Scandium: An efficient dopant to modulate the optical spectrum of vanadium dioxide (VO₂)

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Abstract

Transparency of VO₂ thin films in the visible region is an important aspect of study for its use in smart window applications. In this regard, we experimentally validate the theoretical prediction regarding the influence of scandium (Sc) doping on modulating the optical spectrum of VO₂. Sc-doped nano-crystalline VO₂, bulk and thin films were synthesised using a two-step process involving a rapid non-equilibrium solution combustion process and ultrasonic nebulised spray pyrolysis of aqueous combustion mixture respectively; followed by a reduction step. The presence of Sc was determined by X-ray photoelectron spectroscopy where a peak observed at 530.06 eV is attributed to Sc–O interaction. Raman spectra showed a shift in 611 cm^{−1} peak position to a lower wavenumber due to tensile strain arising from Sc doping. Sc-doped VO₂ thin films showed semiconductor to metal transition of four orders of magnitude change in resistance. Sc-doping increased the band gap from 1.76 eV for undoped to 2.02 eV with 2.0 at. % of doping thereby making the films more transparent in the visible region of the optical spectrum. This shift in the band gap of VO₂ was consistent with the theoretical reports. Thus, Sc is a potential dopant for modulating the optical spectrum of VO₂ for its application in smart windows.

Keywords Vanadium dioxide · Doping · Smart windows · Optical spectrum · Scandium

1 Introduction

Vanadium dioxide (VO₂) is a transition metal oxide which finds use in various applications like thermochromic devices [1], micro-bolometer [2], IR-photodetector [3], metamaterial [4, 5], smart windows [6, 7], thermal switching [8], batteries [9, 10], memristic devices [11], THz modulation devices [12] etc. It is been extensively studied due to its ability to undergo a first order phase transition accompanied by semiconductor-to-metal transition (SMT) at 68 °C (T_{SMT}). During the phase transition, a change in crystal structure from monoclinic (M1) phase (P2₁/c) to tetragonal (R) phase (P4₂/mnm) is observed which leads to change in the V–V bond length [13]. During the SMT transition, VO₂ shows a change in electrical resistivity, high resistance

(T < T_{SMT}) to low resistance (T > T_{SMT}) as well as in the optical response with a slight hysteresis which is attributed to the stress involved due to structural change and the change in latent heat [14]. VO₂ acts as IR transparent at T < T_{SMT} and acts as IR reflector at T > T_{SMT} [15]. Due to this property, it is been for used as a coating material on windows called as smart windows [6, 16]. Various methods like sol–gel [17], pulsed laser deposition [18–20], chemical vapour deposition [21], sputtering [22, 23] etc. have been employed for fabrication of doped as well as undoped VO₂ thin films.

There are few limitations to use VO₂ for smart window applications: (a) High T_{SMT}, which has been overcome by adding dopants in vanadium site [17, 24–30] and the minimum value for T_{SMT} has been observed to be ~ 25

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°C, when W is doped into the system. Many reasons have been reported where the choice of dopant depends on its effect on the crystal structure. This influence of dopant on the crystal structure decides the reduction of transition temperature (T_{SMT}). It is reported in the literature that, when the structure of doped VO_2 is close to that of tetragonal phase, a reduction in T_{SMT} will be observed. This is attributed to reduction in β -angle [31]. (b) The reduced transmission in visible range after coating VO_2 on the glass resists its use as a smart window material [27, 32]. The dopants added either reduce the T_{SMT} or manipulate the optical spectrum. When W, Mo is doped into VO_2 , T_{SMT} decreases (~ 25 °C) but the optical band gap is very low thereby making the film to be dark in colour. When dopants like Mg, F [27, 33, 34] etc., are doped the band gap increases making the film transmit more light, but these dopants do not induce any change in T_{SMT} . In order to come up with a better solution, co-doped system have been introduced [28] which enhances the visible transmittance but not up to the extent that it can be commercially used. To use VO_2 as an efficient smart window material, both the problems need to be overcome at the same time.

Sun et al. [35], depending upon the results obtained from DFT calculations suggests that of all the different transition metal that can be used for doping, scandium (Sc) is the best dopant. Doping Sc into VO_2 reduces the β -angle so that the structure is closer to tetragonal phase of VO_2 thereby reducing the T_{SMT} as well as it enhances the optical spectrum as the interaction between Sc^{3+} and O^{2-} is weaker than V^{4+} and O^{2-} , thereby will induce a blue shift in the absorption spectrum [35].

Herein, we validate these theoretical prediction experimentally. We have synthesised bulk of scandium doped V_2O_5 using rapid solution combustion synthesis (SCS) followed by a reduction step to get scandium doped VO_2 . Thin films were deposited using simple, cost-effective

method i.e., Ultrasonic Nebulised Spray Pyrolysis of Aqueous Combustion Mixture (UNSPACM), first to get phase pure Sc-doped V_2O_5 thin films on quartz substrate, followed by reduction step to get VO_2 . Bulk and thin film samples were further characterized to determine the effect of Sc doping on T_{SMT} and optical spectrum.

2 Experimental section

2.1 Synthesis of bulk materials

For synthesis of bulk material, solution combustion synthesis method was employed. Aqueous combustion mixture (ACM) was prepared using ammonium metavanadate (NH_4VO_3), scandium nitrate ($Sc(NO_3)_3$) as metal source (Oxidizer, O) and urea (CH_4N_2O) as the fuel (F). Stoichiometric amounts of the precursors were dissolved in dilute nitric acid and water calculated using Eq. 1 so that the oxidiser to fuel ratio is equal to 1 [36],

where x is the amount of scandium doped into the system as mentioned in Table 1. The schematics is shown in Fig. 1.

ACM was kept in a furnace pre-heated at 500 °C. The yellow bulk Sc-doped V_2O_5 obtained from self-propagating combustion reaction was ground and subjected to reduction treatment in N_2 atmosphere saturated with hydrocarbon at 550 °C for 30 min [37]. In order to compare the optical results with W- and Mo-doped VO_2 , the bulk samples for 2.0 at. % W doped and 1.8 at. % Mo doped were also synthesised. 2.0 at. % W doping and 1.8 at. % Mo doping was considered as these are the highest dopant levels for W- and Mo-doping respectively, that leads to reduction in T_{SMT} [24, 38].

Table 1 Sample code for doped as well as undoped samples

Doping at. %	Composition x	Elements	Sample code			
			Bulk		Thin film	
			V_2O_5	VO_2	V_2O_5	VO_2
0	0	–	BV	RBV	TV	RTV
0.5	0.005	Sc	BVS0.5	RBVS0.5		
1.0	0.01	Sc	BVS1.0	RBVS1.0	TVS1.0	RTVS1.0
1.5	0.015	Sc	BVS1.5	RBVS1.5		
2.0	0.02	Sc	BVS2.0	RBVS2.0	TVS2.0	RTVS2.0
6.25	0.0625	Sc	BVS6.25	RBVS6.25		
2.0	0.02	W	BVW2.0	RBVW2.0		
1.8	0.018	Mo	BVM1.8	RBVM1.8		

Fig. 1 **a** Schematics for solution combustion synthesis, **b** UNSPAM setup

2.2 Synthesis of thin films

Scandium doped vanadium dioxide thin films were synthesised via UNSPACM using a home built setup [39], schematics for which is shown in Fig. 1. Sc-doped V_2O_5 was synthesized on a quartz substrate. The ultrasonically nebulised mist, containing the redox mixture, was carried to the hot substrate by N_2 gas flowing at 1000 sccm. The micrometer sized droplets instantaneously pyrolysed on encountering with the quartz substrate. The substrate maintained at 600 °C. The films were synthesised at high temperature to get a crystalline phase of V_2O_5 . The films were deposited for 10 min. The films thus obtained were reduced by treating the product in N_2 atmosphere saturated with hydrocarbon [40] at 550 °C for 2.5 h. The sample codes are listed in Table 1.

2.3 Characterization

Phase confirmation was done on both bulk and thin film samples by XRD using PANALYTICAL with $\text{Cu-K}\alpha$ as the X-ray radiation ($\lambda = 1.5418 \text{ \AA}$). Raman measurements were done to confirm the phase formation using Horiba JobinYvon HR-Raman-123microPL spectrometer with a green laser having a wavelength of 523 nm. The surface morphology was determined using a F50 Inspect Field Emission SEM and Carl-Zeiss scanning electron microscope, accelerating voltage of 25 kV. Transmission electron microscope, JEOL 2100F (TEM) was used at an accelerating voltage of 200 kV to determine the morphology of bulk samples. To determine SMT for bulk samples, DSC measurements were carried out in METTLER-TOLEDO DSC1 system. For thin films, electrical measurements were carried out on a DC probe station equipped with an ATT thermal controller coupled with a B1500A semiconductor device analyser. UV Visible measurements were done using Perkin-Elmer spectrophotometer (Lambda 750) for determination of band gap. FTIR measurements were done as a function of temperature for the thin films using Agilent Carry 600 Fourier Transform infrared

spectrometer in reflectance mode. XPS measurements were done using Axis Ultra DLD from Kratos to study the influence of doping on the structural environment using $\text{Al-K}\alpha$ X-ray source. The peak fitting was done using Fityk software.

3 Results and discussions

3.1 Bulk samples

3.1.1 Structural characterization

Doping VO_2 is a better way to reduce the T_{SMT} and is mostly due to the alteration in the crystal structure. DFT calculations suggests that whenever the crystal structure is near to tetragonal phase, a reduction in transition temperature is observed [35].

In order to determine the crystal structure, X-Ray diffraction studies were done. As seen in Fig. 2a, the peaks perfectly match with JCPDS file no: 01-077-2498 for V_2O_5 , showing an orthorhombic crystal system with space group, Pmmn . The peaks match with JCPDS file no: 00-19-1398 for VO_2 (Fig. 2b) showing a monoclinic crystal system with space group $\text{P2}_1/\text{c}$. The BV sample is crystalline in nature. The crystalline nature reduces with increasing doping concentration of scandium in VO_2 bulk sample (Fig. 2b). During synthesis of V_2O_5 by SCS, though the ignition temperature is maintained at 500 °C, it is reported that at the microscopic scale the temperature can be as high as 1500 °C. This is achieved at an optimum equivalence ratio of fuel (F, urea) and oxidizer (O, metal nitrate) (defined as oxidizer to fuel ratio; O/F) of unity [41, 42]. Due to this effect, the crystallites are well formed, leading to sharp peaks in the XRD pattern. However, the reduction step to get phase pure VO_2 , is carried out at 550 °C. This temperature is probably too low to develop well defined crystallites, thereby resulting in broader, or low crystallinity as seen from XRD pattern.

Fig. 2 XRD pattern of doped as well as undoped **a** V_2O_5 and **b** VO_2 bulk samples

Fig. 3 SEM images of **a** RBV, **b** RBVS1.0, **c** RBVS2.0 and **d** RBVS6.25 samples

3.1.2 Morphology: SEM

Figure S1 (supplementary information) show the SEM images of the doped and undoped VO_2 formed before reduction process. The powder samples shows porous morphology which is due to the release of gases as explained from Eq. 1. Figure 3 shows the SEM images of the doped and undoped VO_2 formed after reduction process. The surface morphology shows presence of agglomerated sheets (Fig. 3a–c), which are porous. Figure 3d shows the presence of porous agglomerated particles for RBVS6.25 sample.

For all the samples a small needle like projection was seen coming out of the surface. TEM of RBVS2.0 shows sheet morphology as seen in Fig. 4a. The polycrystalline nature of the sample is confirmed by the electron diffraction pattern (Fig. 4a). The presence of scandium is confirmed by the EDS data (Fig. 4b).

Fig. 4 **a** TEM image for RBVS2.0; **b** EDS data for RBVS2.0

3.1.3 DSC on bulk samples

Phase transition for bulk samples was determined by DSC. The measurement was carried out for both heating and cooling from -80 to 130 °C for these samples. DSC curves are shown in Fig. 5. The data is shown only for 10 to 100 °C. VO_2 sample showed a transition at 68 °C with a heating onset at 60 °C whereas a for cooling the onset was around 62 °C and the peak was observed at 60 °C thereby leading to a hysteresis. As the dopant concentration was increased into the system, broader transition was observed which is probably due to the lower crystallinity as seen from Fig. 2b. For better understanding of the T_{SMT} , electrical measurement of thin films was considered. This is discussed in Sect. 3.2.4.

Fig. 5 DSC of bulk samples

3.1.4 Optical measurements: band gap determination

Scandium doping into VO_2 was supposed to induce a blue-shift in the absorption spectrum [35] as suggested by the DFT calculation. To validate that UV measurement was done on the powder samples by diffuse reflectance spectroscopy (DRS). Using Tauc's plot i.e., $(\alpha h\nu)^n$ vs $h\nu$ plot (Fig. 6a) where $\alpha = 2.303 \log(\text{Absorbance (A)})$, band gap was determined for the powder samples. n was considered to be 2 as VO_2 is a direct band gap semiconductor.

Sc-doping gives a blue shift in the spectrum thereby making it more transparent the reason being that Sc^{3+} possesses no d-electrons. Because of that, $\text{Sc}^{3+}-\text{O}^{2-}$ electrostatic attraction is weaker than $\text{W}^{6+}-\text{O}^{2-}$, $\text{Mo}^{6+}-\text{O}^{2-}$ and $\text{V}^{4+}-\text{O}^{2-}$ thereby increasing the band gap and hence inducing a blue shift [35]. Figure 6b shows that the band gap value increases for scandium doping till 2.0 at. % thus showing a blue shift in the absorption edge, but the band gap decreases when dopant concentration is varied from 2 to 6.25 at. % (theoretical value) thereby showing that the properties are deteriorating when scandium doping concentration increases further.

We can see that as compared to W and Mo, the Sc-doped VO_2 shows higher band gap values thereby validating the reason (Fig. 6b). Thus, it can be inferred that 2.0 at. % of scandium in vanadium dioxide system is the best dopant concentration to get maximum blue shift.

3.2 Thin film samples

For smart windows applications thin film of VO_2 are usually used. As seen from the UV data for bulk samples (Fig. 6), the optical band gap for bulk samples reduced as the concentration of scandium increased from 2.0 to 6.25 at. %. Thus, for the thin films, synthesis (explained

Fig. 6 **a** Tauc's plot for determining band gap. **b** Comparison of band gap of Sc-doping in VO_2 with W- and Mo-doping

in “Experimental section”) and measurements were limited to 2.0 at. % dopant concentration.

3.2.1 Structural characterization: XRD

The XRD data for V_2O_5 thin film perfectly match with JCPDS file no: 01-077-2498 (Fig. 7a) showing an orthorhombic crystal system with space group $Pmmn$ and peaks match with JCPDS file no: 00-19-1398 for VO_2 (Fig. 7b) showing a monoclinic crystal system with space group $P2_1/c$ as seen for the powder sample. The V_2O_5 thin film on the quartz substrate seem to show an orientation about (00l) direction as can be seen from XRD (Fig. 7a). After reduction no such orientation is observed in XRD thereby giving us a polycrystalline VO_2 film (Fig. 7b). The broad peak at $2\theta = 21.525^\circ$ is due to quartz substrate for thin films (Fig. 7a, b).

3.2.2 Morphology: SEM

Figure 8 shows the SEM of undoped (RTV) as well as Sc-doped thin film (RTVS1.0 and RTVS2.0) obtained after reduction. The films are highly porous in nature due to the release of gases during the pyrolysis process as explained by Eq. 1. A slight change in the morphology was observed with increasing Sc doping in VO_2 thin films.

3.2.3 Raman and XPS measurements

The Raman peaks for thin film (Fig. 9) exactly match with the values reported in the literature as shown in Table S1 (supplementary information). In Raman spectra the lower wavenumber bands ($< 400\text{ cm}^{-1}$) are allocated to V–O–V bending modes; intermediate wavenumber bands ($400\text{--}800\text{ cm}^{-1}$) are observed due to V–O–V stretching modes; and higher wavenumber bands ($> 800\text{ cm}^{-1}$), are assigned to V = O stretching modes of distorted octahedra and distorted square-pyramids. The phonon modes in

Fig. 7 XRD pattern of doped as well as undoped **a** V_2O_5 and **b** VO_2 of thin films

Fig. 8 SEM images of **a** RTV; **b** RTVS1.0 and **c** RTVS2.0 thin film

Table 3 Oxidation states along with the peak position, FWHM values and area ratio determined after deconvoluting XPS data

Sample	Element	Peak position (B.E. in eV)	Oxidation state	FWHM	Area ratio (V2p _{3/2}) V ⁺⁵ :V ⁺⁴ :V ⁺³
RTV	V2p _{3/2}	516.35	V ⁺³	0.92	0.82 : 1.0 : 0.065
		517.60	V ⁺⁴		
		518.72	V ⁺⁵		
	V2p _{1/2}	524	V ⁺³	2.4	
		525.10	V ⁺⁴		
		525.65	V ⁺⁵		
	O1s	530.413		1.2	
		531.544			
		532.889			
RTVS2.0	V2p _{3/2}	516.35	V ⁺³	1.2	0.097: 1.0 : 0.231
		517.60	V ⁺⁴		
		518.72	V ⁺⁵		
	V2p _{1/2}	524	V ⁺³	3.0	
		525.10	V ⁺⁴		
		525.65	V ⁺⁵		
	O1s	530.03		1.4	
		530.41			
		531.66			
533.07					

Fig. 10 **a** Resistance versus temperature, **b** derivative plot for Sc-doped VO₂ thin film, **c** Ln R versus 1/K_BT plot, **d** E_a as a function of scandium doping

Similar trend was observed in the metallic phase though an increased value of activation energy was observed when compared with the semiconducting phase.

3.2.5 Optical measurements:UV-visible and FTIR

Figure 11 shows that the band gap value increases for scandium doped VO₂ thin films which shows a blue shift in the absorption edge as observed for powder samples and the results are in good agreement with the theoretical reasoning.

VO₂ upon transition from semiconducting phase to metallic phase shows a change in IR reflectance i.e. shows high reflectance in metallic phase and low reflectance in semiconducting phase as stated earlier [6]. To study the influence of scandium doping on the reflectance, temperature-dependent FTIR measurements were done on the

RTV and RTVS2.0 (Figure S3, supplementary information) thin films in reflectance mode. The measurement was carried out after an interval of 5 °C with an equilibrating time of 5 minutes before each measurement was carried out.

For undoped VO₂ (RTV), 80 % change in the reflectance was observed at $\lambda = 9.31 \mu\text{m}$ and for 2.0 at. % Sc-doped VO₂ (RTVS2.0), 60 % change in the reflectance was observed at $\lambda = 8.48 \mu\text{m}$ as seen in Fig. 12a. Figure 12b shows the derivative plot as a function of temperature thus showing the tunability in the spectral range upon doping and hence making it suitable for a metamaterial type of application. In metallic phase, change in surface plasmon is only observed at $\lambda > 2.0 \mu\text{m}$ [40]. The dip in the reflectance observed in the range of $\lambda = 2.5\text{--}4 \mu\text{m}$ is basically due to the interference of atmospheric CO₂ [46]. Dip around $\lambda = 10 \mu\text{m}$ is attributed to the substrate (quartz).

4 Conclusions

In this study, we gave experimental evidence for the theoretical prediction on the influence of Sc-doping in modulating the optical spectrum of VO₂. We synthesised Sc-doped VO₂ (M1) bulk and thin films by SCS and UNSPACM respectively, in two steps. XPS and Raman measurements confirmed the structural influence of Sc doping into VO₂ thin films. Lowering of 611 cm⁻¹ peak position to 606 cm⁻¹ in Raman spectra was attributed to tensile strain resulting from Sc doping. A blue shift in the optical spectrum from 1.7 eV (undoped) to 2.02 eV (2.0 at. %) was observed for both bulk as well as thin films which is in agreement with the theoretical report. Sc-doped VO₂ showed four orders of magnitude change in resistance and an increased transition width maintaining the T_{SMT} of semiconductor to metal transition. 60 % change in the IR reflectance was observed at $\lambda = 8.48 \mu\text{m}$ with 2.0 at. % of Sc-doping. Sc-doping only

Fig. 11 Band gap as a function of scandium doping for VO₂ thin films

Fig. 12 **a** Change in reflectance as a function of temperature, **b** derivative of reflectance as a function of temperature for RTV and RTVS2.0 thin films

altered the optical spectrum of VO₂ contrary to the theoretical prediction where changes in both T_{SMT} and band gap were reported. Tuning of both optical spectrum and T_{SMT} of VO₂ may be possible by co-doping with other dopants for smart window applications.

5 Supplementary information

See Supplementary information for: SEM image of the undoped as well as Sc-doped V₂O₅ powder samples. Raman modes for V₂O₅ and VO₂ as compared with the literature values; Temperature dependent reflectance plots for undoped (RTV) and 2.0 at. % Sc-doped (RTVS2.0) VO₂ thin films and V2p and O1s spectra for RTV and RTVS2.0 thin films that have been deconvoluted using Fityk software.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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