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Effect of In_2O_3 Dopant on the Properties of V_2O_5 Thin Films Prepared by Vacuum Deposition on ITO Substrates

P. Yuvaraj¹, Anil Midathada², T.S. Senthil³, S. Pavithra⁴, N. Sivakumar⁵

^{1,4,5}PG and Research Department of Physics, Chikkaiah Naicker College, Erode, Tamilnadu 638004, India

²Fujairah Men's College, Higher College of Technology (HCT), P.O.Box: 4114, Fujairah, United Arab Emirates.

³Department of Physics, Erode Sengunthar Engineering College, Perundurai, Erode, Tamilnadu, 638057, India.

Abstract: Pure and In_2O_3 doped (4, and 8 wt. %) V_2O_5 thin films were deposited on ITO substrates at 300 °C by a vacuum deposition technique. The single phase relation of the In_2O_3 doped V_2O_5 systems were investigated by X-ray diffraction analysis. The crystallite size extracted from the XRD data supports the change in full width at half maximum due to the variation in In_2O_3 doping and the structure indexed with lattice parameters as orthorhombic. The FESEM images revealed the In_2O_3 doped V_2O_5 thin films showed granular. The obtained red shift in wavelength of UV absorption peak 300 to 900 nm confirmed the quantum confinement effect of In_2O_3 takes place in the V_2O_5 thin films at high dopant concentration level. Optical measurement showed that the band gap decreasing (from 3.96 to 3.6 eV) occurred dopant concentration increased.

I. INTRODUCTION

The ambition of the present investigation is the search for new phases showing properties of intellectual and eventual practical interest. Among the various metal oxides the promising candidate, which possesses an interesting catalytic properties of divalent metal vanadates (V) [1, 2], including cobalt (II) vanadates (V) [3, 4] have been recognized for many years. The variety of vanadium oxidation states ranging from 2+ to 5+, wide band gap, good thermal, chemical stability and also the unevenness of oxygen co-ordination geometry causes the two phases such as magnolia ($\text{V}_n\text{O}_{2n-1}$) and Wadsley ($\text{V}_{2n}\text{O}_{5n-2}$) helps to improve the performance of V_2O_5 cathode in lithium ion batteries [5, 6, 7]. The most stable form of the V-O system in the V_2O_5 was constructed the orthorhombic unit cell structure and also it shows a good resistive property to corrosion because of formation of a surface oxide film, hence it is not affected by water, air, acids at room temperature [8, 9]. Even though V_2O_5 system acquires all supporting qualities of the survival, the modest electronic conductivity is challenging one of the good electrodes [10, 11, 12]. Recently, indium oxide promoted vanadium pentoxide has been applied for various purposes, such as photo electrode conductive thin films. In the present investigation provides basic insights of V_2O_5 - In_2O_3 based upon their significance in the field energy storage as a primary concern. Amidst of various deposition techniques for film growth, the vacuum evaporation method which yields a high homogeneity surface and controls the deposition parameters gains attention [13-16]. Hence, this work focused to prepare the thin film for cathode application through the vacuum evaporation method and also it portrays structural, morphological and optical properties of the prepared film.

II. EXPERIMENTAL DETAILS

V_2O_5 powder (99.999% source powder purchased from Aldrich) were thermally deposited on the chemically cleaned ITO glass substrates in a vacuum of around 5.5×10^{-5} Torr using a HIND HIVAC coating unit (Model no. 12A4D). The size of substrates was 1.5cm x 9 cm x 0.1 cm and these substrates were cleaned before deposition with acetone followed by isopropyl alcohol and rinsed in deionized water. Source material was evaporated from a molybdenum boat at deposition rate 1 \AA/s and got a thickness of around 100 nm. The distance between molybdenum source and substrate holder was about 18 cm and also the thickness and deposition rates of the films were monitored in the Quartz crystal thickness monitor.

X-ray diffraction (XRD) measurements were carried out by Bruker AXS (D8 ADVANCE) under Cu $K\alpha$ (30 kV, 30 mA) radiation. The morphology of the surface, top-view and the fracture cross section of the specimens were observed using a Field Emission Scanning Electron Microscope (FE-SEM: SIGMA HV – Carl Zeiss with Bruker Quantax 200–Z10 EDS Detector). UV–VIS double beam absorbance spectra of the films were recorded in a Hitachi Corporation UV-2700 spectrophotometer. The vibration of samples were recorded by Raman Spectrometer using X-plora Horiba spectrometer (Horiba Jobin-Yvon, France) equipped with 532 nm solid state laser source and holographic grating of 1200 grooves/mm.

III. RESULTS AND DISCUSSION

A. XRD Analysis

The structural properties of the thin films were investigated by XRD measurements. Figure 1 shows the XRD patterns of pure and In_2O_3 doped V_2O_5 thin films. The characteristic peaks at 2θ values of 20.292° , 33.285° and 45.367° can be associated with (0 0 1), (1 1 1) and (4 1 1) planes respectively and it revealed the polycrystalline nature of the V_2O_5 thin films. The strong and dominant (0 0 1) orientation for the samples indicated that the thin film particles had a (0 0 1) growth direction, which were indexed to orthorhombic V_2O_5 phase (JCPDS 89-2482) having lattice parameters $a=11.544\text{\AA}$, $b=3.571\text{\AA}$ and $c=4.383\text{\AA}$. [17]

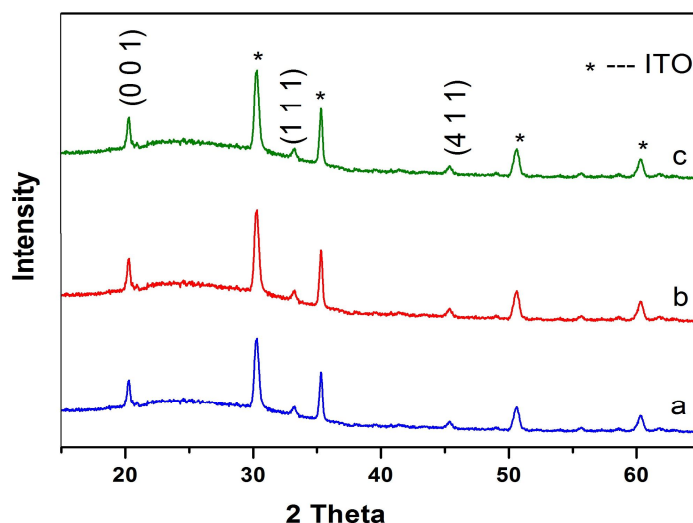


Fig.1. XRD patterns of Undoped V_2O_5 and In_2O_3 doped V_2O_5 thin films
(a) Undoped (b) 4 at % In_2O_3 (c) 8 at % In_2O_3

The diffraction peak at 20.38° indicated the crystalline of V_2O_5 phase with the space group $C2/c$. The d-spacing values of all diffraction peaks were identical to those of the orthorhombic crystalline phase V_2O_5 (Space Group: $Pmmn$) There is no significant change has been observed in the lattice parameters of the In_2O_3 doped V_2O_5 films which has been compared from the previous article[18]. From this study the absence of other peaks exposed the impurity was nil. Ashvani kumar et al [19] has observed that the high substrate temperature leads to higher oxygen vacancy in the V_2O_5 phase causing shift to lower valence state. The induced vacancy can go ahead to partial collapse of the V-O layer assisting the formation of VO_2 phase [20, 21].

The crystallite size is estimated using the Debye-Scherrer formula for the (0 0 1) reflection [22].

$$D = 0.9\lambda/\beta\cos\theta$$

where D is the crystallite size, λ is the wavelength of radiation (1.5406\AA), β is the full width half maximum (FWHM) in radian, and θ is the Bragg's angle of diffraction. It is observed that the crystallite size decreases from 46 to 32 nm with increase in In_2O_3 dopant concentration.

B. Surface Morphology studies

Figure 2 showed the magnified FESEM micrographs of typical V_2O_5 nanoparticles deposited at pure V_2O_5 thin films. It was seen that the variety of nanoparticles morphology of is inter connected with the formation of porous space in between them. From this, a large variety of nano structures randomly distributed over the film surface[23]. Figure 2(a) showed undoped V_2O_5 particles which had smooth and the formation of spherical shape with spongy bush like structure of different sizes aligned horizontally and distributed over the film surface also with different grain size and free of grain boundaries [24, 25]. By increasing In_2O_3 doped (4 and 8 wt %) in V_2O_5 samples (Fig. 2b and 2c), it was shown that the shape of the grains change into the mixed cubical and monoclinic phases. From the FESEM images, it was observed that the particle size range $\sim 32\text{ nm}$ for pure V_2O_5 samples and for In_2O_3 doped (4 and 8 wt %) samples $\sim 28\text{ nm}$ and $\sim 23\text{ nm}$ respectively. Therefore the addition of In_2O_3 in V_2O_5 resulted in a decrease in the average particle size.

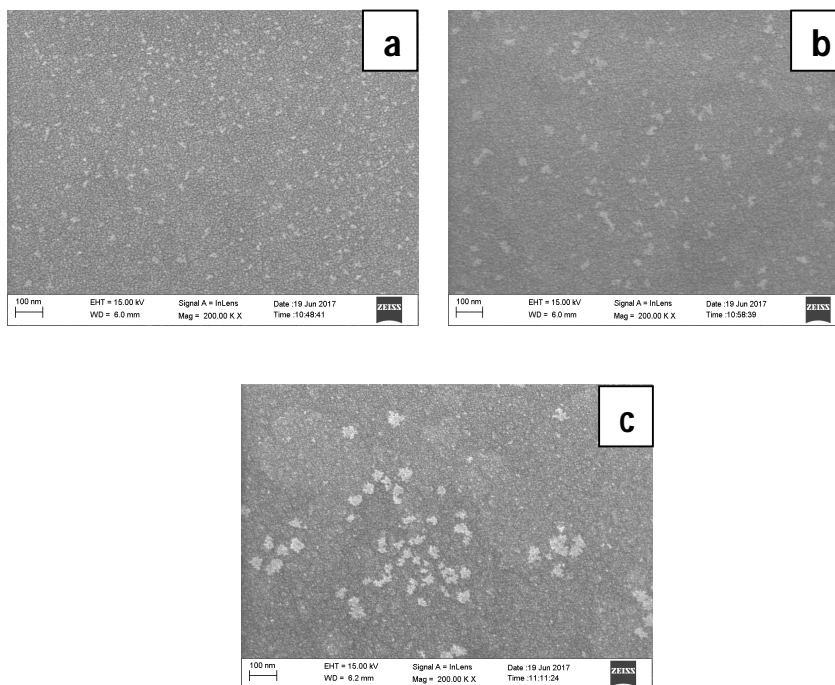


Fig.2. SEM images of Undoped V_2O_5 and In_2O_3 doped V_2O_5 thin films
(a) Undoped (b) 4 at % In_2O_3 (c) 8 at % In_2O_3

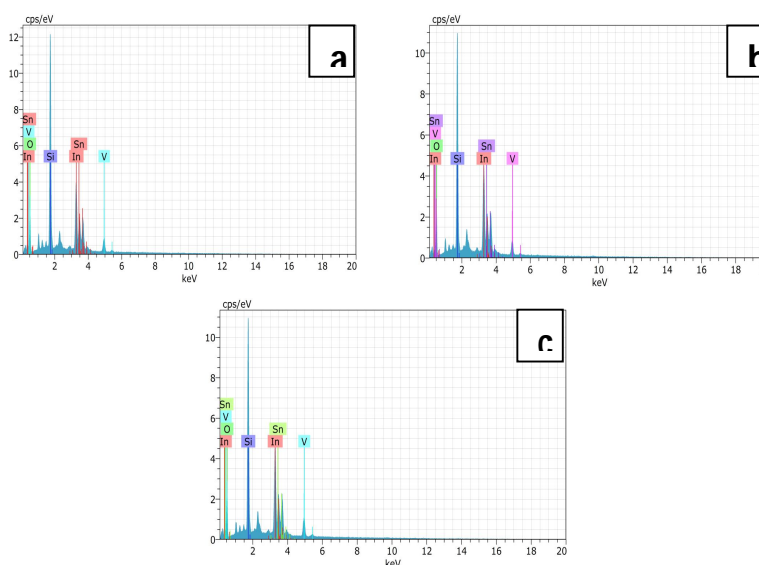


Fig.3. EDAX images of Undoped V_2O_5 and In_2O_3 doped V_2O_5 thin films
(a) Undoped (b) 4 at % In_2O_3 (c) 8 at % In_2O_3

Figure 3 shows the quantitative element compositions of the pure V_2O_5 and In_2O_3 doped samples were analyzed using an energy dispersive spectrometer. The scan shows (Fig. 3b and 3c) that indium peaks implying incorporation of niobium ions into V_2O_5 lattice.

C. Optical Properties

The UV absorbance spectra of the pure and In_2O_3 doped V_2O_5 thin film samples in the wavelength range of 300 to 900 nm are shown in figure 4. From the spectra, it has been clearly observed that the absorption edge shifted towards higher wavelengths with

an increase in doped of In_2O_3 . The value of absorbance is purely dependent on various factors like the size of particles, flaws, or deformities in grain structure and oxygen deficiency. As the doping concentration is increased from 0 to 8 mol % of In_2O_3 , the absorption edge is starting to shift towards higher wavelength (red shift) which means the band gap increases which results due to defects (strain) and hence leads to the reduction in crystallite size as discussed in the XRD analysis. Fig. 3 shows the absorption spectra of the pure and In_2O_3 doped V_2O_5 thin film with the absorption peaks at 313, 326 and 344 nm respectively. The band gap energy of pure and In_2O_3 doped V_2O_5 thin film has been calculated by using the relation $E_g = hc/\lambda$ and the calculated values 3.96, 3.8 and 3.6 are correspond to pure, 4, and 8% In_2O_3 doped V_2O_5 thin films respectively. The observed E_g value is in good agreement with the E_g value determined in literature [26]. From these values it is concluded that the band gap energy decreases with In_2O_3 doping, which shows a red shift in wavelength. The decrease in band gap from 3.96 to 3.6 eV is due to decrease or reduction in particle size due to changing of various dopants In_2O_3 , respectively, on V_2O_5 . This phenomenon of decrease in band gap energy (E_g) and absorption at the lesser wavelength can be explained on the basis of quantum confinement effect among the individual In_2O_3 doped V_2O_5 thin films.

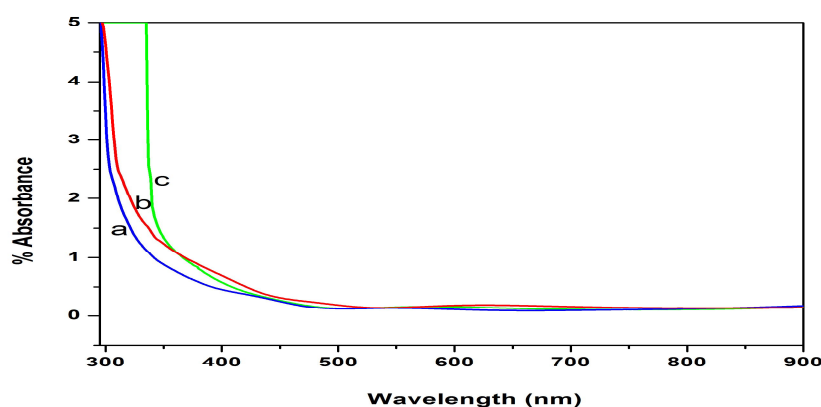


Fig.4. The Variation of % of Absorbance with Wavelength
(a) Undoped (b) 4 at % In_2O_3 (c) 8 at % In_2O_3

D. Raman Studies

The Raman spectra of the pure and In_2O_3 doped V_2O_5 thin film samples in the wavenumber range of 100 to 1100 cm^{-1} are shown in figure 5. The internal modes include V-O stretching vibrations in the 500-1000 cm^{-1} region and V-O-V bending vibrations in the range 200-500 cm^{-1} . The Raman spectrum of micro sized V_2O_5 exhibits seven peaks at 140, 270, 310, 390, 680, 840, 960 and 1090 cm^{-1} [27].

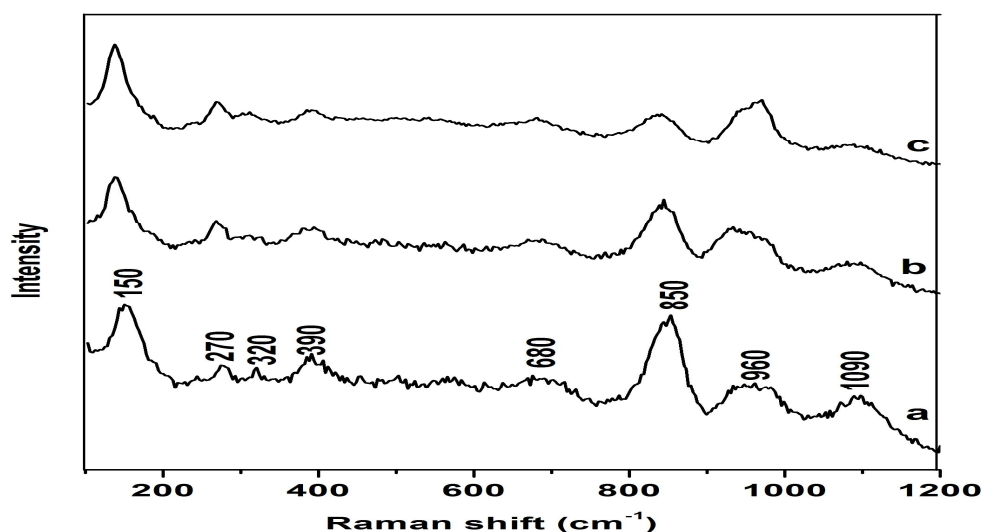


Fig.5. Raman spectra of Undoped V_2O_5 and In_2O_3 doped V_2O_5 thin films

(a) Undoped (b) 4 at % In_2O_3 (c) 8 at % In_2O_3

In our present studies, a band at 1090 cm^{-1} has been assigned to stretching vibration mode of V-O₁ bond along O axis. The narrow peaks 960 cm^{-1} are attributed to the stretching mode related to the A_g symmetric vibrations of the shortest vanadium-oxygen bond (vanadyl V=O). The new peak observed at 850 cm^{-1} is due to oxygen deficiency [28]. The band showing at 680 cm^{-1} has been assigned to (V₂-O) stretching mode which results from corner shared oxygen common to two pyramids. Each layer of V₂O₅ consists of VO₅ square pyramids that share edges and corners. The absence of two major bands at 520 cm^{-1} and 650 cm^{-1} confirms that V₄O bonds are not formed in this oxide film which as previously reported [29]. The lattice vibration mode seems to be very powerful at 140 cm^{-1} , indicating the organization of the long-range order in the mixed oxide film. The shifting of the 1090 cm^{-1} band to 1100 cm^{-1} for the In_2O_3 doped in V₂O₅ (Figure 6 c) indicating the lengthening of the O-V-O bond.

IV. CONCLUSION

Pure and In_2O_3 doped (2%, 4%, 6% and 8%) V₂O₅ thin films were developed on ITO substrates using the vacuum deposition technique at $300\text{ }^\circ\text{C}$. XRD analysis confirms the formation of polycrystalline orthorhombic structure with preferential orientation of (0 0 1). The surface morphology has been carried out using FE-SEM, and the image reveal, the particle size was decreases with the dopant of In_2O_3 . The elemental confirmation has been done by using EDAX for both pure and In_2O_3 doped V₂O₅. After In_2O_3 doping, the grain size was decreased and grain boundaries increased as the scattering center of lights increased which has been confirmed by UV. From the UV result, the optical band gap energy decreases from 3.96 to 3.6 eV. The Raman study indicates that, the shifting of 1092 cm^{-1} band to 1100 cm^{-1} for the doped In_2O_3 in V₂O₅ which represent the lengthening of O-V-O bond.

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