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Studies on Pure and Fluorine doped Vanadium Pentoxide Thin Films Deposited by Spray Pyrolysis Technique

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Abstract: Vanadium pentoxide (V_2O_5) thin films were deposited by spray pyrolysis technique. Precursor solution was prepared in two ways:(i) ammonium meta-vanadate (AMV) was dissolved in distilled water to prepare 0.1 M precursor solution; (ii) required amount of AMV was taken in a beaker and a few ml of concentrated nitric acid was added to it, which was then heated and maintained at 60° C for 10 minutes. After naturally cooling the solution to the room temperature, required amount of distilled water was added to this to prepare 0.1 M aqueous solution. Fluorine doped vanadium oxide films were prepared adding ammonium fluoride of 5 wt. % and 15 wt. % in separate solution. These precursor solutions were used to deposit V_2O_5 and fluorine doped V_2O_5 films on the microslide glass substrate at 400°C. X-ray diffraction results show that the deposited films are in the mixed phase of V_2O_5 and VO_2.Increasing the concentration of ammonium fluoride in the precursor solution suppresses the growth of VO_2phaseand effectively modifies the surface morphology of the prepared thin films. The average visible transmittance of theVanadium oxide films in the wavelength range of 500-800 nm increases due to fluorine doping. Further, fluorine doping in V_2O_5film does not alter the band-gap energy appreciably.
Keywords: Spray pyrolysis, vanadium oxide thin films, structural and optical properties, morphology analysis.

Introduction

Transparent Conducting Oxide (TCO) thin filmsare transparent in the visible region of the solar spectrum and possess high electrical conductivity. These properties make them useful in various fields such asgas sensors, display panel, thin film resistors, light emitting diodes, solar cells and photovoltaic windows[1]. The efficiency of the solar cells is increased by utilizingTCO films possessing sheet resistance ~10Ω/cm^{2}and optical transmittanceof ~80%[2].The vanadium oxide materials exhibit crystallographic transformation which accompanies a reversible semiconductor-to-metal transitionat a critical temperaturewith a change in optical and electrical properties[3,4]. The vanadium oxides exist in the V^{2+}, V^{3+}, V^{4+} and V^{5+} oxidation states and form the

VO, V_2O_3, VO_2 and V_2O_5materials[5]. Among the vanadium oxides, vanadium pentoxide (V_2O_5) is the most stable formwhich exists in orthorhombic structure and possesses higher electrical and optical properties[6]. V_2O_5 thin film exhibits electrochromic propertiesandfind applications in various optical devices such as electro-chromic displays, color filters and smart windows[7,8,9].

Vanadium pentoxide thin films were prepared using various physical and chemical techniques such as spray pyrolysis[10,11,12], thermal evaporation[13], electron beam evaporation[14] andsol-gel[15,16,17] methods. Different dopants were added to prepare doped V_2O_5 thin films to study the effect of dopants on the structural, electrical and optical properties. Molybdenum and tantalum doped V_2O_5 thin films were subjected to various studies to characterize their structural, optical, electro-chemical and electrochromic properties[15,17]. Fluorine doping in the TCO films improves electrical conductivity andoptical transmittance. Previous reports show that doping fluorine inzinc oxide (ZnO)[18], cadmium stannate (Cd_2SnO_4)[19]and in tin oxide (SnO_2)[20]films enhances the electrical and optical properties of these films. In this work, pureandfluorine doped V_2O_5 thin films are deposited by spray pyrolysis method from the precursor solution prepared in two different ways. The effect of fluorine doping on the structural, surface morphology and optical properties of the deposited films is reported for the first time.

Experimental

Preparation of V_2O_5 and F: V_2O_5 thin films

A simple homemade spray pyrolysis experimental setup was employed to prepare V_2O_5 and fluorine doped V_2O_5 (F: V_2O_5) thin films. Precursor solution was prepared in two ways to deposit V_2O_5 and F:V_2O_5 thin films: (i) Ammonium meta vanadate (NH_4VO_3 – AMV) of the required amount was dissolved in distilled water to get 0.1M precursor solution (S_1) and the solution was stirred well; (ii) Ammonium meta vanadate was taken in a beaker and a few ml of nitric acid was added with the ammonium meta vanadate and the same was kept at ~60° for 10 minutes. Then the solution was allowed to cool to the room temperature and thenthe required amount of distilled water was added to get 0.1 M precursor solution (S_2). Fluorine doped vanadium oxide thin films were prepared by adding separately ammonium fluoride (NH_4F) of 5 wt. % (S_3)and 15 wt. % (S_4)in the above precursor solution S_2. Well cleaned microslide glass substrates were used for depositing thin films. The prepared precursor solution was sprayed onto the heated substrate at 400°C and the distance between spray nozzle and substrate was set to 35 cm. The spray time was 3 seconds, spray interval was 20 seconds and the compressed gas (purified air) pressure is 40 kg/cm^2. The structural properties of the deposited films were studied usingX-pert powder XRD system using Cu Kα radiation (λ=1.5405Å) in Bragg-Brentano (θ/2θ coupled) geometry. The morphology and compositional analysis of the deposited thin films were studied by Scanning Electron Microscopic (SEM) and Energy Dispersive X-ray Analyses (EDAX) using FEI Quanta FEG200. Optical transmittance of the deposited films was studied by UV-Vis-NIR spectrophotometer (Perkin-Elmer Lamda-35) in the wavelength range of 300-1100nm.

Result and Discussion

Structural Analysis of V_2O_5 Thin Films

The X-ray diffraction (XRD) patterns of vanadium oxidethin films deposited at 400^{0}C from 0.1 M precursor solution is presented in Fig. 1. The XRD results show that the deposited films are in the mixed phase of V_2O_5 and VO_2.V_2O_5 phase belongs to orthorhombic system (JCPDS card 41-1426) and VO_2 phase belongs to monoclinicsystem (JCPDS card 81-2393). The thin film prepared by S_1 solution is nearly amorphous in nature. Film prepared from S_2solution shows (001) and (002) XRD peak at 20.03° and 41.2° (2θ) respectively which confirm the presence of V_2O_5 phase and the XRD peak at 28.8° (2θ)represents the (202)* plane of the VO_2 phase. The film deposited from the precursor solution S_3 (5 wt. % ammonium fluoride) shows (001) XRD peak at 20.06° (2θ)and (002) peak at 41.16° (2θ) due to V_2O_5 phaseand (202)* peak at 28.8° (2θ) due to VO_2 phase. The film prepared from precursor solution S_4(15 wt. % ammonium fluoride) shows an intense (001) XRD peak and a weak (002) XRD peak of the V_2O_5 phase. This shows that increase in ammonium fluoride concentration in the solution to 15 wt. %,suppresses the growth of VO_2 phase and favors the growth of V_2O_5 phase only.The intensity of the XRD peak of films prepared from S_3 and S_4 solution is less when compared to that of the film obtained from S_2 solution. Addition of ammonium fluoride in the precursor solution, as evidenced from Table 1, shifts the (002) peak to relatively less 2θ value. Previous report on depositing vanadium oxide by dc reactive magnetron sputtering shows the formation of V_2O_5 and VO_2 mixed phase[21]. The lattice parameter '*c*' of

orthorhombic system of V_2O_5 films is obtained from the (001) and (002) XRD peaks using the relation $\mathbf{d_{(hkl)} = \frac{n\lambda}{2sin\theta}}$ $\mathbf{_{(hkl)} = 1/(h^2/a^2 + k^2/b^2 + l^2/c^2)^{1/2}}$where $d_{(hkl)}$isthe interplannar distance corresponding to (hkl) Miller indices[22]. In this work, the obtained value of '*c*' from (001) and (002) peak is 4.42 Å and 4.3750 Å respectivelyand the value compared well with the reported value of 4.38 Å[10,14].

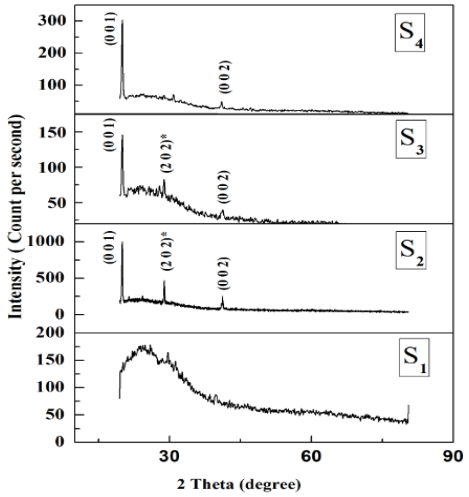


Fig.1: X-ray pattern of vanadium oxide thin films deposited at 400°C from S_1,S_2,S_3 andS_4solutions.

The grain sizewas calculated for the prepared thin films using Debye's Scherrer's formula[23] $\mathbf{D = \frac{k\lambda}{\beta cos\theta}}$ where k = 0.9, λ is the wavelength of X-rays (1.5406 Å) used, β is the full width at half maximum in radian and θ is Bragg's angle. The crystallite size derived from(001) peak of the films deposited from the precursor solutionS_2, S_3 and S_4 is 40.22 nm, 22.83 nm and 34.35 nm respectively and for (002) peak the corresponding crystallite sizesis58.53nm, 46.76nm and 28.34nm respectively.The present results show that the crystallite size of the film calculated from (002) XRD peak decreases with increase in the fluorine concentration. Thus one canconclude that inclusion of ammonium fluoride in the precursor solution reduces the crystallite size of V_2O_5as evidenced from Table 1.

Table 1:Structural parameter of vanadium oxide thin films

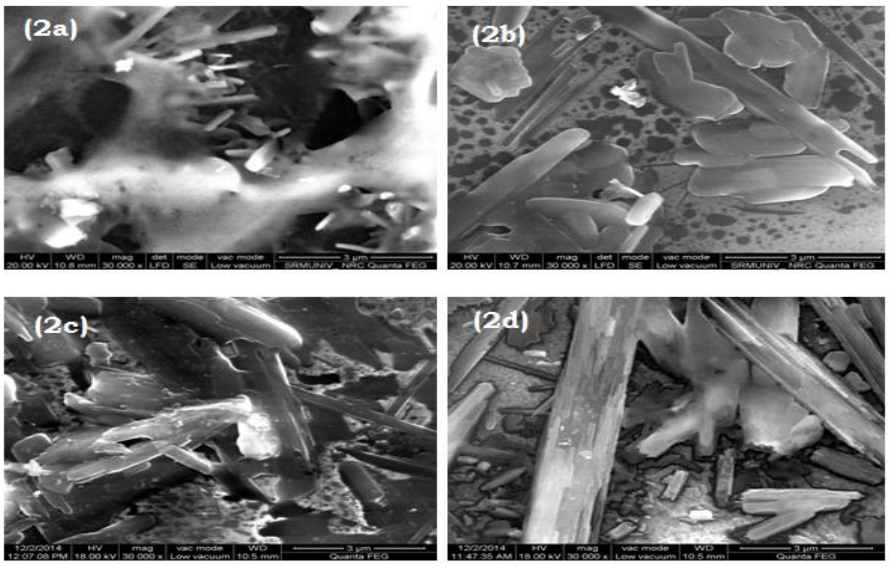
Sample	(h k l)	2θ (°)	FWHM (°)	d Spacing (Å)	D (nm)	Phase
S_2 (Distilled water + HNO_3)	(001)	20.03	0.2007	4.42	40.22	V_2O_5
	(202)*	28.87	0.1729	3.09	47.45	VO_2
	(002)	41.24	0.1451	2.18	58.53	V_2O_5
S_3 (S_2 + 5 wt. % NH_4F)	(001)	20.06	0.3534	4.42	22.83	V_2O_5
	(202)*	28.85	0.2832	3.09	28.96	VO_2
	(002)	41.16	0.1840	2.19	46.76	V_2O_5
S_4 (S_2 + 15 wt. % NH_4F)	(001)	20.05	0.2348	4.42	34.35	V_2O_5
	(002)	41.03	0.2992	2.19	28.34	V_2O_5

'*' indicates VO_2 phase.

Morphological studies

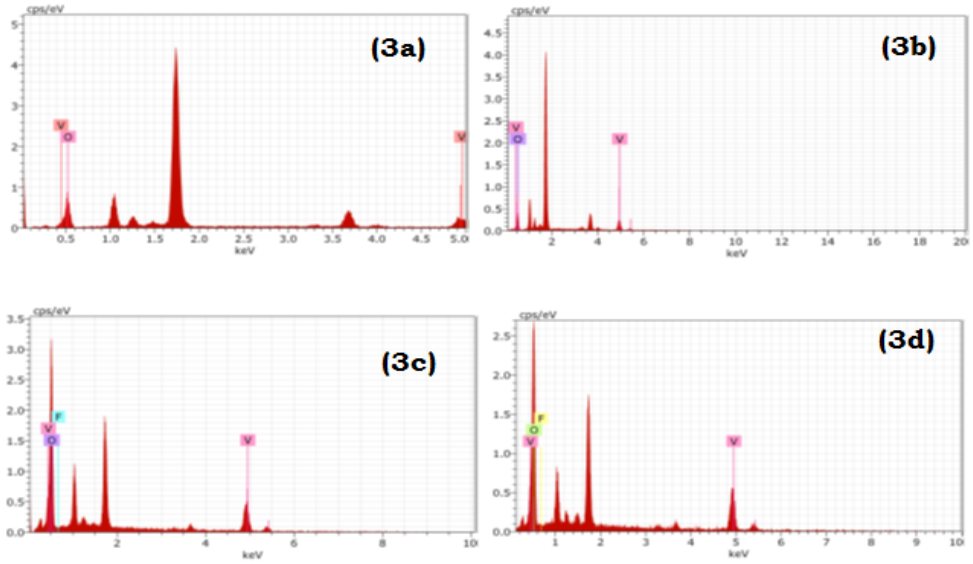
Figs. 2a-d show SEM images for pure vanadium oxide films prepared by the precursor solutionsS_1, S_2,S_3 andS_4at substrate temperature of 400°C. The surface of the film prepared from the precursor solution S_1contains small flake structures whereas the surface of film prepared from the precursor solution S_2contains long flake like structures and voids. When ammonium fluoride concentration is 5 wt. % (S_3solution) bunch of

flakes are spread on the surface of the substrate and voids are reduced. For 15 wt. % ammonium fluoridein the solution (S_4 solution), long flakes along with small rod shaped structures are formed on the surface of the film and no voids are observed. The synthesis of $V_2O_5$by hydrothermal method using AMV and ethanol solution containing 0.02 M oxalic acid (reductant) show that the bulk material formed is split into many layers[24]. In present work, film prepared by S_2 solution contains long flake like structures split on the surface with voids. The breadth of flakes formed on the surface is increased for 15 wt. % (NH_4F) compared to that of 5 wt. % (NH_4F) due to the growth of the V_2O_5 along the (001) and (002) directions.



Figs. 2a-d:SEM image of vanadium oxide thin films prepared by S_1, S_2,$S_3$and S_4 solution.

The composition of elements in the deposited vanadium oxide thin films prepared from the precursor solutions is estimated using Energy Dispersive X-ray Analysis (EDAX) and is shown in Figs. 3a-d. The atomic weight percentage of the oxygen and vanadium is 85.9 % and 14.1 % respectively for film deposited from the precursor solution S_1 and 86.4 % and 13.6 % respectively for film coated from the precursor solution S_2. For the film deposited from S_3solution (5 wt. % NH_4F), the atomic weight percentage of oxygen, vanadium and fluorine is 79.4 %,19.9 % and 0.69 % respectively. Similarly, the atomic weight percentage of oxygen, vanadium and fluorine is 76.4 %, 22.4 % and 1.10 % for films prepared from S_4 precursor solution.



Figs. 3a-d: Compositional analysis of vanadium oxide thin films prepared by S_1, S_2, S_3 and S_4 solution.

Optical Properties

The transmittance spectra of the pure and fluorine doped vanadium oxide thin films recorded using Perkin-Elmer lamda-35 UV-Vis-IR spectrometer are shown in the Fig. 4. The average visible transmittance of the deposited thin films was calculated in the visible region of the wavelength between 500 and 800 nm. Average visible transmittance for the film prepared from the precursor solution S_1, S_2, S_3 and $S_4$is 32.1%, 37.1%,55.3% and 50.4% respectively.

The average visible transmittance (AVT)of the vanadium oxide film prepared from 5 wt. % NH_4F added precursor solution (S_3) increases but AVT of the film prepared from 15 wt. % NH_4F addedprecursor solution (S_4) decreases. Maximum transmittance of the films prepared from S_1, S_2, S_3 and S_4 solution with the respective wavelength of the spectrum is presented in Table 2 which shows that the film deposited from S_3 (5 wt. % NH_4F) possesses the maximum transmittance.The optical band gap of the vanadium oxide films was calculated from the relation $(\alpha h\upsilon)^2 = A(h\upsilon - E_g)$ where A is the constant, υ is the frequency of the radiation, E_g is the band gap and α is the absorption co-efficient[25]. Fig. 5 shows the extrapolation of the graph plotted between $(\alpha h\upsilon)^2$ and energy ($h\upsilon$). The optical band gap value calculated is 2.08 eV, 1.93 eV, 1.99 eV and 1.97 eV respectively for the films deposited from the precursor solution S_1, S_2, S_3 and S_4.

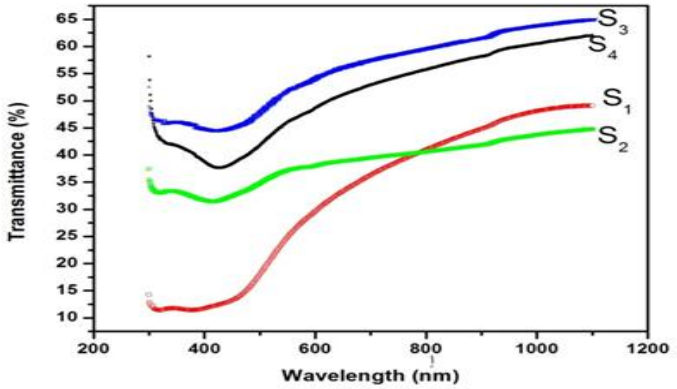


Fig 4: Transmittance spectra of vanadium oxide thin films prepared by S_1, S_2,S_3 andS_4 solutions.

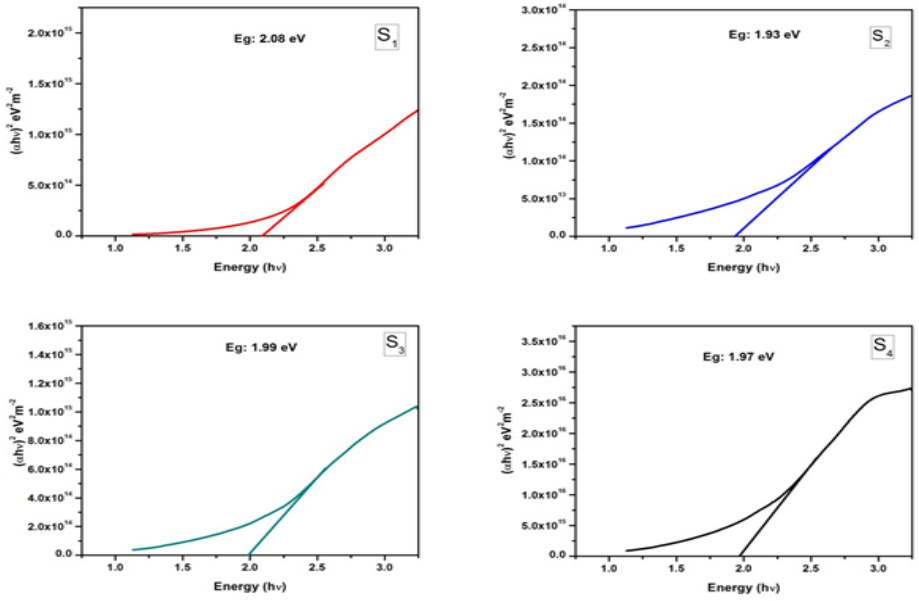


Fig 5: Band gap of vanadium oxide thin films prepared from S_1, S_2,S_3 andS_4 solutions.

Table 2:Transmittance and band gap of Vanadium oxide thin films

Sample	500 (nm)	600 (nm)	700 (nm)	800 (nm)	AVT (%) (500-800 nm)	Band gap (eV)
S_1	17.96	29.59	36.29	40.98	32.1	2.08
S_2	34.78	37.99	39.46	40.57	37.1	1.93
S_3	47.69	54.01	57.45	59.55	55.3	1.99
S_4	41.84	48.66	52.96	55.78	50.4	1.97

Further one can observe that doping of fluorine doesn't alter the band gap of the prepared vanadium oxide thin films appreciably. The reported band gap value of V_2O_5 thin film prepared by spray pyrolysis is 2.34 eV[26].

Conclusion

In the present work, pure and fluorine doped vanadium oxide thin films were deposited by spray pyrolysis techniqueat substrate temperature of 400°C. XRD studiesshow that the deposited films are in mixed phase of V_2O_5 (orthorhombic system) and VO_2(monoclinic system). Addition of ammonium fluoride in the solution suppresses the VO_2 phase and modifies the crystallite size. Ammonium fluoride concentration in precursor solution influences the surface morphology of the vanadium oxide films. Elemental compositional analysis confirms the presence of vanadium, oxygen and fluorine in the prepared thin films. Optical transmittance of the film prepared from 5 wt. % ammonium fluoride in the solution exhibits higher transmittance in the visible region compared to other deposited films. Influence of fluorine doping doesn't alter the band gap of vanadium oxidethin film.

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