films, Thin Solid Films, 2002, 406,79-86.

- 13. Baserga A, Russo V, Di Fonzo F, Bailini A, Cattaneo D, Casari C. S, Li Bassi A, Bottani C. E, Nano structured tungsten oxide with controlled properties: Synthesis and Raman characterization, Thin Solid Films, 2007, 515,6465-6469.
- 14. Muthu Karuppasamy K and Subramanyam A, Results on the electrochromic and photocatalytic properties of vanadium doped tungsten oxide thin films prepared by reactive dc magnetron sputtering technique, Journal of Physics D: Applied Physics, 2007,41, 035302.
- 15. Guery C, Choquet C, Dujeancourt F, Tarascon J. M, Lassegues J. C, Infrared and X-ray studies of hydrogen intercalation in different tungsten trioxides and tungsten trioxide hydrates, Journal of Solid State Electrochemistry, 1997, 1,199-207.
- 16. Ahsan M, Tesfamichael T,Ionescu M, Bell J, Motta N, Low temperature CO sensitive nano-structured WO3 thin films doped with Fe, Sensors and Actuators B, 2012, 162,14-21.
- 17. Navas I, Vinodkumar R, Detty A. P, Mahadevan Pillai V. P, Intense photoluminescence from nanostructured MoO3 films, ICOP International Conference on Optics and Photonics, 2009.
- 18. Feng M, Pan A L, Zhang H R, Li Z A, Liu F, Liu H. W, Shi D. X, Zou B. S, Gao H. J, Strong photoluminescence of nano-structured crystalline tungsten oxide thin films, Appl. Phys. Lett., 2005, 86,141901.
- 19. Kunquan Hong, Maohai Xie, Rong Huand Huasheng Wu, Synthesizing tungsten oxide nanowires by a thermal evaporation method, Appl. Phys. Lett., 2007, 90,173121.
- 20. Sunghoon Park, Hyunsu Kim, Changhyun Jin, Chongmu Lee, Intense ultraviolet emission from needle like WO3 nanostructures synthesized by non-catalytic thermal evaporation, Nanoscale Research Letters, 2011, 6,451.
- Lin C Y, Hsiao C H, Huang B R, Young S J, Chang S J, Chen T P, Synthesis of tungsten oxide thin film by Sol-Gel method and the fabrication UV photodetector, The Electrochemical Society, Abstract #91, 219 th ECS Meeting, 2011.
- 22. Chin Wei Laiand Srimala Sreekantan, Optimized sputtering power to incorporate WO3 into C-TiO2 nanotubes for highly visible photoresponse performance, NANO: Brief Reports and Reviews, 2012, 7, 6, 1250051.
- 23. Anup Thakur, Hanbyeol Yoo, Se-Jun Kang, Jae Yoon Baik, Ik-Jae Lee, Han-Koo Lee, Kijeong Kim, Bongsoo Kim, Seonghoon Jung, Jaehun Park, and Hyun-Joon Shinb Effects of Substrate Temperature on Structural, Electrical and Optical Properties of Amorphous In-Ga-Zn-O Thin Films, ECS Journal of Solid State Science and Technology, 2012, 1,Q11-Q15.
- 24. Gyorgy E, Perezdel Pino A, Tunable optical and nano-scale electrical properties of WO3 and Ag WO3 nano-composite thin films, J. Mater. Sci., 2011, 46, 3560-3567.
