Role of V-V dimerization in the insulator-metal transition and optical transmittance of pure and doped VO₂ thin films

S. S. Majid,¹ S. R. Sahu,² A. Ahad,¹ K. Dey,² K. Gautam,² F. Rahman,¹
 P. Behera,² U. Deshpande,² V. G. Sathe,² and D. K. Shukla^{2,*}

¹*Department of Physics, Aligarh Muslim University, Aligarh-202002, India*

²*UGC-DAE Consortium for Scientific Research, Indore-452001, India*

(Received 14 June 2019; revised manuscript received 5 December 2019; published 17 January 2020)

An insulator to metal (IMT) transition ($T_i \sim 341$ K) in the VO₂ accompanies a transition from an infrared (IR) transparent to IR opaque phase. Tailoring of the IMT and associated IR switching behavior can offer potential thermochromic applications. Here we report on effects of the W and the Tb doping on the IMT and associated structural, electronic structure, and optical properties of the VO₂ thin film. Our results show that the W doping significantly lowers IMT temperature (~ 292 K to ~ 247 K for 1.3% W to 3.7% W) by stabilizing the metallic rutile, *R*, phase while Tb doping does not alter the IMT temperature much and retains the insulating monoclinic, *MI*, phase at room temperature. It is observed that the W doping albeit significantly reduces the IR switching temperature but is detrimental to the solar modulation ability, contrary to the Tb doping effects where higher IR switching temperature and solar modulation ability is observed. The IMT behavior, electrical conductivity, and IR switching behavior in the W and the Tb-doped thin films are found to be directly associated with the spectral changes in the V $3d_{||}$ states.

DOI: [10.1103/PhysRevB.101.014108](https://doi.org/10.1103/PhysRevB.101.014108)

I. INTRODUCTION

Vanadium dioxide (VO₂) is known to undergo first-order insulator to metal transition (IMT) from the low-temperature monoclinic insulating phase ($P2_1/c$) to the high temperature rutile metallic ($P4_2/mnm$) phase around the transition temperature $T_i \sim 341$ K. Structural transformation of VO₂ from the rutile, *R*, structure to the monoclinic, *MI* structure transforms the equally spaced V atoms, oriented along the rutile *c* axis, into paired (dimerized) and tilted V atoms in the monoclinic structure [1–3]. The IMT in VO₂ is accompanied by a dramatic modification in optical properties like switching in transmittance/reflectance of the IR radiations with the insulating phase being transparent to the IR while the metallic phase blocks them. This property of VO₂ is potentially useful for designing thermochromic smart windows which can serve as the best energy-management devices as these windows switch the solar heat gain [4–6].

Changes in the IR and visible transmittance of the VO₂ thin films across the IMT can be explained in terms of changes in the band structures, explained in context of the Goodenough model [7,8]. According to this model, in the rutile metallic phase of the VO₂ the octahedral crystal field splits the V $3d$ degenerate orbitals into doubly degenerate e_g^σ and triply degenerate t_{2g} orbitals. The t_{2g} orbitals are further split into the doubly degenerate e_g^π orbitals and the single $d_{x^2-y^2}$ ($d_{||}$) orbital. Both the e_g^π and e_g^σ states hybridize with O $2p$ orbitals to form antibonding π^* and σ^* molecular orbitals while the $d_{||}$ orbitals are oriented along the rutile *c* axis. In the

insulating phase, pairing and tilting of the vanadium atoms along the rutile *c* axis results in splitting of the $d_{||}$ orbitals into filled bonding and empty antibonding orbitals. A band gap of ~ 0.65 eV in the VO₂ insulating phase arises due to energy differences between the bonding V $3d_{||}$ and the π^* bands while, in the metallic phase, the energy gap vanishes due to overlapping of the nonbonding $3d_{||}$ and π^* bands at the Fermi level. Decrease in the IR transmittance of the VO₂ with increase in temperature is directly associated with vanishing of the VO₂ insulating band gap (~ 0.65 eV) and increase in the free carrier concentration in the high-temperature metallic phase. Optical transitions in the visible spectral range occur between lower O $2p$ valence states to the π^* conduction bands [9,10].

For practical applications of the VO₂ material such as thermochromic smart windows, the IMT temperature of the VO₂ requires that it be tailored down to room temperature (RT). Chemical doping of electron-rich valence shell metal ions viz. W⁶⁺, Mo⁶⁺, and Nb⁶⁺ and optimizing the amount of strain in epitaxial VO₂ thin films have been found to be effective ways to reduce the T_i of the VO₂ to RT [9,11–14]. Doping of electron-doped ions tungsten (W⁶⁺) have been found effective in reducing the transition temperature to RT, while doping of the hole-doped ions terbium (Tb³⁺) has no significant impact on the transition temperature lowering [15]. There is always a trade-off between the transition temperature reduction, solar modulation ability, and the luminous transmittance in VO₂ thin films [6]. W doping is found to reduce the solar modulation ability and the luminous transmittance [16,17] while Tb doping enhances the luminous transmittance accompanied by the decrease in the solar modulation ability [15]. Two systems (W- and Tb-doped VO₂) show contrasting

*dkshukla@csr.res.in

effects on the electrical and optical properties of the VO₂ thin films. It is essential to completely study both the W and the Tb VO₂ systems and explore the role of W and Tb in modifying the VO₂ IMT and optical properties.

We have synthesized the pure VO₂ and W- (1.3%, 2.9%, and 3.7%) and Tb- (1.3%, 3.3%, and 4.6%) doped VO₂ thin films on the quartz substrates using the pulsed laser deposition technique. By combining structural, electrical, optical, and electronic structure studies, we present an insightful of the effects of the W and Tb doping on the IMT and optical properties of the VO₂. Our results directly show the doping-induced alterations to the V-V dimerization in the VO₂ thin film, on which electrical and optical properties are largely dependent.

II. EXPERIMENTAL DETAILS

KrF excimer laser ($\lambda = 248$ nm, repetition rate of 5 Hz and pulse energy of 210 mJ) was focused onto a target (pressed pure, W- and Tb-doped V₂O₅) with a fluence of 1.1 J/cm². Ultrasonically cleaned quartz substrates were maintained at a temperature of 700 °C during the deposition. All depositions were performed in an oxygen partial pressure of 10 mTorr. X-ray diffraction (XRD) was carried out with a Bruker D8 x-ray diffractometer with Cu K α radiation. Temperature-dependent resistivity measurements were performed in the standard four-point configuration. Temperature-dependent Raman spectra were collected in backscattering geometry using a 10 mW Ar (475 nm) laser as an excitation source coupled with a Labram-HRF micro-Raman spectrometer equipped with a 50X objective. The x-ray photoelectron spectroscopy (XPS) measurements were performed using an Omicron energy analyzer (EA-125) with a Al K α (1486.6 eV) x-ray source. Soft x-ray absorption spectroscopy (SXAS) across the V $L_{3,2}$ and the O K edges were carried out in the total electron yield mode at the beamline BL-01, Indus-2 at RRCAT, Indore, India. Energy resolution during SXAS measurements at the oxygen K -edge energy was ~ 250 meV. Bulk VO₂ was measured for reference. V- K -edge x-ray absorption near edge spectroscopy measurements were performed at beamline P64, PETRA III, DESY, Hamburg, Germany in fluorescence mode. Optical transmittance spectra were collected using UV-VIS-NIR spectrometer, Perkin Elmer USA Model: Lambda 950, operating in the spectral range of 175 to 3300 nm having resolution ~ 0.02 nm (UV-VIS) and ~ 0.2 nm (NIR). Doping percentages used throughout the paper are calculated using the XPS spectra of Tb and W.

III. RESULTS AND DISCUSSIONS

Figure 1(a) shows XRD of pure and W-doped thin films. XRD confirms growth of the VO₂ monoclinic (*M1*) phase in the undoped thin films, visualized from the diffraction peaks observed at $2\theta \sim 27.97^\circ$ and 57.79° , corresponding to the reflections from the VO₂ monoclinic (0 1 1) and (0 2 2) planes, respectively [18,19]. Tungsten-doped VO₂ thin films are grown in the rutile (*R*) phase, evident from 2θ positions of the diffraction peaks at $\sim 27.78^\circ$ and 57.27° , which correspond to reflections from the rutile (1 1 0) and

FIG. 1. Room-temperature XRD patterns of (a) pure and W-doped VO₂ thin films, (b) pure and Tb-doped VO₂ thin films. Room temperature Raman spectra of (c) pure and W-doped VO₂ thin films and (d) pure and Tb-doped VO₂ thin films.

(2 2 0) planes, respectively [19]. Further confirmation about grown phases in pure and W-doped VO₂ thin films comes from the Raman spectra shown in the Fig. 1(c). The pure VO₂ thin film shows seven A_g and three B_g Raman modes at ~ 139 , 192, 222, 309, 337, 389, 613 cm⁻¹ and 260, 441, 496 cm⁻¹, respectively, which belong to the VO₂ monoclinic, *M1*, phase [20]. The A_g symmetry Raman modes ω_{v1} and ω_{v2} at ~ 192 and 222 cm⁻¹ are assigned to the V-V vibrations while the rest of the observed Raman peaks are related to V-O vibrations [21,22]. Complete disappearance of the *M1* vibrational modes observed in all W-doped thin films confirm growth of the rutile phase, consistent with earlier reports [18,23]. XRD patterns of the Tb-doped thin films shown in Fig. 1(b) exhibit a slight decrease in crystalline nature and shifting of the monoclinic, *M1*, (0 1 1) diffraction peak toward higher 2θ , compared to the pure VO₂ thin film. Shifting of the diffraction peaks to higher 2θ values with increase in the Tb-doping percentage is attributed to decrease in unit cell size of the VO₂. The nonproportionality of (0 1 1) intensity with Tb doping may be attributed to the misalignment of the 3.3% Tb-doped sample during the XRD measurements, which is clear from the background behavior too. XRD studies reveal the highly oriented growth of the VO₂ thin films on the amorphous quartz substrate. Raman spectra shown in Fig. 1(d) further confirms growth of the monoclinic, *M1*, phase in the Tb-doped thin films and substantiates to XRD results. In contrast to the W doping, no phase transformation is visualized due to the Tb doping.

Temperature-dependent resistivity (ρ) measurements of the pure and the W-/Tb-doped VO₂ thin films are shown

FIG. 2. Temperature-dependent resistivity of (a) pure and W-doped VO₂ thin films (b) pure and Tb-doped VO₂ thin films.

in Figs. 2(a) and 2(b). The characteristic IMT is observed in all the thin films. To infer quantitative information from temperature-dependent resistivity measurements, the IMT in all the thin films were fitted by the Boltzmann function [$f(T) = 1 - \frac{1}{1 + e^{\frac{T - T_0}{dT}}}$ Eq. (1)]. f is the resistivity, (ρ), T_0 is the transition temperature and dT signifies the transition width. IMT temperature (T_i) is defined as an average of transition

temperatures measured in the cooling and the heating cycles. The IMT temperature for the pure and doped VO₂ thin films are illustrated in Table I. Tungsten doping has effectively reduced the IMT transition temperature of the VO₂ thin film. In the $\sim 1.3\%$ W-doped VO₂ thin film, IMT is observed near RT (~ 292 K), which is consistent with the earlier reports [24,25]. Tb doping has small impact on the IMT temperature of the VO₂ thin film compared to the W doping. Resistivity measurements are also used to calculate the IMT strength defined as resistivity ratio $\rho(T_i - dT)/\rho(T_i + dT)$. Calculated values of the IMT strength of the pure and the doped VO₂ thin films are listed in Table I.

For the correct estimation of chemical states of the vanadium and the dopant elements, we carried out XPS measurements, shown in Fig. 3. XPS of the pure VO₂ thin film [Fig. 3(a)] confirms the +4 oxidation state of the vanadium, which is visible from the binding energy positions of the spin-orbit split features V 2p_{3/2} ~ 516 eV and V 2p_{1/2} ~ 523 eV. The features at ~ 531.3 eV, ~ 530 eV, and ~ 527 eV correspond to the OH concentration, O 1s, and the V 2p_{3/2} satellite peak, respectively [26,27]. VO₂ contains satellite features for both the V 2p_{3/2} and V 2p_{1/2} states due to strong hybridization between the V 3d and the O 2p states [27]. The V 2p_{3/2} satellite peak, S1, ~ 527 eV is found in between the V 2p_{1/2} and O 1s spectral features while V 2p_{1/2} satellite peak is located on the higher binding energy side of O 1s peak and is mixed with the states corresponding to the OH concentration. The spectral feature, S2, at ~ 520 eV is assigned to x-ray satellite peak of Al K α_3 source and arises from a nonmonochromatic x-ray radiation source [28]. W doping [Figs. 3(b) and 3(c)] induces the spectral features at binding energies ~ 514 eV and ~ 522 eV, belonging to V³⁺ 2p_{3/2} and 2p_{1/2} states, while Tb [Figs. 3(d)–3(f)] doping results in the inclusion of V⁵⁺ 2p_{3/2} and V⁵⁺ 2p_{1/2} states at the binding energy values ~ 517 eV and ~ 524 eV. XPS spectra shown in Figs. 4(a)–4(c) confirm the +6 oxidation state of the W which is evident from the binding energy positions of 4f_{7/2} ~ 35 eV and 4f_{5/2} ~ 37 eV features, while Figs. 4(d)–4(f) represent +3 oxidation state of the Tb which is visualized from the spectral features at ~ 1241 eV and ~ 1276 eV belonging to Tb 3d_{5/2} and 3f_{3/2} states. The multiple valency of vanadium states is difficult to observe from the V 3p XPS spectra because of the strong multiplet splitting due to the large spatial overlap with the V 3d shell [26], hence the feature at ~ 41.5 eV is assigned to V 3p states, consistent with earlier reports [15,29].

TABLE I. Parameters T_i , T_{sc} , T_{oc} and IMT strength obtained from the temperature-dependent resistivity, Raman (cooling cycle), and transmittance spectroscopy (cooling cycle) in pure and doped VO₂ thin films. The $d_{||}$ intensity in the pure and doped VO₂ thin films is manifested from the XAS measurements.

Sample	T_i (K) resistivity	T_{sc} (K) Raman	T_{oc} (K) transmittance	IMT strength resistivity	$d_{ }$ intensity XAS
VO ₂	340.1	322.3	320.7	56.6	0.55 ± 0.03
1.3%W	292.2	241.8	285.2	21.4	0.42 ± 0.04
2.9%W	275.8	198.9	246.2	18.8	0.45 ± 0.03
3.7%W	247.3	122.5	217.1	11.1	0.46 ± 0.03
1.3%Tb	339.2	329.3	341.6	271.4	0.64 ± 0.06
3.3%Tb	335.7	328.2	338.5	142.5	0.62 ± 0.07
4.6%Tb	335.5	322.3	330.5	109.9	0.66 ± 0.06

FIG. 3. O 1s and V 2p XPS of (a) the pure VO₂ (b) 1.3% W, (c) 2.9% W, (d) 1.3% Tb, (e) 3.3% Tb, and (f) 4.6% Tb-doped VO₂ thin films

To maintain charge neutrality in the W and Tb-doped VO₂ thin films, some vanadium atoms change their oxidation state to +3 and +5 to compensate the higher (W^{6+}) and the lower (Tb^{3+}) charge states. Figure 4(g) shows a decrease in the V^{4+} percentage content with an increase in the doping percentage of the W and Tb atoms and the decrease in the V^{4+} content is found to be accompanied by an increase in the contents of the V^{3+} and V^{5+} for the W- and Tb-doped VO₂, respectively.

Temperature-dependent Raman spectra of the pure and the W-/Tb-doped VO₂ thin films are shown in Figs. 5(a)–5(g), measured in the cooling cycles. Temperature-dependent structural transition from the low-temperature monoclinic (*M1*) structure to the high-temperature rutile (*R*) structure is observed in all the thin films without presence of any intermediate structures (*M2* and *T*) which are usually accessible via chemical doping in the VO₂ [18]. Temperature-dependent frequency position of the Raman mode ω_0 , of the pure and the W-/Tb-doped VO₂ thin films are plotted in Figs. 5(h) and 5(i). There is not any anomalous change observed in the temperature-dependent frequency position of the Raman mode, ω_0 . Softening of the Raman mode positions due to lattice thermal expansion is accompanied by a large and sudden change at the structural transition temperature. In the Tb-doped VO₂ thin films, frequency shift of the ω_0 mode from ~ 613 cm⁻¹ (observed in the pure VO₂ thin film, to

FIG. 4. (a)–(c) W 4f XPS of the 1.3%, 2.9%, and 3.7% W-doped VO₂ thin films. (d)–(f) Tb 3d XPS of the 1.3%, 3.3%, and 4.6% Tb-doped VO₂ thin films. (g) Variation of the V^{5+} and V^{3+} contents for the Tb- and W-doping concentrations, along with the doping dependent V^{4+} content variation in the VO₂ thin film.

~ 619 cm⁻¹) reflects significant influence of the Tb doping on the V-O vibrational mode compared to the W doping, where the ω_0 mode stays around ~ 613 cm⁻¹. Normally, the higher frequency shift of the ω_0 mode position in the pure VO₂ thin film is considered a fingerprint for identification of the VO₂*M2* and *T* structures [18,21,30]; however, in the Tb-doped VO₂ thin films, higher frequency shift of the ω_0 mode to ~ 619 cm⁻¹ is much less compared to that observed for the *T* phase (~ 629 cm⁻¹) and for the *M2* phase (~ 642 cm⁻¹).

Recently, Kalcheim *et al.* [31] used XRD and IR spectroscopic techniques to understand coupling between the IMT and the structural phase transition in the V₂O₃ thin films and discussed the nonreliability of the resistance measurements in determination of the correct insulating and metallic phase fractions. We have extracted the the monoclinic phase fraction (MPF) and the insulating phase fraction (IPF) from temperature-dependent Raman and optical transmittance spectra (discussed later, see Fig. 7), respectively. The following formula has been used to calculate the IPF (in the range, 2000 cm⁻¹ to 2500 cm⁻¹).

$$IPF(T) = \frac{T_r(T) - T_{rM}}{T_{rI} - T_{rM}} \quad (1)$$

where T_{rI} and T_{rM} are transmittance of the pure insulating and the pure metallic phases and $T_r(T)$ is the transmittance at temperature, T . The calculated IPF of the pure and the W-/Tb-doped VO₂ thin films are compared with the MPF obtained from temperature-dependent integrated intensity of the ω_0 Raman mode in Figs. 6(a)–6(f). Calculated transition temperatures, T_{oc} and T_{sc} , from the optical transmittance

FIG. 5. (a)–(g) Temperature-dependent Raman spectra of the pure and the W-/Tb-doped VO₂ thin films collected in the cooling cycle. Temperature-dependent frequency shift of the ω₀ Raman mode positions obtained from Lorentz fitting in (h) W-doped (i) pure, and Tb-doped VO₂ thin films.

measurement and the Raman spectroscopy data, using Eq. (1), are listed in Table I. In the pure VO₂ thin film, IMT is found to be coupled with the structural transition while W and Tb doping are found to stabilize the rutile structure prior to the metallic state. Impact of the W doping in the rutile structure stabilization is much more significant compared to the Tb doping.

For thermochromic applications, optical properties of the pure and the doped VO₂ thin films are characterized using temperature-dependent UV-VIS-NIR transmittance spectra shown in Fig. 7. The spectral transmittance in the wavelength range of ~250 nm to ~2500 nm of the pure [Fig. 7(a)], W-doped [Figs. 7(b)–7(d)], and the Tb-doped [Figs. 7(e)–7(g)] VO₂ thin films are used to calculate the solar transmittance, T_{sol} . For the luminous transmittance, T_{lum} , calculations in

FIG. 6. (a)–(f) Temperature-dependent variation of the insulating phase fraction (IPF) obtained from optical transmittance measurements and monoclinic phase fraction (MPF) obtained through the ω₀ Raman mode in the pure and the W-/Tb-doped VO₂ thin films. Data shown in these graphs are from the cooling cycles.

the spectral range ~382 nm to ~732 nm are used. Both the solar and the luminous transmittance are calculated using the following formula:

$$T_{\text{sol/lum}} = \frac{\int \phi_{\text{sol/lum}}(\lambda) T_r(\lambda) d\lambda}{\int \phi_{\text{sol/lum}}(\lambda) d\lambda}, \quad (2)$$

where $T_r(\lambda)$ is the spectral transmittance at wavelength λ . $\phi_{\text{sol}}(\lambda)$ is the solar spectral irradiance for the sun standing 37° above the horizon (for the air mass 1.5) and ϕ_{lum} is the standard luminous efficiency function for the photopic vision of human eyes [6,32]. Using the integrated solar and luminous transmittance, we can calculate the solar and luminous modulation of the pure and doped VO₂ thin films using the following formulas:

$$\Delta T_{\text{sol}} = T_{r(\text{sol},I)} - T_{r(\text{sol},M)}, \quad (3)$$

$$\Delta T_{\text{lum}} = T_{r(\text{lum},I)} - T_{r(\text{lum},M)}, \quad (4)$$

where $T_{r(\text{sol},I)}$, $T_{r(\text{sol},M)}$, $T_{r(\text{lum},I)}$, and $T_{r(\text{lum},M)}$ are the solar and the luminous transmittance of the insulating and the metallic states, respectively. Parameters obtained from transmittance spectra of the pure and the W-/Tb-doped VO₂ thin films

FIG. 7. (a)–(g) Temperature-dependent optical transmittance spectra of the pure and W-/Tb-doped VO₂ thin films. (h) Temperature-dependent IR transmittance at ~ 2500 nm of the pure and W-/Tb-doped VO₂ thin films in the cooling cycles.

are illustrated in Table II. IR switching in the pure and the W-/Tb-doped VO₂ thin films can be visualized from Fig. 7(h), where temperature-dependent change in the IR transmittance at the wavelength, $\lambda \sim 2500$ nm is plotted in the cooling cycle. The IR switching transition temperatures for the pure and the W-/Tb-doped VO₂ thin films are calculated from the

TABLE II. Parameters obtained from the temperature-dependent optical transmittance measurements of the pure and W-/Tb-doped VO₂ thin films.

Sample	$T_{\text{lum,I}}$	$T_{\text{lum,M}}$	ΔT_{lum}	$T_{\text{sol,I}}$	$T_{\text{sol,M}}$	ΔT_{sol}
VO ₂	20.8	19.5	1.3	32.4	17.0	15.4
1.3%W	20.6	19.4	1.2	30.2	16.4	13.7
2.9%W	28.1	26.4	1.67	32.7	23.4	9.2
3.7%W	30.9	30.8	0.07	32.6	26.6	5.9
1.3%Tb	17.1	14.9	2.2	28.9	13.6	15.2
3.3%Tb	28.8	26.1	2.6	38.9	23.7	15.1
4.6%Tb	31.4	27.9	3.5	38.8	25.4	13.4

IR transmittance vs T curve, measured in the cooling cycle, using Eq. (1), and is found equivalent to T_{oc} (see Table I). The near RT T_{oc} , $T_{\text{r(lum)}} \geq 40\%$, and the $\Delta T_{\text{sol}} \geq 10\%$ are considered the best criteria for the VO₂ thin films to be employed in thermochromic windows applications [6,33]. From Table II, it is found that the W doping in the VO₂ thin film effectively reduces the IR switching temperature to near RT ~ 282 K (measured in the cooling cycle) but is accompanied with a decrease in the solar modulation ability, consistent with earlier reports [16,34]. With the Tb doping, IR switching occurs at higher T_{oc} , while the solar modulation ability is maintained around $\sim 15\%$ which is much large compared to the earlier report on Tb-doped VO₂ thin films [15]. There is always a trade-off between the solar modulation ability and the luminous transmittance in the VO₂ thin films, i.e., an increase in the luminous transmittance is accompanied by the decrease in the solar modulation [16,17]. However, in the Tb-doped VO₂ thin films, increase in the luminous transmittance is accompanied with the good and stable solar modulation ability (see Table II).

To understand the transmittance observations, it is essential to calculate the band gap of the pure and W-/Tb-doped VO₂ thin films corresponding to the visible and the IR transparency, which can be extracted from the Tauc plot shown in Figs. 8(a) and 8(b). The Tauc plot is a graphical description between $(\alpha h\nu)^n$ vs $h\nu$ obtained from the Tauc's equation [35] given as

$$(\alpha h\nu)^n = A(h\nu - E_g), \quad (5)$$

where $n = 1/2, 1/3, 2$, and $2/3$ for the indirect allowed, indirect forbidden, direct allowed and direct forbidden optical transitions, respectively, α is the absorption coefficient obtained from the transmittance spectra, A is a constant, and $h\nu$ is the photon energy. Usually, in the optical experiments, direct band gap is visualized because of the lower excitation probability among different symmetry points during the optical transition [36]. The band gap is obtained by extrapolating the linear portion of the curve while the y ordinate is zero. Two types of band gaps are observed, i.e., E_{g1} and E_{g2} . E_{g2} corresponds to energy gap between the V $3d_{||}$ and π^* bands while the E_{g1} is due to the optical transition between the O $2p$ and π^* bands [37,38] [Figs. 8(a) and 8(b)]. The IR switching temperature in all the thin films is found to depend on the energy band gap E_{g2} . The lowering of the IR switching temperature in the W-doped VO₂ thin films (see Table II) is attributed to a decrease in the energy band gap, E_{g2} , from ~ 0.63 eV in the pure to ~ 0.24 eV in the 1.3% W-doped VO₂ thin film, while in the Tb-doped VO₂ thin films we have observed the highest IR switching temperature ~ 341.6 K in the $\sim 1.3\%$ Tb-doped VO₂ thin film having the largest band gap $E_{g2} \sim 0.74$ eV.

The band gap E_{g1} corresponds to the luminous transparency of the thin films, the higher the E_{g1} value, the higher the visible transparency will be [37–39]. Figures 8(a)(ii) and 8(b)(ii) show the variation of the luminous transmittance along with the absorption edge (λ_K) obtained from the derivative of the transmittance spectra. The blueshift in the absorption edge along with an increase in the luminous transmittance in the VO₂ thin film due to W and Tb doping are found to be consistent with an increase in the energy band-gap values E_{g1} .

FIG. 8. (a) Tauc plot $[(\alpha hv)^2 \text{ vs } hv]$ of the pure and W-doped VO_2 thin films at room temperature. Insets: (i) Tauc plot in the IR range of photon energies and (ii) variation in the T_{lum} and the λ_K with the W-doping percentage. (b) Tauc plot of the pure and Tb-doped VO_2 thin films at room temperature. Insets: (i) Tauc plot in the IR range of photon energies and (ii) variation in the T_{lum} and the λ_K with the Tb-doping percentage.

In the following, we will discuss the origin of doping-induced changes in the electrical conductivity and optical properties of VO_2 . The V $L_{2,3}$ edge x-ray absorption spectra of the pure and the W-/Tb-doped VO_2 thin films are shown in Fig. 9(a). The vanadium $L_{2,3}$ spectrum arises due to the transition from the V $2p$ core level (spin orbit split V $2p_{3/2}$ and $2p_{1/2}$) to the unoccupied V $3d$ states and consists of two pronounced features at $\sim 518.8 \text{ eV}$ (L_3) and $\sim 525.5 \text{ eV}$ (L_2). The features at $\sim 516.0 \text{ eV}$ and $\sim 522.6 \text{ eV}$ are due to the transitions to the crystal field split t_{2g} part of the V $3d$ states [40,41]. The energy positions of the $L_3 \sim 518.8 \text{ eV}$ and $L_2 \sim 525.5 \text{ eV}$ features confirm $4+$ oxidation state of the vanadium. With the W and Tb doping in the VO_2 thin film, the slight shift in the energy positions of the L_3 and L_2 states is observed, which is due to the additional V^{3+} and V^{4+} states created by the W and Tb doping, as inferred from the XPS measurements also.

FIG. 9. Room temperature (a) V $L_{2,3}$ (b) O K -edge XAS measurements of pure and W-/Tb-doped VO_2 thin films. Normalized O K -edge XAS of (c) pure and Tb-doped, (d) pure and W-doped VO_2 thin films. The V K -pre-edge XAS (e) of 1.3% Tb-doped and (f) of 1.3% W-doped VO_2 thin films at 300 K and 373 K.

The O K -edge spectrum, see Fig. 9(b), results from transition of the O $1s$ electrons to the O $2p$ states which are hybridized with the V $3d$ orbitals and form the conduction band. Peaks at $\sim 530.3 \text{ eV}$ and $\sim 532.8 \text{ eV}$ are due to transitions into the π^* and the σ^* hybridized bands [8,42]. Doping of the W has clearly resulted in a shift of the π^* band toward the lower energies as compared to the pure VO_2 thin film, which signifies the stabilization of the metallic state. The Tb doping shifts the π^* band toward higher energy, signifying the stabilization of the insulating state. The crystal-field splitting energy (ΔE_{CF}) which is the energy separation between the π^* and the σ^* states is found to vary with the W and the Tb doping. Variations in the crystal-field splitting energy values due to the W and the Tb doping in the VO_2 thin film are also susceptible to a different extent of V-V interactions. The π^* orbitals in the VO_2 thin film point in between the ligands and have less orbital overlap with the O $2p$ orbitals, while the σ^* orbitals are directed toward the ligand having a higher overlap with the O $2p$ orbitals. Therefore, spectral weight of the π^* band is highly sensitive to the V-V interactions while spectral weight of the σ^* band is related to the direct V-O interactions [43]. To clearly visualize the spectral changes

among the XAS spectra of pure and doped VO₂ thin films, we have carried out the normalization and horizontal shift of the π^* states to ~ 532.8 eV as shown in Figs. 9(c) and 9(d). The asymmetry observed in the π^* bands around ~ 531 eV, which is marked in both Figs. 9(c) and 9(d), is assigned to the unoccupied $d_{||}$ states, whose spectral weight is related to V-V dimerization [43–45]. The decrease and an increase in the intensity of the $d_{||}$ feature is observed in the W and Tb doping, respectively, and for better visualization and comparison pure VO₂ spectra is shown by the dotted line. In the insulating VO₂ phase, we did not observe splitting of the $d_{||}$ feature, as observed by Koethe *et al.* [44] during their polarized XAS measurements on VO₂ single crystal because the spectral weight of the $d_{||}$ feature measured in the highly oriented VO₂ thin films is an averaged $d_{||}$ intensity of the randomly oriented VO₂ crystallites in the plane perpendicular to the surface normal [0 1 1] as the polarization vector of the incident photons was perpendicular to the surface normal during the experiments and probes all the randomly oriented V 3 $d_{||}$ states along the monoclinic a axis (or rutile c axis, as $a_M = 2c_R$). Due to this averaging effect, the splitting of the $d_{||}$ feature is obscured in the VO₂ thin films. The integrated intensity of the $d_{||}$ states for the pure and the doped VO₂ thin films is noted in Table I. The pre-edge structures at ~ 5468.3 eV from the V K -edge XAS observed in 1.3% Tb and W-doped VO₂ thin films at the temperatures 330 K and 373 K are shown in Figs. 9(e) and 9(f). The pre-edge peak intensity is highly sensitive to the local geometrical structure around the absorbing atom (V) and increases directly with increase in distortion of the regular octahedral VO₆ units [18]. The VO₂ rutile, R phase has less distorted octahedron compared to the monoclinic, $M1$ phase, hence an increase in intensity in the 300 K spectra compared to the 370 K spectra of the Tb-doped VO₂ thin film represent the transition from the R phase to the $M1$ phase while no such signature is observed in the W-doped VO₂ thin film, indicating a stable rutile phase at RT and 373 K. By combining the resistivity and XAS measurements, we find that the IMT strength of the pure and W-/Tb-doped VO₂ thin films is directly related to the unoccupied spectral weight of the V 3 $d_{||}$ states. W doping is found to decrease the IMT strength while Tb doping increases the IMT strength which is accompanied by a decrease and an increase in the spectral weight of the V 3 $d_{||}$ states [see Table I and Figs. 9(c) and 9(d)]. The changes in the IMT strength and the spectral weight of the $d_{||}$ states within the error limits are not systematic with the W and the Tb dopings, however, we can clearly visualize respective increase and decrease in both the IMT strength and the $d_{||}$ spectral weight with the Tb and W dopings, as compared to the pure VO₂ thin film.

Spectral weight of the $d_{||}$ states observed in the XAS measurements is directly related to the vanadium-vanadium dimerization along the rutile c axis [44,45]. The V-V dimerization in the VO₂ can be directly visualized from the ω_{v_1} and the ω_{v_2} vibrational modes in Raman spectra shown in Figs. 10(a)–10(g) as both these modes are assigned to V-V vibrations and the ω_{v_1} frequency mode gives the twisting vibration of the vanadium dimers along the rutile c axis. Raman mode ω_{v_1} in the pure and Tb-doped VO₂ thin films is fitted with a single Lorentzian while in the W-doped VO₂ thin films, the vibrational mode is fitted with two Lorentzian

FIG. 10. (a)–(d) Room temperature (300 K) Raman-integrated intensity of the ω_{v_1} and ω_{v_2} vibrational modes in pure and Tb-doped VO₂ thin films. (e)–(g) Raman integrated intensity of the ω_{v_1} and ω_{v_2} vibrational modes in the 1.3%, 2.9%, and 3.7% W-doped VO₂ thin films at 200 K, 150 K, and 130 K, respectively. (h) Raman intensity variation of the V-O and V-W modes with the increase in the W% concentration.

peaks at ~ 186 and 195 cm^{-1} . The additional peak at the lower frequency value ~ 186 cm^{-1} is assigned to the V-W vibrational mode as effective mass of the V-W system is larger as compared to the V-V system. Presence of the V-W vibrational modes in the W-doped VO₂ thin films signify replacement of the V atoms by the doped W atoms along the VO₂ rutile c axis, hence the loss of V-V dimerization. On the contrary, in the Tb-doped VO₂ thin film absence of any such extra mode signify that the Tb is not doped along the rutile c axis therefore there is no loss of V-V dimerization. Figure 10(h) shows the intensity variation of the V-V and the V-W vibrational modes in the W-doped sample. Increase in intensity of the V-W vibrational mode and corresponding decrease in intensity of the V-V vibrational mode with increase in the W doping can be visualized. According to

FIG. 11. Variation in the spectral position of the π^* states, IR band gap (E_{g2}), and the IR switching temperature (T_{oc}) with the W% and the Tb% concentration in the VO_2 thin films.

Tang *et al.* [46], electron dopant W atoms break the $\text{V}^{4+}\text{-V}^{4+}$ dimers and result in formation of the $\text{V}^{3+}\text{-W}^{6+}$ and $\text{V}^{3+}\text{-V}^{4+}$ pairs along the rutile c axis due to electron transfer from the W to the V ions. The electronic charge transfer from the W atoms resulting in formation of V^{3+} ions (see Fig. 3) stabilizes the metallic state and the loss of the vanadium dimerizations favors the rutile symmetry [13,46].

XAS and optical transmittance results reveal that the IR switching temperature, T_{oc} , is strongly related to the spectral weight and position of the $\text{V } 3d_{||}$ and π^* states (see Figs. 9 and 11). IR switching temperature (T_{oc}) in all thin films, which is sensitive to the energy gap E_{g2} (energy gap between the $d_{||}$ and the π^* states), is found to be directly related to the spectral position of the π^* states (see Fig. 11). The spectral weight and position of the π^* band is directly sensitive to the V-V interactions and reflects the extent of the V-V hybridization [47]. Larger V-V hybridization will stabilize the π bonding states and simultaneously shift the π^* antibonding states toward the higher photon energy. The decreasing T_{oc} and E_{g2} with increasing W-doping concentration and increasing T_{oc} and E_{g2} with increasing Tb concentration are found to be concomitant with shift of the π^* states spectral weight toward lower and higher energies, respectively. The solar modulation ability of all the thin films can be directly associated with their IMT strength. In the W-doped VO_2 thin films, ΔT_{sol} decreases with decrease in the IMT strength. In the Tb-doped VO_2 thin films, an increase and the stabilized ΔT_{sol} values (contrary to a previous report [15]) can be attributed to an increased IMT strength observed from the resistivity measurements. Hence the solar modulation ability, ΔT_{sol} , is found to be largely

dependent on stabilization of the VO_2 monoclinic, $M1$ phase, and therefore on preservation of the V-V dimers.

IV. CONCLUSIONS

In summary, changes in electrical, structural, optical, and electronic structure properties of the pure and W-/Tb-doped VO_2 thin films have been studied. Electron dopant W atoms are found to significantly reduce the IMT temperature in the VO_2 thin film by stabilizing the rutile metallic phase, contrary to the hole dopant Tb atoms which favor and stabilize the insulating monoclinic phase. Loss of the V-V dimerization is clearly observed due to the W doping while the Tb doping is found to strengthen the V-V dimerization. Loss of the V-V dimerization has been found to directly influence the spectral weight of the $\text{V } 3d_{||}$ states, a decrease and an increase in spectral weight of the $d_{||}$ states has been observed due to the W and the Tb doping, respectively. Changes in strength of the IMT, the electrical conductivity, the IR switching temperature, and the solar modulation ability due to the W and Tb doping are found directly related to the spectral changes in the $d_{||}$ states. Conclusions which are directly related to thermochromic applications of doped VO_2 thin films are as follows: (i) A decrease in the IR switching temperature is observed due to the W doping while an increase in the IR switching temperature is visualized due to the Tb doping. Near RT, IR switching temperature (~ 285 K, cooling cycle) is observed at an optimum 1.3% W concentration. (ii) An increase in the luminous transmittance is observed for both the W and the Tb doping. Luminous transmittance of $\sim 30.9\%$ and 31.4% is observed for the highest 3.7% W and 4.6% Tb dopings. (iii) An increased and stabilized solar modulation ability (~ 15.2) is observed with the 1.3% Tb doping and a decrease in the solar modulation ability (~ 13.7) due to an optimum 1.3% W doping. Our results also clearly indicate that the W and the Tb codoping may be a potential candidate to get a combination of lowered IMT temperature, large ΔT_{sol} , and high T_{lum} essential for smart window applications.

ACKNOWLEDGMENTS

Authors are thankful to Sharad Karwal, Rakesh Sah, and Ajay Rathore for help during XPS, XAS, and Raman measurements, respectively. R.J. Choudhary is gratefully acknowledged for providing the PLD setup. E. Welter is gratefully acknowledged for his support during hard x-ray absorption spectroscopy measurements, performed under India-DESY collaboration. K.G. thanks Council of Scientific and Industrial Research, New Delhi, India, for support in form of SRF. D.K.S. acknowledges support from SERB, India, in the form of an early-career research award (Award No. ECR/2017/000712).

- [1] A. Zylbersztein and N. F. Mott, *Phys. Rev. B* **11**, 4383 (1975).
- [2] M. Imada, A. Fujimori, and Y. Tokura, *Rev. Mod. Phys.* **70**, 1039 (1998).
- [3] D. Adler, *Rev. Mod. Phys.* **40**, 714 (1968).

- [4] J. Zhou, Y. Gao, Z. Zhang, H. Luo, C. Cao, Z. Chen, L. Dai, and X. Liu, *Sci. Rep.* **3**, 3029 (2013).
- [5] C. Wu, F. Feng, and Y. Xie, *Chem. Soc. Rev.* **42**, 5157 (2013).

- [6] L. Zhao, L. Miao, C. Liu, C. Li, T. Asaka, Y. Kang, Y. Iwamoto, S. Tanemura, H. Gu, and H. Su, *Sci. Rep.* **4**, 7000 (2014).
- [7] J. B. Goodenough, *J. Solid State Chem.* **3**, 490 (1971).
- [8] J. Goodenough and H. Y. Hong, *Phys. Rev. B* **8**, 1323 (1973).
- [9] M. K. Dietrich, F. Kuhl, A. Polity, and P. J. Klar, *Appl. Phys. Lett.* **110**, 141907 (2017).
- [10] A. Gavini and C. C. Kwan, *Phys. Rev. B* **5**, 3138 (1972).
- [11] C. Batista, J. Carneiro, R. Ribeiro, and V. Teixeira, *J. Nanosci. Nanotechnol.* **11**, 9042 (2011).
- [12] C. J. Patridge, L. Whittaker, B. Ravel, and S. Banerjee, *J. Phys. Chem. C* **116**, 3728 (2012).
- [13] X. Tan, T. Yao, R. Long, Z. Sun, Y. Feng, H. Cheng, X. Yuan, W. Zhang, Q. Liu, C. Wu *et al.*, *Sci. Rep.* **2**, 466 (2012).
- [14] Y. Muraoka and Z. Hiroi, *Appl. Phys. Lett.* **80**, 583 (2002).
- [15] N. Wang, M. Duchamp, R. E. Dunin-Borkowski, S. Liu, X. Zeng, X. Cao, and Y. Long, *Langmuir* **32**, 759 (2016).
- [16] L. Hu, H. Tao, G. Chen, R. Pan, M. Wan, D. Xiong, and X. Zhao, *J. Sol-Gel Sci. Technol.* **77**, 85 (2016).
- [17] W. Burkhardt, T. Christmann, S. Franke, W. Kriegseis, D. Meister, B. Meyer, W. Niessner, D. Schalch, and A. Scharmann, *Thin Solid Films* **402**, 226 (2002).
- [18] S. S. Majid, D. K. Shukla, F. Rahman, S. Khan, K. Gautam, A. Ahad, S. Francoual, R. J. Choudhary, V. G. Sathe, and J. Strempfer, *Phys. Rev. B* **98**, 075152 (2018).
- [19] N. Sepúlveda, A. Rúa, R. Cabrera, and F. Fernández, *Appl. Phys. Lett.* **92**, 191913 (2008).
- [20] K. Shibuya and A. Sawa, *J. Appl. Phys.* **122**, 015307 (2017).
- [21] C. Marini, E. Arcangeletti, D. Di Castro, L. Baldassare, A. Perucchi, S. Lupi, L. Malavasi, L. Boeri, E. Pomjakushina, K. Conder, and P. Postorino, *Phys. Rev. B* **77**, 235111 (2008).
- [22] X.-B. Chen, *J. Kor. Phys. Soc.* **58**, 100 (2011).
- [23] Y. Ji, Y. Zhang, M. Gao, Z. Yuan, Y. Xia, C. Jin, B. Tao, C. Chen, Q. Jia, and Y. Lin, *Sci. Rep.* **4**, 4854 (2014).
- [24] H. Takami, T. Kanki, S. Ueda, K. Kobayashi, and H. Tanaka, *Phys. Rev. B* **85**, 205111 (2012).
- [25] K. Shibuya, M. Kawasaki, and Y. Tokura, *Appl. Phys. Lett.* **96**, 022102 (2010).
- [26] R. Zimmermann, R. Claessen, F. Reinert, P. Steiner, and S. Hüfner, *J. Phys.: Condens. Matter* **10**, 5697 (1998).
- [27] G. Silversmit, D. Depla, H. Poelman, G. B. Marin, and R. De Gryse, *J. Electron Spectrosc. Relat. Phenom.* **135**, 167 (2004).
- [28] J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, Eden Prairie, MN, 1992).
- [29] Y. Zhang, W. Li, M. Fan, F. Zhang, J. Zhang, X. Liu, H. Zhang, C. Huang, and H. Li, *J. Alloys Compd.* **544**, 30 (2012).
- [30] J. M. Atkin, S. Berweger, E. K. Chavez, M. B. Raschke, J. Cao, W. Fan, and J. Wu, *Phys. Rev. B* **85**, 020101(R) (2012).
- [31] Y. Kalcheim, N. Butakov, N. M. Vargas, M.-H. Lee, J. del Valle, J. Trastoy, P. Salev, J. Schuller, and I. K. Schuller, *Phys. Rev. Lett.* **122**, 057601 (2019).
- [32] L. Kang, Y. Gao, Z. Zhang, J. Du, C. Cao, Z. Chen, and H. Luo, *J. Phys. Chem. C* **114**, 1901 (2010).
- [33] S.-Y. Li, G. A. Niklasson, and C.-G. Granqvist, *Thin Solid Films* **520**, 3823 (2012).
- [34] C. G. Granqvist, *Sol. Energy Mater. Sol. Cells* **91**, 1529 (2007).
- [35] J. Tauc and A. Menth, *J. Non-Cryst. Solids* **8**, 569 (1972).
- [36] G.-H. Liu, X.-Y. Deng, and R. Wen, *J. Mater. Sci.* **45**, 3270 (2010).
- [37] M. Wan, M. Xiong, N. Li, B. Liu, S. Wang, W.-Y. Ching, and X. Zhao, *Appl. Surf. Sci.* **410**, 363 (2017).
- [38] S.-Y. Li, N. R. Mlyuka, D. Primetzhofer, A. Hallén, G. Possnert, G. A. Niklasson, and C. G. Granqvist, *Appl. Phys. Lett.* **103**, 161907 (2013).
- [39] J. Zhou, Y. Gao, X. Liu, Z. Chen, L. Dai, C. Cao, H. Luo, M. Kanahira, C. Sun, and L. Yan, *Phys. Chem. Chem. Phys.* **15**, 7505 (2013).
- [40] M. W. Haverkort, Z. Hu, A. Tanaka, W. Reichelt, S. V. Streltsov, M. A. Korotin, V. I. Anisimov, H. H. Hsieh, H.-J. Lin, C. T. Chen, D. I. Khomskii, and L. H. Tjeng, *Phys. Rev. Lett.* **95**, 196404 (2005).
- [41] J. Zaanen, G. A. Sawatzky, J. Fink, W. Speier, and J. C. Fuggle, *Phys. Rev. B* **32**, 4905 (1985).
- [42] D. Ruzmetov, S. D. Senanayake, and S. Ramanathan, *Phys. Rev. B* **75**, 195102 (2007).
- [43] D. Ruzmetov, S. D. Senanayake, V. Narayanamurti, and S. Ramanathan, *Phys. Rev. B* **77**, 195442 (2008).
- [44] T. C. Koethe, Z. Hu, M. W. Haverkort, C. Schüßler-Langeheine, F. Venturini, N. B. Brookes, O. Tjernberg, W. Reichelt, H. H. Hsieh, H.-J. Lin, C. T. Chen, and L. H. Tjeng, *Phys. Rev. Lett.* **97**, 116402 (2006).
- [45] N. F. Quackenbush, H. Paik, M. J. Wahila, S. Sallis, M. E. Holtz, X. Huang, A. Ganose, B. J. Morgan, D. O. Scanlon, Y. Gu, F. Xue, L.-Q. Chen, G. E. Sterbinsky, C. Schlueter, T.-L. Lee, J. C. Woicik, J.-H. Guo, J. D. Brock, D. A. Muller, D. A. Arena, D. G. Schlom, and L. F. J. Piper, *Phys. Rev. B* **94**, 085105 (2016).
- [46] C. Tang, P. Georgopoulos, M. E. Fine, J. B. Cohen, M. Nygren, G. S. Knapp, and A. Aldred, *Phys. Rev. B* **31**, 1000 (1985).
- [47] D. Ruzmetov and S. Ramanathan, *Thin Film Metal Oxides: Fundamentals and Applications in Electronics and Energy* (Springer, New York, 2010).