Structural, Morphological, and Optical Transitions in Pulsed Laser deposited V$_2$O$_5$–TiO$_2$ Transition Metal Oxide Nanocomposite Thin Films

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Abstract

We studied the influence of titanium dioxide (TiO$_2$) concentration on the structural and optical properties of vanadium pentoxide (V$_2$O$_5$) thin films deposited on amorphous glass substrate using pulsed laser deposition technique. TiO$_2$ doping into V$_2$O$_5$ matrix revealed an interesting morphological change from an array of high density pure V$_2$O$_5$ nanorods (~140 nm) to granular structure in TiO$_2$-doped V$_2$O$_5$ thin films. The results showed a significant improvement in the transmittance and refractive index in TiO$_2$ doped V$_2$O$_5$ thin films.

Keywords: Pulsed laser deposition; Nanocomposite thin films; Structural properties; Optical properties.

Introduction

The transition metal oxides attract a lot of attention due to their interesting physical, chemical, electronic, and optical properties which arise from the narrow d states as well as their hybridization with the ligand p orbital. The vanadium pentoxide (V$_2$O$_5$) has attracted considerable interest owing to their multivalency, layered structure, wide optical band gap, good chemical and thermal stability, and excellent thermoelectric property [1-3]. Scientific and technological applications of V$_2$O$_5$ thin films form includes electronic and optical switches [4], electro chromic devices [5], window for solar cell [6, 7], microelectronic devices [8], thin film batteries (TFB) [9]. V$_2$O$_5$ crystallizes with an orthorhombic unit cell structure and belongs to Pmmn space group with the lattice parameters a=11.51Å, b=3.56 Å and c= 4.3Å [10]. It is fundamentally comprised of VO$_6$ pyramids which form alternating double chain along the b-axis. Alternating double chains of pyramids up/pyramids-down are connected laterally by bridging oxygen to form a sheet or zig-zag ribbon in the a-b plane. The planes themselves are connected by Vander Waals bonds and this looser bonding creates easy cleavages parallel to that plane. V$_2$O$_5$ is an indirect semiconductor with a band gap of 2.3-2.4 eV, which stems from the split-off oxygen 2$p$ band up to vanadium 3$d$ band. Electronic conduction in V$_2$O$_5$ is highly anisotropic with conduction within the a-b planes considerably higher than conduction perpendicular to these planes.
Understanding the unique properties of V$_2$O$_5$ requires a great structural investigation especially in case of doping the oxide with other elements that may result in a change of morphology, structural arrangement and optical properties of this material. The structural stability of this V$_2$O$_5$ doped with guest atoms is also important because small amount of admixtures may strongly affect the reactivity of this oxide. The novel technology of the nanostructure material assembling provides the possibility of tailoring such materials with unique microstructure properties. The proper amount of transition metal doping could lead to optimal degree of non-stoichiometry for better performance. Since composites and mixed phases can have different properties than their constituent phases. Various metals like W, Pd, Mo, Mn have been used to dope the V$_2$O$_5$ for several applications like enhanced electrochemical performance, better intercalation property, improved cyclic stability, and various other electronic applications. But doping with Titanium dioxide (TiO$_2$) may significantly improve the photo catalytic applications of V$_2$O$_5$.

TiO$_2$ has been proven to be an effective material for applications such as photocatalysis [11], dye sensitized solar cell (DSSC) for photon harvesting [17]. Moreover, TiO$_2$ offers the advantage of energy alignment between the conduction and valance bands in the energy scale [16]. In the thin film form, TiO$_2$ is usually used in photovoltaic applications such as photo electrochemical system (PEC) and dye sensitized solar cell (DSSC) for photon harvesting [17].

Optical properties of the deposited films were studied using Varian Cary 5000 UV-VIS/NIR spectrometer with specular reflection attachment in the range between 300 nm and 800 nm having wavelength accuracy of ±2 nm and with scan speed 90 nm/min. The microstructure of the films was investigated using field emission scanning electron microscopy (FESEM) with an operating voltage of 20 keV and NTMDT atomic force microscopy (AFM) in semi-contact mode with silicon nitride (Si$_3$N$_4$) tip of 10 nm radius.

**Experimental Details**

For the deposition of pure V$_2$O$_5$, TiO$_2$, and V$_2$O$_5$-TiO$_2$ composite films (TiO$_2$ content from x = 0 to x = 100), 1-inch circular targets of these materials were prepared by the conventional solid-state reaction method. High purity V$_2$O$_5$ and TiO$_2$ powders were thoroughly mixed and calcined at 400°C and 1100°C respectively for 6 h in air. After calcination, V$_2$O$_5$ and TiO$_2$ powders were pressed into pellets and sintered at 650°C for 12 h and 1400°C for 4 h in air respectively. These target materials along with cleaned glass substrates were mounted in a pulsed laser deposition chamber followed by vacuum pumping to a base pressure of 10$^{-6}$Torr. The target-to-substrate distance was kept at 40 mm and substrates were heated to a temperature of 400°C. For thin film deposition, a pulsed laser beam generated by a KrF excimer laser at a wavelength of 248 nm and pulse duration of 25 ns was introduced into the deposition chamber through a quartz window and focused using an optical lens onto the target surface. The laser fluence on the target was 2-3 J/cm$^2$, while the repetition rate was fixed at 8 Hz. Before target ablation, pure oxygen was introduced and maintained at a pressure of 50 mTorr. Before every deposition, the target was pre-ablated for 2 min in order to ascertain the same state of the target in every deposition. The target holder was scanned in X-Y direction for uniform erosion of the target material. A post deposition annealing at 600°C for 30 min was performed after deposition.

Structural characterization of the films was carried out using a Bruker X-Ray of Cu Kα radiation (1.54Å) with the scanning speed of 2θ = 1°/min in the angle range between 10° and 60°. To obtain a profile fitting with good signal, a polycrystalline Si powder was used for instrumental correction.

**Results and Discussion**

**Structural properties**

Figure 1 shows the XRD pattern of bulk samples corresponding to pure V$_2$O$_5$, TiO$_2$, and V$_2$O$_5$/TiO$_2$ composite target materials used for the fabrication of nanocomposite films. Figure 2 shows the X-ray diffraction (XRD) pattern of composite (V$_2$O$_5$)$_{100-x}$-(TiO$_2$)$_x$ thin films with different TiO$_2$ content varying from x=0 to x=100. Samples A, B, C, D, and E represents the films with different TiO$_2$ contents, i.e. x=0, x=20, x=50, x=80, and x=100 respectively. Room temperature XRD pattern of pure V$_2$O$_5$ thin film (sample A) deposited at substrate temperature (T$_s$) of 400 °C exhibits peaks at 2θ=13.2°, 19.4° and 25.2°, which are attributed to the Bragg reflections from the (200), (001), and (102) planes, respectively and is indicative of the polycrystalline V$_2$O$_5$ films with orthorhombic crystal structure. It is worth noting that no
additional peaks of vanadium oxide phases were present in the XRD pattern, indicating the phase purity of these films. The XRD pattern of composite sample B with TiO$_2$ content ($x = 20$) shows dominant peaks at 14.5° and 28.82°, which corresponds to the (200) reflection from V$_2$O$_5$ and R(110) from TiO$_2$ planes, respectively. When TiO$_2$ content was increased to 50% (sample C), a significant increment in the intensity of both the planes were observed. The intensity of the peaks (200) & R (110) increases with the doping level, due to superior crystalline quality. With further increase in TiO$_2$ content ($x = 80$, sample D) peak at 28.82° (corresponds to rutile TiO$_2$) starts dominating and an additional peak at 44.081° corresponding to rutile TiO$_2$ of plane (111) is observed. It is worth noting that there is no peak corresponding to anatase phase when TiO$_2$ concentration is 50% and 80%. Thus, incorporation of TiO$_2$ in V$_2$O$_5$ leads to formation of rutile phase only.

XRD pattern of pure TiO$_2$ ($x = 100$ – sample E) shows peaks at 25.4°, 38.2° and 38.85° which corresponds to the reflections from anatase (101), (004) and rutile (200) respectively. It is observed that in pure TiO$_2$ anatase phase dominates above rutile phase at $T_S = 400$ °C. It could be attributed to different surface free energies associated with different phases. The crystallite size of different samples was estimated using Debye Sherrer’s formula:

$$d = \frac{0.9\lambda}{B\cos\theta_B}$$  \hspace{1cm} (1)

Where $\lambda$, $\theta_B$, and $B$ are the X-ray wavelength (1.54Å), Bragg diffraction angle and line width at half-maximum (FWHM), respectively [20]. The calculated values of crystallite size are depicted in Table 1. Figure 3(a–e) shows the FESEM images of films for samples A–E, respectively. A nanorod formation is clearly evident from the FESEM image of pure V$_2$O$_5$ film. It is because the annealing treatment provides sufficient thermal energy to activate crystallization. The observed nanorods formation can be interpreted as recrystallization process driven by minimization of surface energy. V$_2$O$_5$ has basal {001} planes bonded weakly to each other. The surface energy of the {001} atomic planes is, therefore, smallest because only a limited number of bonds is destroyed when the material is cleaved along these planes. According to the numerical simulation [21], the {001} planes have a value of surface energy of about 0.7 Jm$^{-2}$, which is significantly smaller than the calculated values for other lower energy surfaces. It is interesting to see that the morphology and the growth mechanism of these V$_2$O$_5$ nanorods are quite similar to those of the formation of zinc oxide nanorods [22]. So, we believe that surface diffusion (migration) plays an important role in the growth process of nanorods.

Table 1. Shows FWHM, crystallite size, grain size, $d$-spacing and phase present of the deposited composite thin films.
Furthermore, it should be noted that nanorods are not directly formed on glass substrate but on the underlying nanocrystalline V$_2$O$_5$ film. This implies that underlying film act as a nucleation site, with a reduced energy barrier, for the formation of nanorods. Due to annealing at high temperature ($T_s$ = 600 °C) the diameter of nanorods increases. It is interesting to note that surface morphology of the films undergoes a transformation from one-dimensional nanorods arrays to two-dimensional film with granular structure after incorporating TiO$_2$ content (20-80%) in V$_2$O$_5$ matrix as shown in Figure 3(a-e). It could be attributed to the fact that in the case of doped systems, the columnar (nanorods type) growth is always inhibited during incorporation of the doping element in to the matrix due to the formation of either defects or aggregation after doping. Thus, for the deposition of composite films, heterogeneous or homogeneous nucleation may occur on the substrate, and the coarsening process (through atomic diffusion) of small particles proceeds with difficulty, in contrast to the undoped V$_2$O$_5$ deposition at the same annealing temperature, due to the presence of TiO$_2$ doping element. Consequently, a granular rather than a columnar structure is formed. Figure 4 shows the crystallite size and grain size of samples calculated by XRD and FESEM analysis. It is worth to note that grain size shown by FESEM is much higher as compared to crystallite size calculated from the XRD results. It could be due to the fact that XRD gives the average mean crystallite size while FESEM showed agglomeration of the grains.

The surface topography of the films as studied by atomic force microscopy (AFM) revealed that laser ablated (V$_2$O$_5$)$_{100-x}$(TiO$_2$)$_x$ composite thin films were homogenous, smooth and uniform [Figure5(a-e)]. The average value of surface roughness was found to increase with increasing TiO$_2$ content [Table 1]. The image shows the different grain growth in shape and size with the changing TiO$_2$ content. The occurrence of the large size particles in our film is due to the incomplete elimination of the crater - like features on the target surface, which is caused by ultra-rapid evaporation of the target material. The AFM results are in agreement with the XRD and FESEM results. The film surfaces have no evident defaults such as impurity holes and cracks.

Figure 3. (a - e) FESEM morphology of (V$_2$O$_5$)$_{100-x}$(TiO$_2$)$_x$ composite thin films deposited at substrate temperature ($T_s$) = 400 °C for different TiO$_2$ composition (a) $x$=0; (b) $x$=20; (c) $x$=50; (d) $x$ = 80; (e) $x$=100.

Figure 4. Variation of crystallite size and grain size with the variation in TiO$_2$ Content.

Figure 5. (a - e) AFM images of (100-x) V$_2$O$_5$ - (x) TiO$_2$ composite thin films deposited at substrate temperature of 400°C for different TiO$_2$ composition (a) $x$=0; (b) $x$=20; (c) $x$=50; (d) $x$ = 80; (e) $x$=100.
Optical properties
Transmittance and absorbance measurements

The spectral variations of absorption and transmission for the \((\text{V}_2\text{O}_5)_{100-x}(\text{TiO}_2)_x\) composite thin films deposited onto glass substrate, with different TiO\(_2\) composition were measured over the wavelength range of 300–800 nm and are shown in [Figure 6(a,b)]. At \(x=0\) (pure V\(_2\)O\(_5\)), films show transmittance up to 50% in the visible range of electromagnetic spectrum. Lack of oscillations suggests that the films so formed are very thin. At \(x=50\) [Figure 6(b)], transmittance is 60%. With the incorporation of TiO\(_2\) there is gradual increase in transmittance as addition of TiO\(_2\) leads to transparency of films which in turn leads to increase in transmittance. When \(x=100\) [Figure 6(b)], films shows four to five fringes and there is a gradual increase of transmittance towards longer wavelength. It is remarkable that a gradual increase in the red-shift is observed with increase in TiO\(_2\) doping. Optical results are in confirmation with AFM and FESEM results. The pure V\(_2\)O\(_5\) films have uniform yellow colour. Such yellow colour indicate that vanadium was incorporated as V\(^{+5}\) in V\(_2\)O\(_5\) lattice, because it is known that V\(^{+4}\) presents a brown and black colour [23].

Refractive index \((n)\) was estimated from the transmission spectrum by using envelope method [24] and following expressions was used to calculate the refractive index

\[
n = \left[ N + (N^2 - N_0^2n_1^2)^{1/2} \right]^{1/2}
\]

\[
N = \frac{n_0^2 + n_1^2}{2} + 2n_0n_1 \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}} + T_{\text{min}}}
\]

Where \(n_0\) is the refractive index of air, \(n_1\) is the refractive index of substrate, \(T_{\text{max}}\) and \(T_{\text{min}}\) are maximum and minimum transmittance values at the same wavelength. The calculated value of the refractive index for all the deposited thin films was found to be in the range from 2.30 to 2.76 as shown in the Table 1. Figure 7 shows the change in refractive index with the variation of TiO\(_2\) content. For each value of refractive index, different applications can be proposed by variation in TiO\(_2\) content doped in V\(_2\)O\(_5\) thin films.

Knowing the refractive index \((n)\), thickness \((t)\) of the films was determined by using the following expression.

\[
t = \frac{M\lambda_1\lambda_2}{2(n_1^2\lambda_1^2 - n_2^2\lambda_2^2)}
\]

Where \(M\) is the number of oscillations between the two extrema and the value of \(M\) is equal to 1 between two consecutive maxima and minima, \(\lambda_1\), \(n_1\) and \(\lambda_2\), \(n_2\) are the corresponding wavelength and indices of refraction [24]. By using the above relation, the thickness of the film was found \(~\) 325 nm.

Conclusion

In summary, pure V\(_2\)O\(_5\), TiO\(_2\) and \((\text{V}_2\text{O}_5)_{100-x}(\text{TiO}_2)_x\) composite thin films were fabricated on amorphous glass substrate at the substrate temperature of 400°C using pulsed laser deposition technique. XRD results revealed polycrystalline nature of undoped V\(_2\)O\(_5\) thin films. SEM results showed the formation of nanorods with the size of \(~\) 140 nm. The formation of granular particles (of few nanometres in size) from nanorods results from either defects or aggregation of particles after doping or due to the coarsening process of small particles. AFM results showed homogeneous, uniform, smooth and crack-free composite films. The TiO\(_2\) content was found to have a significant impact on the transmittance and refractive index of the films. The transmittance was significantly...
improved from 56% to 71% with the incorporation of TiO$_2$. The film colouration is found to have stable over several tens of hours claiming high colouration memory. TiO$_2$ doped V$_2$O$_5$ films could play an important role in various photo catalytic, electro chrome and antireflective coatings applications.

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References


