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## MoO<sub>3</sub> nanowire growth on VO<sub>2</sub>/WO<sub>3</sub> for thermochromic applications†

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This study explores the structural, electronic, and optical properties of sandwich-structured thin films composed of WO<sub>3</sub>, MoWO<sub>3</sub>, and MoO<sub>3</sub> as window layers on VO<sub>2</sub>/WO<sub>3</sub> via a physical vapor deposition method. Morphological analysis demonstrates the evolution of distinct nanowires, offering insights into the lattice strain of the VO<sub>2</sub> layer toward high-performance thermochromic devices. Temperature-dependent sheet resistivity is investigated, showcasing significant improvements in conductivity for samples with MoO<sub>3</sub> as a window layer. The electrical and optical properties of the MoO<sub>3</sub>/VO<sub>2</sub>/WO<sub>3</sub> device showed a phase transition temperature ( $T_c$ ) of 36.8 °C, a transmittance luminous ( $T_{lum}$ ) of 54.57%, and a solar modulation ability ( $\Delta T_{sol}$ ) of 12.43. This comprehensive analysis contributes to understanding the growth of nanowires on multi-layered thin films, offering valuable insights into potential applications in bright windows.

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### I. Introduction

Building services use more energy than the transportation and industrial sectors, accounting for over half of all energy consumption. Most energy is used to run different heating, ventilation, and air conditioning (HVAC) systems.<sup>1,2</sup> The development of efficient energy conversion technologies is of utmost importance in the modern era, and thermochromic materials are a promising avenue in this regard.<sup>3</sup> In particular, the thermochromic properties of VO<sub>2</sub> have received significant attention in recent years due to their potential for use in various applications, such as temperature sensors, energy harvesting, and cooling devices. The ability of VO<sub>2</sub> to undergo a reversible phase transition from an insulating to a metallic state with a change in temperature makes it an ideal candidate for thermochromic applications.<sup>4,5</sup> However, in the real-world implementation of VO<sub>2</sub>-based thermochromic bright windows, issues

with high  $T_c$ , balancing the  $T_{lum}$ , and  $\Delta T_{sol}$  still persist. Since high  $T_c$  limits the practical usage of monolayer VO<sub>2</sub> films,  $T_c$  is reduced by a variety of techniques, including strain engineering,<sup>6</sup> element doping,<sup>7</sup> and multilayer construction.<sup>8–10</sup> Monoclinic VO<sub>2</sub> has been synthesized using various fabrication methods, each of which has proven successful in producing high-performance materials, such as chemical vapor deposition (CVD),<sup>11</sup> pulsed laser deposition (PLD),<sup>12</sup> molecular beam epitaxy (MBE),<sup>13</sup> and liquid phase synthesis (LPS).<sup>14</sup> These various methods have each demonstrated remarkable performance characteristics.

The thermochromic properties of VO<sub>2</sub> can be further enhanced through sandwich structures, consisting of layers of different materials stacked on top of each other. In addition to significantly improving the VO<sub>2</sub> crystal's quality, window layers with lattice characteristics equivalent to VO<sub>2</sub> can act as a barrier against particle diffusion between the intermediate layer and the substrate and act as an antireflecting layer (ARL).<sup>15,16</sup> The  $T_c$  and thermal hysteresis width ( $\Delta H$ ) of the VO<sub>2</sub> layer can be altered by the internal tension brought on by a lattice mismatch.<sup>17,18</sup> In general, carefully considering the materials employed is necessary to attain the appropriate optical characteristics in constructing sandwich structures. The materials selected will be determined by the particular application and the required performance standards.<sup>19</sup> In a particular way, the envisioned advantage of nanowire structures for smart windows lies in the potential to fine-tune the metal–insulator transition at lower temperatures, facilitating better control over the window's transparency in response to external stimuli. Nanowires, with their higher aspect ratio and altered optical properties, can influence the transmittance luminosity of smart

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windows. Their unique geometry and changed interaction with light might enhance light scattering or absorption properties compared to nanoparticles such as the recently reported, plasmonic Au nanowires,<sup>20</sup> silver nanowires,<sup>21,22</sup>  $\text{WO}_3$  nanowires,<sup>23</sup>  $\text{Sb}_2\text{Se}_3$  ultrathin nanowires,<sup>24</sup> and  $\text{VO}_2$  nanowires.<sup>25</sup>

This article investigates the effect of Mo, W, and Mo-W oxide window layers in the ARL coating on the thermochromic properties of  $\text{VO}_2/\text{WO}_3$  sandwich structures on the FTO glass substrate. Our study focuses on understanding the impact of Mo concentration on the shape of the nanowires, the electrical and optical properties of sandwich structures, and how these properties affect the overall thermochromic performance of the  $\text{VO}_2$ . The surface morphology plays a significant role in thermochromic applications, particularly in enhancing parameters like transmittance luminous ( $T_{\text{lum}}$ ) and solar modulation ability ( $\Delta T_{\text{sol}}$ ).

## II. Materials and methods

### 1. Deposition of sandwich structures

The thin film multi-layers comprising vanadium (V), molybdenum (Mo), and tungsten (W) were prepared using metallic targets of three inches with a purity of 99.9%. The deposition process involved reactive radio frequency (RF) and direct current (DC) magnetron sputtering, utilizing a combination of argon and oxygen gases, as detailed in Table 1. Before sputtering, the chamber underwent a vacuum pump down to a pressure of  $7 \times 10^{-7}$  Torr. Cleaned FTO ( $6 \Omega \text{ square}^{-1}$ ) substrates were utilized for depositing the thin films. These FTO glass substrates were cleaned under ultrasonic conditions with acetone and isopropyl alcohol for 15 min, followed by rinsing with deionized water and high-purity nitrogen gas. All samples were heated to the desired temperature in the sputtering chamber and left for 30 minutes to stabilize the substrate temperature. A working pressure of  $5.1 \times 10^{-3}$  Torr was maintained throughout the processes. The thicknesses of the V-O, W-O, and Mo-O films were controlled by adjusting the deposition time. By keeping constant film deposition times, the film thicknesses of V-O, W-O, Mo-O, and Mo-W-O films were consistent across all samples. The deposition parameters are illustrated in Table 1. The deposition parameters control the window layer's nanowire growth through the materials' deposition rate.

While  $\text{Mo}_{0.2}\text{W}_{0.8}\text{O}_3$  was a composite film combining Mo and W, the film was created under specific conditions, with an oxygen environment of 12.1 sccm and an argon flow of 50 sccm, and the power applied to the Mo and W targets during the

Table 1 The deposition parameters of the deposited multilayer films

Parameters	V-O	W-O	Mo-O	Mo-W-O
Power (W)	DC <sub>V</sub> /190	RF <sub>W</sub> /137	RF <sub>M</sub> /137	RF <sub>M-W</sub> /137
Ar (sccm)	41	37.1	37.1	37.1
O <sub>2</sub> (sccm)	2.2	12.1	12.1	12.1
Time (min)	7.5	7.5	16.7	16.7
Thickness (nm)	50	100	100	120

deposition process was 27 W and 110 W, respectively. The entire deposition process lasted 16.7 minutes for both Mo and W targets. The primary objective of this layer was to incorporate a small quantity of Mo atoms into the  $\text{WO}_3$  film to produce a high-quality layer with anti-refractive and anti-oxidative properties. Our previous research<sup>26–28</sup> has indicated that this layer exhibits exceptional transmission characteristics and favorable electrical performance. It is worth noting that the optimization of the Mo content within the  $\text{WO}_3$  film has been thoroughly explored in previous studies.<sup>28</sup> Moreover, following the sputtering process,  $\text{VO}_2$  was subjected to an *in situ* treatment at a temperature of 400 °C for 2 hours, with an argon flow rate of 50 sccm.

For simplicity, V, W-V-W, MoW-V-W, and Mo-V-W are used which represented the  $\text{VO}_2$ ,  $\text{WO}_3/\text{VO}_2/\text{WO}_3$ ,  $\text{Mo}_{0.2}\text{W}_{0.8}\text{O}_3/\text{VO}_2/\text{WO}_3$ , and  $\text{MoO}_3/\text{VO}_2/\text{WO}_3$  samples.

### 2. Characterization techniques

The optical transmission (T) was evaluated using a UV-Vis-NIR spectrophotometer attached to a heating stage, specifically the UV-3600i Plus model by Shimadzu. The surface morphology was analyzed using a field emission scanning electron microscope (FESEM), specifically the ZEISS GeminiSEM 500. Raman vibrational modes were captured using a Renishaw inVia confocal Raman microscope with a 532 nm laser beam. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific K-alpha XPS system, employing an Al K $\alpha$  source and a spot size of 400  $\mu\text{m}$ . A source meter system measured the electrical I-V phase transition under temperature changes, including a connected heating stage. An *in situ* Quartz crystal monitor within the sputtering system collected the thickness measurements. Additionally, a Filmetrics F20 Thin Film Analyzer is used to corroborate the sample thickness, showcasing a minimal deviation of around 1 nm.

## III. Results and discussion

### 1. Structural properties (Raman spectroscopy)

In Fig. S2(b) (ESI†), in the additional information section, the XRD pattern of the deposited  $\text{VO}_2$  thin film is presented, indicating a monoclinic phase with a JCPDS card number [#96-153-0871] and a space group of C12/m1(12). Various diffraction peaks appear at  $2\theta = 15.45^\circ, 20.49^\circ, 31.28^\circ, 47.69^\circ$ , and  $62.32^\circ$ . The unit cell parameters are  $a = 12.03000 \text{ \AA}$ ,  $b = 3.69300 \text{ \AA}$ , and  $c = 6.42000 \text{ \AA}$ , with an angle of  $\beta = 106.100^\circ$ . Fig. S2(c) (ESI†) in the additional information section shows the Raman spectra of  $\text{VO}_2$  thin films. The most crucial peaks within the  $\text{VO}_2$  layer are related to lattice motion involving V-V bonds (at 132 and 229  $\text{cm}^{-1}$ ), along with the vibrational modes of V-O bonds in the  $\text{VO}_2$  monoclinic insulating phase (at 500 and 828  $\text{cm}^{-1}$ ).<sup>29–31</sup>

It is also more interesting to present the Raman spectra of  $\text{MoO}_3$ ,  $\text{WO}_3$ , and  $\text{Mo}_{0.2}\text{W}_{0.8}\text{O}_3$  thin films, as represented in Fig. S3 (ESI†) in the additional information section. In the



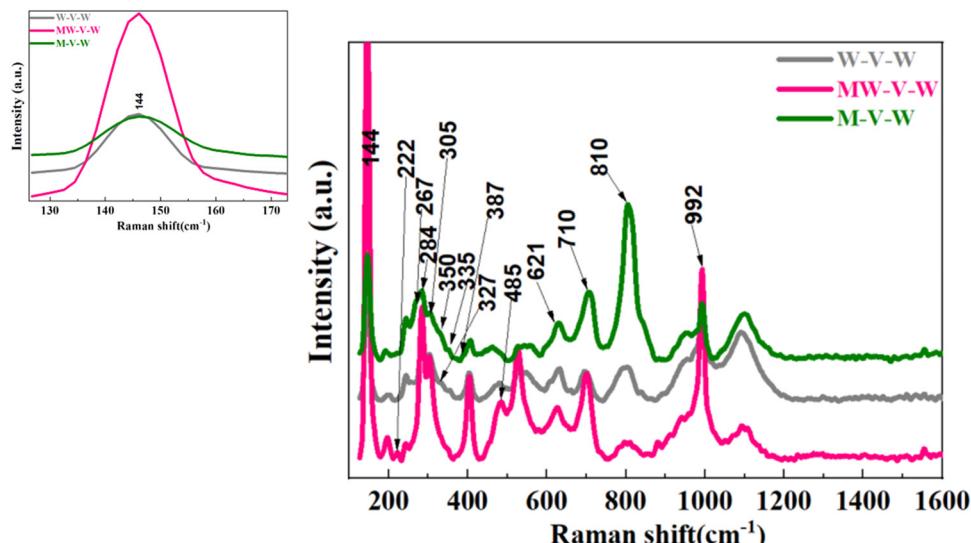


Fig. 1 Raman spectra of W-V-W, MoW-V-W, and Mo-V-W samples. The inset shows the main  $\text{VO}_2$  peak at  $144\text{ cm}^{-1}$ .

$\text{MoO}_3$  thin film, the prominent peaks at  $820$ ,  $860$ , and  $994\text{ cm}^{-1}$  correspond to the  $\alpha$ - $\text{MoO}_3$  crystal phase and M-O stretching modes.<sup>32–34</sup> Weaker peaks at  $190$ ,  $283$ ,  $336$ , and  $352\text{ cm}^{-1}$  are linked to Mo-O bending mode,<sup>35,36</sup> while the  $658\text{ cm}^{-1}$  peak relates to triply coordinated oxygen  $\text{Mo}_{3-\text{O}}$  stretching.<sup>37</sup> In the  $\text{WO}_3$  layer, the monoclinic phase is characterized by peaks at  $270$  and  $326\text{ cm}^{-1}$ .<sup>38</sup> The  $\text{WO}_3$  structure is confirmed through the lattice mode peak at  $132\text{ cm}^{-1}$ <sup>39</sup> and stretching mode peaks of W-O-W bonding at  $711$  and  $810\text{ cm}^{-1}$ .<sup>38</sup> For  $\text{Mo}_{0.2}\text{W}_{0.8}\text{O}_3$  thin films, Raman peaks are weak, whereas distinguishable prominent peaks for  $\text{WO}_3$  imply significant structural disruption caused by the introduction of Mo.

Nevertheless, examining the multilayer sandwich structures of the prepared samples can provide additional insights into the strain effects of  $\text{VO}_2$ , as illustrated in Fig. 1. Within the  $\text{VO}_2$  layer, specific peaks play a crucial role in characterizing the lattice motion involving V-V bonds ( $132$ ,  $144$ ,  $387$ ,  $305$  and  $222\text{ cm}^{-1}$ ), as well as the vibrational mode of V-O bonds in the  $\text{VO}_2$  monoclinic insulating phase ( $500$  and  $828\text{ cm}^{-1}$ ).<sup>29–31,40,41</sup> In the case of the top  $\text{MoO}_3$  thin layer, the most robust peaks observed at  $820$ ,  $860$ , and  $992\text{ cm}^{-1}$  correspond to the  $\alpha$ - $\text{MoO}_3$  crystal phase and the M-O stretching modes.<sup>32–34</sup> Additionally, weaker peaks are detected at  $191$ ,  $284$ ,  $335$ , and  $350\text{ cm}^{-1}$ , which are attributed to the bending mode of Mo-O,<sup>35,36</sup> while the peak at  $658\text{ cm}^{-1}$  is associated with the triply coordinated oxygen  $\text{Mo}_{3-\text{O}}$  stretching.<sup>37</sup> Moving on to the  $\text{WO}_3$  layer, the monoclinic phase is identified by peaks at  $267$  and  $327\text{ cm}^{-1}$ .<sup>38</sup> The  $\text{WO}_3$  lattice mode is confirmed by the peak observed at  $133\text{ cm}^{-1}$ ,<sup>42</sup> and the stretching mode peaks of W-O-W bonding are scanned at  $710$  and  $810\text{ cm}^{-1}$ .<sup>43</sup> Finally, the Raman peaks of  $\text{Mo}_{0.2}\text{W}_{0.8}\text{O}_3$  thin films exhibit moderate intensity.

## 2. Surface morphology of the top window-layer

It is known that  $\text{VO}_2$  is one of the attractive, strongly correlated oxides that involve high lattice strain effects that can easily control the deposition of various materials on its surface.

Different studies show that reactive DC magnetron sputtering is used to deposit nanowires and nanorods with a high aspect ratio.<sup>44</sup> The growth of different morphologies of  $\text{VO}_2$  has been controlled in the sputtering system, as reported before.<sup>45</sup> Our previous research<sup>28</sup> delved into the growth patterns of various metal oxides at  $400\text{ }^\circ\text{C}$ . Fig. S1(a) and (b) (ESI†) in the additional information section show the surface structures of  $\text{VO}_2$  and  $\text{MoO}_3$  thin films. By employing high vacuum conditions during deposition, coupled with an optimal sputtering temperature of  $40\text{ }^\circ\text{C}$ , we achieved the ideal setting for generating nanostructures and uniformly distributed thin films. Notably, nanowires manifest in  $\text{VO}_2$ , while  $\text{MoO}_3$  exhibits growth in the form of nanosheets. However, depositing the sandwich structure affects the surface growth of the  $\text{VO}_2$  layer due to its lattice strain, which can influence the growth of  $\text{MoO}_3$  on its surface.

The top FE-SEM images of W-V-W, MoW-V-W, and Mo-V-W sandwich samples unveil a fascinating evolution of nanowire-based structures, shedding light on the intricate nature of these composite materials. In Fig. 2(a) and (b), the W-V-W sample exhibits an initial morphology characterized by a dense and compact structure, with large grains (approximately  $139\text{ nm}$  in size) uniformly distributed. However, in Fig. 2(c) and (d), with an increased concentration of Mo in the top layer of the MoW-V-W sample, the presence of delicate nanowires becomes evident, signifying the early stages of surface morphology transformation. Observations indicate the presence of nanostructured wires, with dimensions of roughly  $60\text{ nm}$  in length and  $20\text{ nm}$  in diameter, which appear to develop atop the grains. This formation results in clearly demarcated regions separated by grain boundaries.

As the process continues, further increasing the Mo atom concentration until reaching  $\text{MoO}_3$  on the top surface, a profound transformation is observed, resulting in a well-defined and visible nanostructured surface. Fig. 2(e) and (f) depicts the Mo-V-W sample, where short nanowires are uniformly distributed across the entire surface. Notably, the



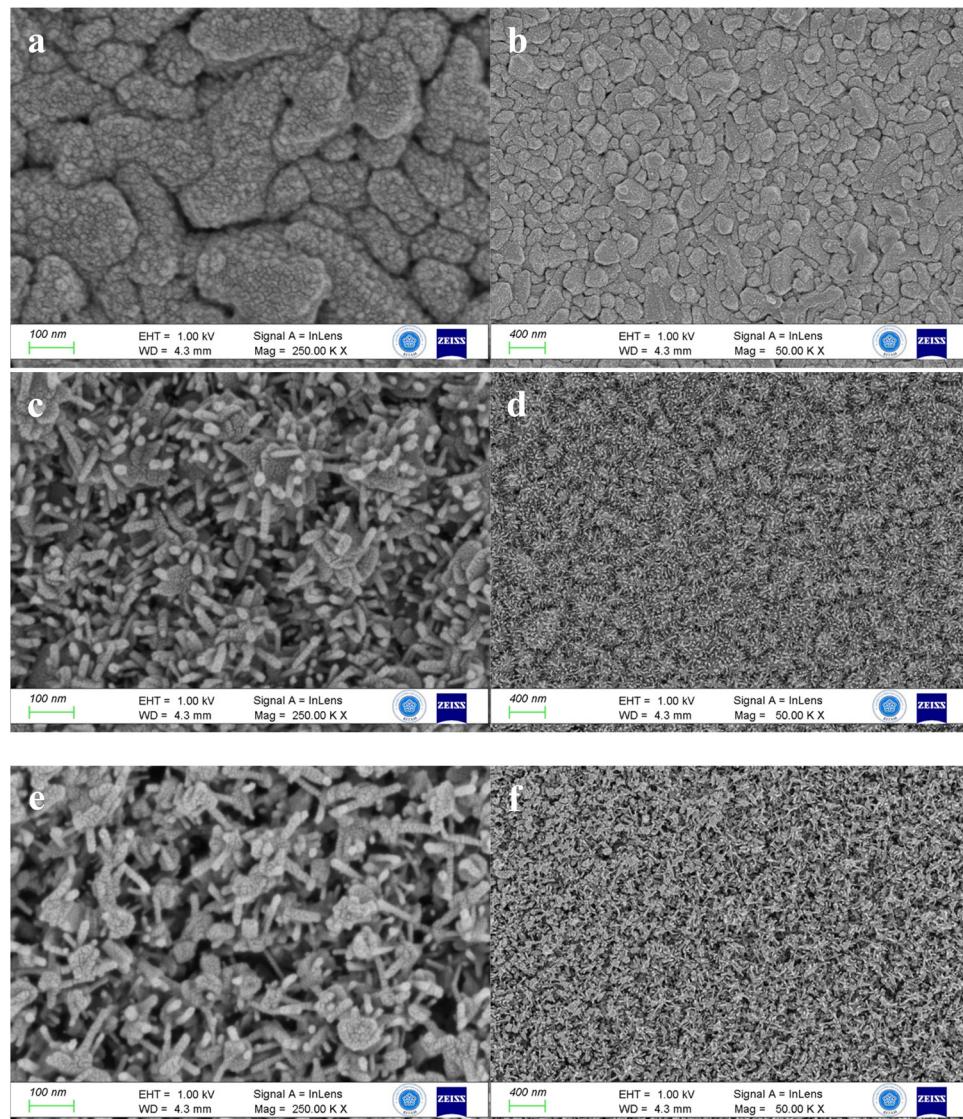


Fig. 2 FE-SEM images of (a) and (b) W-V-W, (c) and (d) MoW-V-W, and (e) and (f) Mo-V-W samples. (a), (c), and (e) show a high resolution of 250 KX, while (b), (d), and (f) represent 50 KX resolutions.

nanoparticles' size remains unchanged compared to the MoW-V-W sample. These short nanowires, characterized by their slender and tapered structures, significantly contribute to the overall surface texture, providing a light-harvesting surface that holds great promise for applications in intelligent windows.

### 3. XPS

To seek the origin of different thermochromic properties of samples upon varying the top layer of the sandwich structure, the XPS analysis is carried out on both the Mo-V-W and W-V-W samples to examine the composition and valence states of the prepared films. The corresponding results are displayed in Fig. 3 and 4. In Fig. 3(a), the analysis of Mo-V-W and the XPS spectra revealed the presence of the V2p, O1s (Fig. 3(b)), and Mo3d (Fig. 3(c)) photoelectron spectra. The peaks were deconvoluted using a Gaussian function to ascertain the films'

chemical state and stoichiometry. Due to spin-orbit splitting, the V2p<sub>3/2</sub> spectra display characteristic two-peak patterns at 517.1 eV and 517.9 eV, corresponding to the oxidation states of V<sup>4+</sup> and V<sup>5+</sup>, respectively. For O1s, the core peak was split into two peaks corresponding to an oxygen ion "O<sup>2-</sup>" at 530 eV and oxygen vacancies "V<sub>O</sub><sup>2+</sup>" at 533.12 eV. High-resolution XPS in Fig. 3(c) showed the enlarged spectra of Mo3d between 227 eV and 240 eV binding energies, which exhibited dual peaks, with Mo3d<sub>5/2</sub> and Mo3d<sub>3/2</sub> peaks. These peaks correspond to molybdenum in Mo<sup>6+</sup> oxidation states. The binding energy difference of Mo3d<sub>5/2</sub> and Mo3d<sub>3/2</sub> is 3.12 eV, which fits well with the reported values.<sup>46,47</sup>

The XPS analysis of the W-V-W sample is presented in Fig. 4. The survey spectrum in Fig. 4(a) shows the existence of O, W, and V. Deconvolution of V2p<sub>3/2</sub> also reveals two peaks at 516.41 eV and 517.11 eV, for V<sup>4+</sup> and V<sup>5+</sup>, oxidation states,

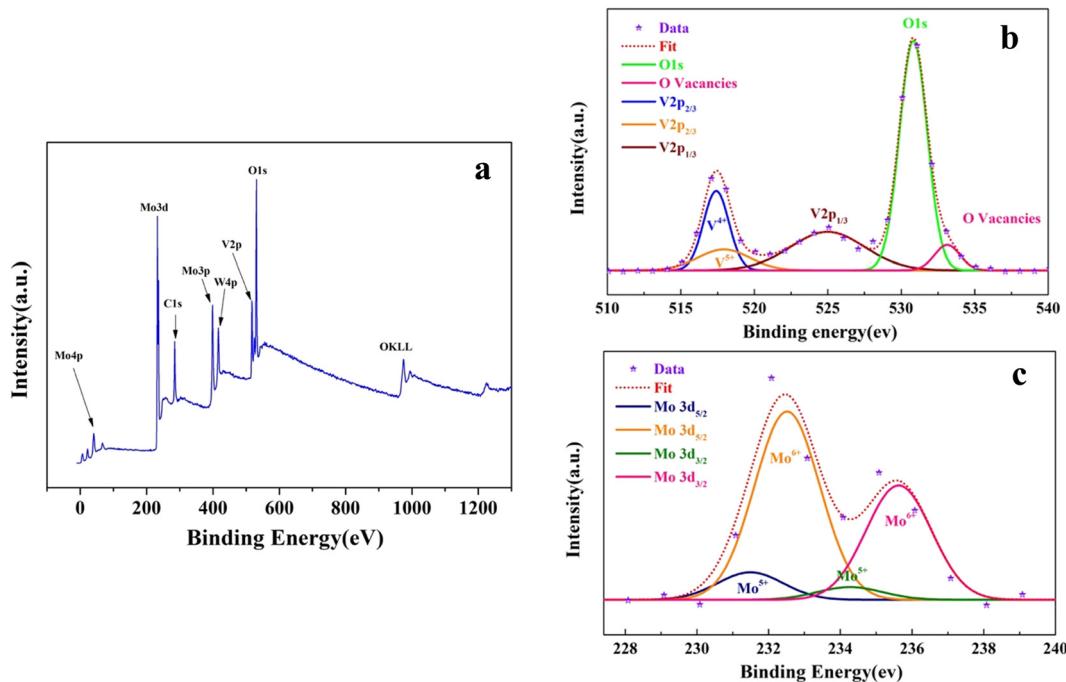


Fig. 3 (a) XPS survey spectrum of the M–V–W sample. (b) Enlarged spectra of V 2p<sub>3/2</sub>, V 2p<sub>1/2</sub>, and O 1s and (c) Mo 3d peaks.

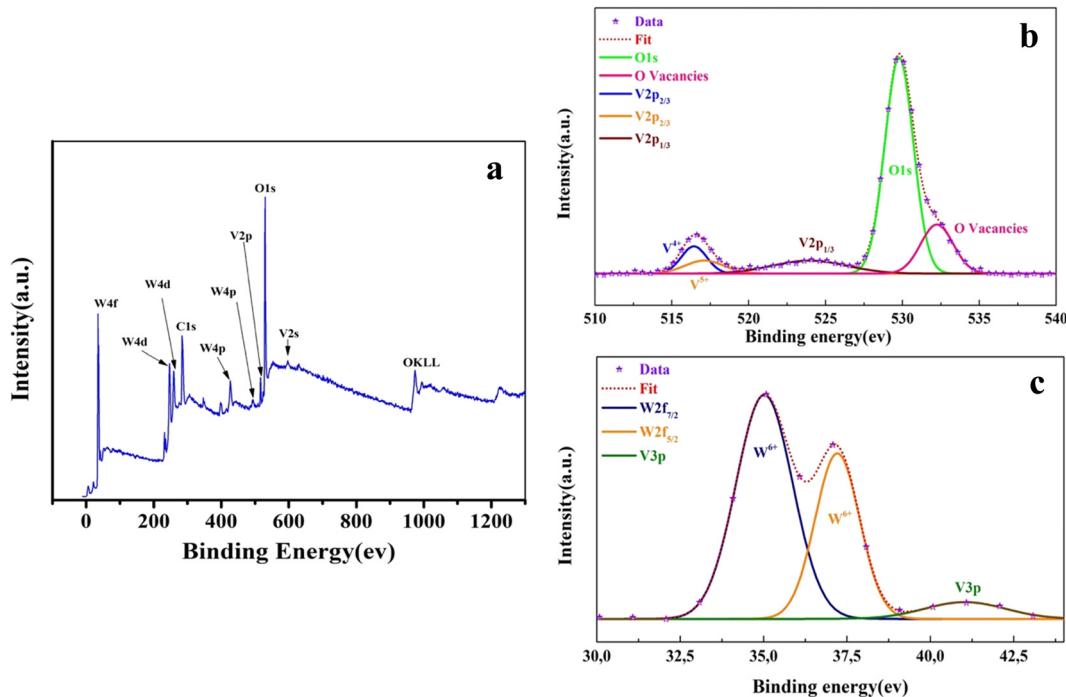


Fig. 4 (a) XPS survey spectrum of the W–V–W sample. (b) Enlarged spectra of V 2p<sub>3/2</sub>, V 2p<sub>1/2</sub>, and O 1s and (c) W 2f and V 3p peaks.

respectively. The high resolution of the O1s core peak shows an oxygen ion peak of “O<sup>2-</sup>” at 529.78 eV and oxygen vacancies “V<sub>O</sub><sup>2+</sup>”, at 532.24 eV (Fig. 4(b)).<sup>48</sup> In addition, from the deconvolution of the W4f core peak in Fig. 4(c), W is present as W<sup>6+</sup> with W4f<sub>7/2</sub> and W2f<sub>5/2</sub> at 35.02 eV and 37.21 eV binding

energies, respectively. These binding energies were consistent with previously published values of the W<sup>6+</sup> oxidation state WO<sub>3</sub>.<sup>38,42</sup>

The integrated surface ratio of V<sup>4+</sup>/V<sup>5+</sup> in Mo–V–W is 1.87, indicating a higher proportion of V<sup>4+</sup> valence than the W–V–W

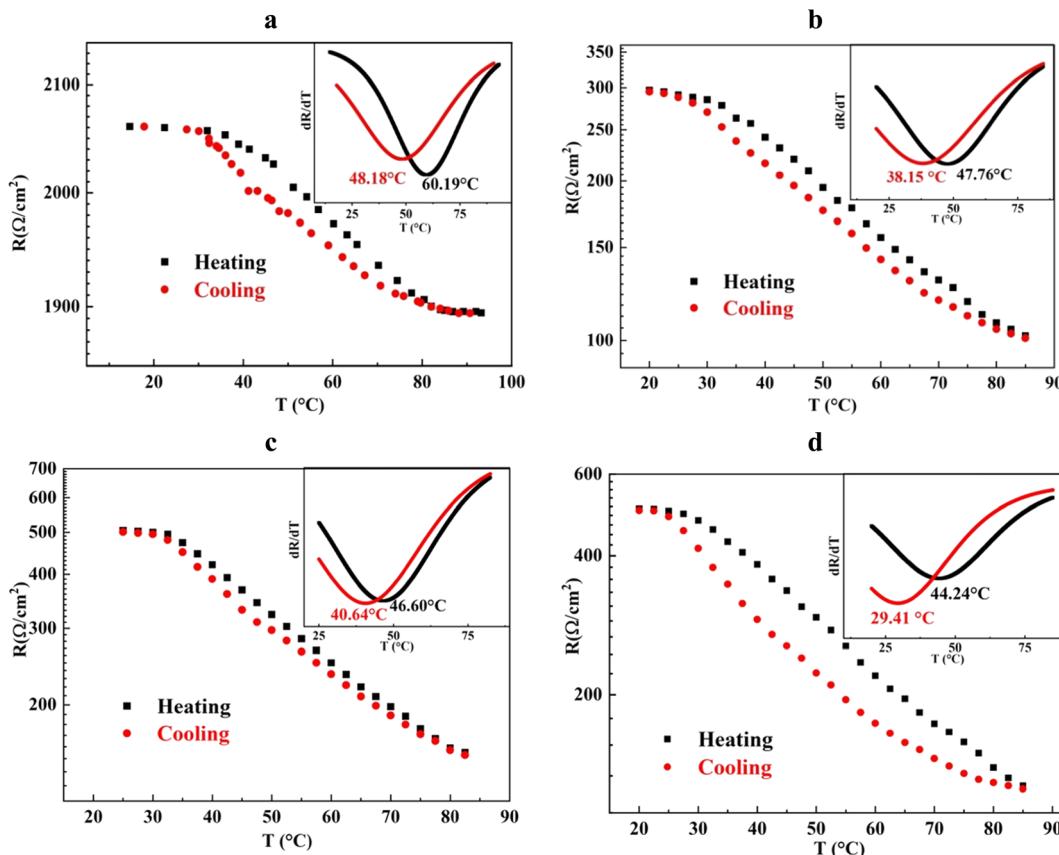


Fig. 5 Temperature-dependent sheet resistivity of (a) V, (b) W-V-W, (c) MoW-V-W, and (d) Mo-V-W samples.  $T_c$  calculated from  $d(\log R)/dT \sim T$  with Gauss fitting plots in insets.

sample, which presents a lower  $\text{V}^{4+}/\text{V}^{5+}$  ratio of 1.37. It is generally thought that  $\text{W}^{6+}$  and  $\text{Mo}^{6+}$  as solutes penetrate the crystal lattice of  $\text{VO}_2$  and substitute the  $\text{V}^{4+}$  ion, creating donor-like defects (both  $\text{W}^{6+}$  and  $\text{Mo}^{6+}$  ions with valences higher than  $\text{V}^{4+}$  ions). The lower  $\text{V}^{4+}/\text{V}^{5+}$  ratio in the W-V-W sample relative to the Mo-V-W sample is attributed to the possibility of over-doping  $\text{VO}_2$  thin films by W atoms migrating from both upper and lower layers.<sup>47</sup> However, in the Mo-V-W sample, the co-doping of  $\text{W}^{6+}$  and  $\text{Mo}^{6+}$  ions contribute separately to the increasing  $\text{V}^{4+}/\text{V}^{5+}$  ratio.<sup>19,49,50</sup>

#### 4. Electrical properties

Fig. 5 illustrates the temperature-dependent sheet resistivity of V, W-V-W, MoW-V-W, and Mo-V-W samples. The graph showcases the variation in sheet resistivity with changing temperatures. Initially, all samples exhibit thermochromic properties with a relatively high sheet resistivity in  $\text{K}\Omega$  order (Table 2). As the temperature increases, a significant decrease in sheet resistivity of up to four orders of magnitude is observed for the samples with  $\text{MoO}_3$  as a window layer. This remarkable change indicates a notable improvement in the electrical conductivity properties of the sandwich samples compared to the reference sample V.

The amplitude of transition ( $\Delta R$ ), representing the resistance change from room temperature above  $85^\circ\text{C}$ , and the

Table 2  $T_c$ ,  $\Delta R$  and  $\Delta H$  of V, W-V-W, MoW-V-W, and Mo-V-W samples

Samples	$T_c$ ( $^\circ\text{C}$ )	$\Delta R$ ( $\Omega \text{ cm}^{-1}$ )	$\Delta H$ ( $^\circ\text{C}$ )
V	54	$1.7 \times 10^2$	12
W-V-W	43	$1.95 \times 10^2$	9.6
MoW-V-W	43.6	$3.5 \times 10^2$	6
Mo-V-W	36.8	$3.78 \times 10^2$	14.8

hysteresis widths ( $\Delta H$ ), calculated as the difference between  $T_c$  values measured during heating and cooling cycles are also discussed. The  $T_c$  value of the W-V-W sample with a  $\text{WO}_3$  window layer is  $43^\circ\text{C}$ , while for the MoW-V-W sample with a  $\text{Mo}_{0.2}\text{W}_{0.8}\text{O}_3$  window layer, it is  $43.6^\circ\text{C}$ . However, Mo-V-W samples presented the lowest recorded  $T_c$  behavior of  $36.8^\circ\text{C}$ . Those values of the three samples are lower than the observed transition temperature of  $\text{VO}_2$  of the order  $54^\circ\text{C}$ .

Furthermore, the  $\Delta R$  and  $\Delta H$  values change according to the window layer used in W-V-W, MoW-V-W, and Mo-V-W samples. Comparatively, the W-V-W sample deposited with a  $\text{WO}_3$  window layer exhibits a lower  $\Delta R$  value of  $1.95 \times 10^2 \Omega \text{ cm}^{-2}$ , while MoW-V-W with the  $\text{Mo}_{0.2}\text{W}_{0.8}\text{O}_3$  window layer presented a narrower  $\Delta H$  of  $6^\circ\text{C}$  with a high  $\Delta R$  of  $3.5 \times 10^2 \Omega \text{ cm}^{-2}$ , indicating superior electrical behavior compared to the V sample with the smallest  $\Delta R$  ( $1.7 \times 10^2 \Omega \text{ cm}^{-2}$ ) and a  $\Delta H$  value of  $12^\circ\text{C}$ . Mo-V-W presented a higher  $\Delta R$  of

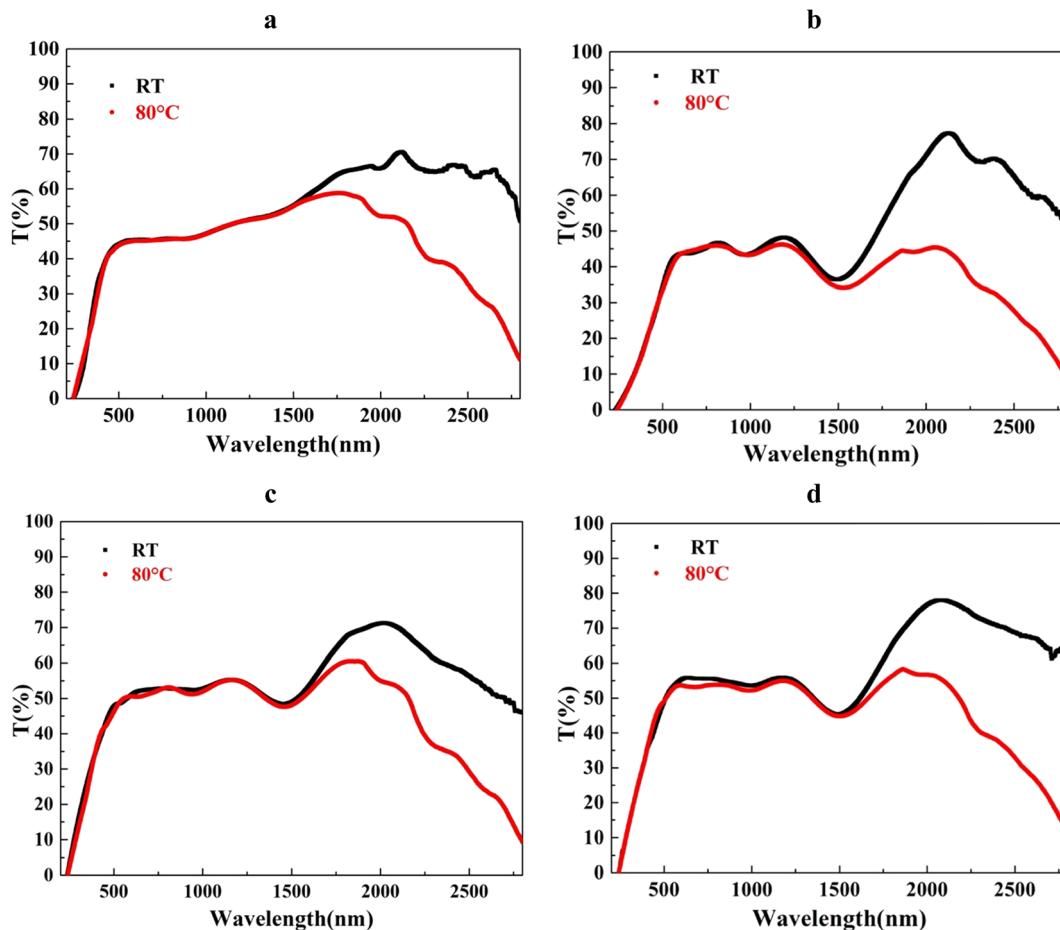


Fig. 6 Transmittance spectra at RT and 80 °C of (a) V, (b) W-V-W, (c) MoW-V-W, and (d) Mo-V-W samples.

$3.78 \times 10^2 \Omega \text{ cm}^{-2}$  and the lowest  $T_c$  of 36.8 °C. However, this sample presents the highest hysteresis  $\Delta H$  of 14.8 °C.

A longstanding debate surrounds the nature of the metal-insulator transition (MIT) in  $\text{VO}_2$ . Some argue for a Mott-type transition, emphasizing strong electron-electron correlations, while others advocate for a Peierls-type transition, focusing on structural changes involving V dimerization. Recently, a hybrid perspective has emerged, proposing that the MIT in  $\text{VO}_2$  might be best described as a Mott-Peierls phase transition, suggesting that electron-electron correlations and  $\text{V}^{4+}$  dimerization contribute significantly to this transition.<sup>51–53</sup> As evidenced by the XPS findings, the W-V-W configuration exhibits a lower  $\text{V}^{4+}/\text{V}^{5+}$  ratio compared to the Mo-V-W configuration. Consequently, the  $T_c$  of the Mo-V-W samples is lower than that of the W-V-W samples. Despite the low  $T_c$  of Mo-V-W, the Mo migration to the  $\text{VO}_2$  lattice results in a broadening of the phase transition peak (bigger  $\Delta H$ ); this effect is likely due to the substitution of V in the  $\text{VO}_2$  lattice by Mo through doping. Mo will replace the position of V in the doping process because the radius of  $\text{Mo}^{6+}$  is more significant than that of  $\text{V}^{4+}$ , which results in the deformation of its crystalline structure due to the size mismatch. This disparity in ionic radii between  $\text{Mo}^{6+}$  and  $\text{V}^{4+}$  leads to decreased activation energy required for MIT, resulting in a bigger  $\Delta H$  and a phase transition sharpness.<sup>49,54–56</sup> The work

done by Fan *et al.*<sup>57</sup> indicated that the high defect concentration would cause a hysteresis loop or disappearance of the shifting effect.

## 5. Optical properties

The optical transmittance of samples was measured in visible (vis) and near-infrared (NIR) regions under two different temperatures (room temperature (RT); 25 °C and 80 °C) of the V, W-V-W, MoW-V-W, and Mo-V-W samples. It is evident from the presented results in Fig. 6 that the transmittance in the visible region remains relatively constant for all the samples. The following formulas were used to calculate the integrated solar transmittance ( $T_{\text{sol}}$ , 300–2500 nm) and luminous transmittance ( $T_{\text{lum}}$ , 380–780 nm)<sup>58</sup>:

$$T_{\text{sol/lum}} = \int_{\text{sol/lum}}^{\phi} (\lambda) T(\lambda) d\lambda \int_{\text{sol/lum}}^{\phi} (\lambda) \varphi_{\text{lum}}(\lambda) d\lambda$$

$$\Delta T_{\text{sol}} = T_{\text{sol}}(25 \text{ °C}) - T_{\text{sol}}(80 \text{ °C})$$

In this case,  $\varphi_{\text{lum}}(\lambda)$  is the standard luminous efficiency function for the human photopic vision,  $T(\lambda)$  indicates the film transmittance at a wavelength ( $\lambda$ ), and  $\varphi_{\text{sol}}(\lambda)$  is the solar irradiance spectrum for air mass 1.5, which corresponds to the sun standing 37° above the horizon and  $\Delta T_{\text{sol}}$  is the solar modulation ability.



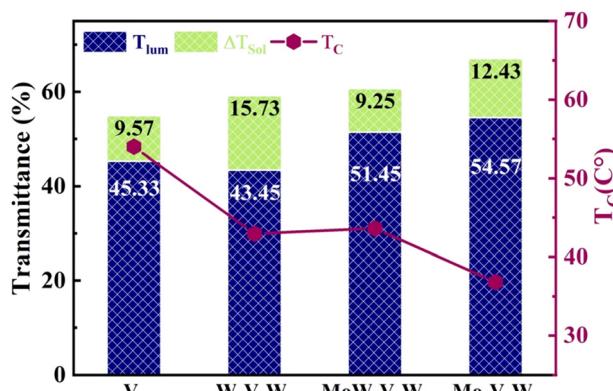


Fig. 7 Bar plots of  $T_{lum}$ ,  $\Delta T_{sol}$  and  $T_c$  of V, W-V-W, MoW-V-W and Mo-V-W samples.

To use  $VO_2$  in smart windows applications, a technological obstacle is to raise the maximum  $T_{lum}$  to a respectable level ( $>50\%$ ) while preserving  $VO_2$ 's high  $\Delta T_{sol}$ .<sup>59</sup> The solar transmittance of each sample was computed as a means of illustrating the solar modulation. The calculated  $T_{sol}$  on the solar spectra present a similar comportment as  $T_{lum}$ . This suggests that the structures under investigation have a large impact on the transmission of not only in the visible light range but also in the entire solar spectra.

As presented in Fig. 7,  $T_{lum}$  calculated from the transmittance spectra at the RT, it presents a slight decrease from 45.33% to 41.65% in the W-V-W sample compared to the  $VO_2$  thin films' reference sample (Table 3). The sandwich structure negatively affected the sample's transmittance in W-V-W due to the additional two  $WO_3$  layers.<sup>48</sup> On the other hand,  $\Delta T_{sol}$  increased to from 9.57% in  $VO_2$  to 15.7%. Nevertheless, a considerable improvement in both MoW-V-W and Mo-V-W of 50.83% and 54.57% was noticed. In contrary to the W-V-W surface, the nanostructured surface of MoW-V-W and Mo-V-W acted as a light-harvesting media reducing the reflectance arrived from the  $VO_2$  surface and acting as an antireflecting layer. Consequently, we notice a very promising improvement in  $T_{lum}$ . Additionally, in Table 3,  $T_{lum}$  improvement can be seen to have a direct relationship with the sandwich samples' optical band gap ( $E_g$ ).<sup>7,54</sup>  $\Delta T_{sol}$  decreases in Mo-V-W and MoW-V-W to 12.43% and 9.25%, respectively, compared to the W-V-W sample. It is believed that the defects generated due to the textured surface negatively affected the solar modulation of these two samples.

Table 3  $T_c$ ,  $T_{lum}$ ,  $T_{sol}$  and  $\Delta T_{sol}$  of V, W-V-W, MoW-V-W and Mo-V-W samples

Samples	$T_{lum}$	$T_{sol}$	$\Delta T_{sol}$	$T_c$ (°C)
V	45.33	46.86	9.57	54
W-V-W	41.65	43.45	15.73	43
MoW-V-W	50.83	51.45	9.25	43.6
Mo-V-W	54.57	52.49	12.43	36.8

## IV. Conclusions

In conclusion, the systematic investigation of nanowire-based sandwich-structured thin films composed of  $Mo_{0.2}W_{0.8}O_3$ ,  $MoO_3$ , and  $WO_3$  top layers *via* physical vapor deposition provides a detailed understanding of their structural, electrical, and optical characteristics. Raman spectroscopy confirms the successful preparation of each thin film, highlighting distinctive vibrational modes and lattice features. FE-SEM images reveal a fascinating evolution of nanostructures, particularly with  $MoO_3$  as the top layer, showcasing potential applications in smart window applications. Electrical properties exhibit significant improvements in conductivity for samples with  $MoO_3$  as a window layer, attributing this enhancement to the migration of Mo atoms into the  $VO_2$  lattice. The observed MIT behavior is rationalized based on XPS findings. Furthermore, optical analysis demonstrates promising improvements in luminous transmittance and solar modulation, especially in configurations with  $MoO_3$  as the top layer. Collectively, these findings contribute to the knowledge base for developing and optimizing multifunctional thin films, paving the way for potential advancements in smart window technologies.

## Data availability

Will be available on request.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

1. P. Huovila, *et al.*, *Buildings and climate change: Summary for decision-makers*, 2009.
2. L. Pérez-Lombard, J. Ortiz and C. Pout, A review on buildings energy consumption information, *Energy Build.*, 2008, **40**(3), 394–398.
3. Z. Zhang, *et al.*, Thermochromic Energy Efficient Windows: Fundamentals, Recent Advances, and Perspectives, *Chem. Rev.*, 2023, **123**(11), 7025–7080.
4. K. Okimura, *et al.*, High luminous transmittance and solar modulation of  $VO_2$ -based smart windows with  $SiO_2$  anti-



reflection coatings, *Sol. Energy Mater. Sol. Cells*, 2023, **251**, 112162.

5 M. K. Shahzad, *et al.*, Influence of  $\text{VO}_2$  based structures and smart coatings on weather resistance for boosting the thermochromic properties of smart window applications, *RSC Adv.*, 2022, **12**(48), 30985–31003.

6 J. Victor, *et al.*, From multilayers to  $\text{V}_{1-x}\text{W}_x\text{O}_2 \pm \delta$  films elaborated by magnetron sputtering for decreasing thermochromic transition temperature, *J. Alloys Compd.*, 2021, **858**, 157658.

7 D. Zhou, *et al.*, Symmetrical  $\text{SnO}_2/\text{W}$ -doped  $\text{VO}_2/\text{SnO}_2$  sandwich structures with high luminous transmittance, excellent solar modulation ability and low phase transition temperature, *Infrared Phys. Technol.*, 2022, **123**, 104198.

8 H. Zhou, *et al.*, Surface plasmon resonance tunability in  $\text{VO}_2/\text{Au}/\text{VO}_2$  thermochromic structure, *Laser Photonics Rev.*, 2014, **8**(4), 617–625.

9 Y. Dang, L. Zhao and J. Liu, Preparation and optical properties of W-doped  $\text{VO}_2/\text{AZO}$  bilayer composite film, *Ceram. Int.*, 2020, **46**(7), 9079–9085.

10 H. Zong, *et al.*, Preparation and characterization of  $\text{HfO}_2/\text{VO}_2/\text{HfO}_2$  sandwich structures with low phase transition temperature, excellent thermochromic properties, and superior durability, *Ceram. Int.*, 2022, **48**(5), 6734–6744.

11 D. Malarde, *et al.*, Optimized atmospheric-pressure chemical vapor deposition thermochromic  $\text{VO}_2$  thin films for intelligent window applications, *ACS Omega*, 2017, **2**(3), 1040–1046.

12 H. Koo, *et al.*, The effect of  $\text{CeO}_2$  antireflection layer on the optical properties of thermochromic  $\text{VO}_2$  film for smart window system, *J. Mater. Eng. Perform.*, 2014, **23**, 402–407.

13 H.-T. Zhang, *et al.*, Wafer-scale growth of  $\text{VO}_2$  thin films using a combinatorial approach, *Nat. Commun.*, 2015, **6**(1), 8475.

14 J. Kim, *et al.*, Two-dimensional  $\text{VO}_2$  nanosheet converted from MXene for flexible thermochromic smart windows, *Chem. Eng. J.*, 2023, **477**, 147014.

15 H. Koo, *et al.*, Thermochromic properties of  $\text{VO}_2$  thin film on  $\text{SiN}_x$  buffered glass substrate, *Appl. Surf. Sci.*, 2013, **277**, 237–241.

16 G. Xu, *et al.*, Optimization of antireflection coating for  $\text{VO}_2$ -based energy efficient window, *Sol. Energy Mater. Sol. Cells*, 2004, **83**(1), 29–37.

17 H. Kim, *et al.*, Strain effect in epitaxial  $\text{VO}_2$  thin films grown on sapphire substrates using  $\text{SnO}_2$  buffer layers, *AIP Adv.*, 2017, **7**(10), 105116.

18 J. Zheng, S. Bao and P. Jin,  $\text{TiO}_2$  (R)/ $\text{VO}_2$  (M)/ $\text{TiO}_2$  (A) multilayer film as smart window: Combination of energy-saving, antifogging and self-cleaning functions, *Nano Energy*, 2015, **11**, 136–145.

19 S. Long, *et al.*, Thermochromic multilayer films of  $\text{WO}_3/\text{VO}_2/\text{WO}_3$  sandwich structure with enhanced luminous transmittance and durability, *RSC Adv.*, 2016, **6**(108), 106435–106442.

20 S.-Z. Sheng, *et al.*, Nanowire-based smart windows combining electro-and thermochromics for dynamic regulation of solar radiation, *Nat. Commun.*, 2023, **14**(1), 3231.

21 L. Veeramuthu, *et al.*, Novel stretchable thermochromic transparent heaters designed for smart window defroster applications by spray coating silver nanowire, *RSC Adv.*, 2019, **9**(61), 35786–35796.

22 L. L. Zhao, *et al.*, Enhanced Thermochromic Properties and Solar-Heat Shielding Ability of  $\text{W}_x\text{V}_{1-x}\text{O}_2$  Thin Films with Ag Nanowires Capping Layers, *J. Nanosci. Nanotechnol.*, 2015, **15**(11), 9192–9196.

23 D. Y. Lu, *et al.*, Raman study of thermochromic phase transition in tungsten trioxide nanowires, *Appl. Phys. Lett.*, 2007, **90**(4), 041919.

24 W. Y. Wu, *et al.*, Thermochromism from Ultrathin Colloidal  $\text{Sb}_2\text{Se}_3$  Nanowires Undergoing Reversible Growth and Dissolution in an Amine–Thiol Mixture, *Adv. Mater.*, 2019, **31**(4), 1806164.

25 K. C. Kam and A. K. Cheetham, Thermochromic  $\text{VO}_2$  nanorods and other vanadium oxides nanostructures, *Mater. Res. Bull.*, 2006, **41**(5), 1015–1021.

26 M. A. Basyooni, *et al.*, Efficient  $\text{MoWO}_3/\text{VO}_2/\text{MoS}_2/\text{Si}$  UV Schottky photodetectors;  $\text{MoS}_2$  optimization and monoclinic  $\text{VO}_2$  surface modifications, *Sci. Rep.*, 2020, **10**(1), 1–18.

27 K. Appavoo, *et al.*, Role of defects in the phase transition of  $\text{VO}_2$  nanoparticles probed by plasmon resonance spectroscopy, *Nano Lett.*, 2012, **12**(2), 780–786.

28 M. A. Basyooni, *et al.*, Fast response of  $\text{CO}_2$  room temperature gas sensor based on Mixed-Valence Phases in Molybdenum and Tungsten Oxide nanostructured thin films, *Ceram. Int.*, 2020, **46**(7), 9839–9853.

29 M. Currie, M. A. Mastro and V. D. Wheeler, Atomic layer deposition of vanadium dioxide and a temperature-dependent optical model, *J. Visualized Exp.*, 2018, **(135)**, e57103.

30 A. Makarevich, *et al.*, Chemical synthesis of high quality epitaxial vanadium dioxide films with sharp electrical and optical switch properties, *J. Mater. Chem. C*, 2015, **3**(35), 9197–9205.

31 X.-B. Chen, Assignment of the Raman modes of  $\text{VO}_2$  in the monoclinic insulating phase, *J. Korean Phys. Soc.*, 2011, **58**, 100–104.

32 T. Nagyné-Kovács, *et al.*, Hydrothermal synthesis and gas sensing of monoclinic  $\text{MoO}_3$  nanosheets, *Nanomaterials*, 2020, **10**(5), 891.

33 P. Martín-Ramos, *et al.*,  $\alpha$ - $\text{MoO}_3$  crystals with a multilayer stack structure obtained by annealing from a lamellar  $\text{MoS}_2/\text{g-C}_3\text{N}_4$  nanohybrid, *Nanomaterials*, 2018, **8**(7), 559.

34 T. Ivanova, K. Gesheva and A. Szekeres, Structure and optical properties of CVD molybdenum oxide films for electrochromic application, *J. Solid State Electrochem.*, 2002, **7**, 21–24.

35 C. W. Kee, Assignment of O–O and Mo = O stretching frequencies of molybdenum/tungsten complexes revisited, *J. Chem.*, 2015, **2015**, 10.

36 A. Klinbunmung, T. Thongtem and S. Thongtem, Characterization of orthorhombic  $\alpha$ - $\text{MoO}_3$  microplates produced by a microwave plasma process, *J. Nanomater.*, 2012, **2012**, 10.



37 F. Haque, *et al.*, Ordered intracrystalline pores in planar molybdenum oxide for enhanced alkaline hydrogen evolution, *J. Mater. Chem. A*, 2019, **7**(1), 257–268.

38 F. Liu, *et al.*, Ultrathin tungsten oxide nanowires: oleylamine assisted nonhydrolytic growth, oxygen vacancies and good photocatalytic properties, *RSC Adv.*, 2015, **5**(94), 77423–77428.

39 J. Díaz-Reyes, *et al.*, Characterization of  $\text{WO}_3$  thin films grown on silicon by HFMOD, *Adv. Condens. Matter Phys.*, 2013, **2013**, 9.

40 H. Choi, *et al.*, Mid-infrared properties of a  $\text{VO}_2$  film near the metal-insulator transition, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**(7), 4621.

41 M. A. B. Mohamed,  *$\text{VO}_2$  İnce Film İçeren İki Boyutlu ve Çok Katmanlı Yapılardaki Arayüzey Gerilmelerinin Termokromik ve Fotodetektör Performanslara Etkisi*, Necmettin Erbakan University, Turkey, 2020.

42 J. Díaz-Reyes, *et al.*, Characterization of  $\text{WO}_3$  thin films grown on silicon by HFMOD, *Adv. Condens. Matter Phys.*, 2013, **2013**, 9.

43 M. A. Basyooni, *et al.*, Tuning the metal-insulator transition properties of  $\text{VO}_2$  thin films with the synergetic combination of oxygen vacancies, strain engineering, and tungsten doping, *Nanomaterials*, 2022, **12**(9), 1470.

44 S.-Y. Li, *et al.*, Thermochromic  $\text{VO}_2$  nanorods made by sputter deposition: Growth conditions and optical modeling, *J. Appl. Phys.*, 2013, **114**(3), 033516.

45 T. D. Vu, *HIPIMS deposition of  $\text{VO}_2$  thermochromic coating for enhanced optical properties*, 2022.

46 Z. Li, L. Gao and S. Zheng, SEM, XPS, and FTIR studies of  $\text{MoO}_3$  dispersion on mesoporous silicate MCM-41 by calcination, *Mater. Lett.*, 2003, **57**(29), 4605–4610.

47 V. Sreelakshmi, A. A. Kaliani and M. Jithin, Photochromic and hydrophilic vanadium oxide–molybdenum oxide composite thin films, *J. Mater. Sci.: Mater. Electron.*, 2023, **34**(3), 179.

48 Z. Fang, *et al.*,  $\text{VO}_2/\text{ZnO}$  bilayer films with enhanced thermochromic property and durability for smart windows, *Appl. Surf. Sci.*, 2021, **540**, 148414.

49 F. Chen, *et al.*, Simultaneous tuning of the phase transition temperature and infrared optical properties of Mo-doped  $\text{VO}_2$  powders for intelligent infrared stealth materials, *Ceram. Int.*, 2023, **49**(15), 25585–25593.

50 D. Li, *et al.*, Influence of the charge compensation effect on the metal–insulator transition of Mg-W co-doped  $\text{VO}_2$ , *Appl. Surf. Sci.*, 2022, **579**, 151990.

51 N. F. Mott, The basis of the electron theory of metals, with special reference to the transition metals, *Proc. Phys. Soc., Sect. A*, 1949, **62**(7), 416.

52 C. Ling, *et al.*, W Doping and Voltage Driven Metal-Insulator Transition in VO Nano -Films for Smart Switching Devices, *ACS Appl. Nano Mater.*, 2019, **2**(10), 6738–6746.

53 S. Biermann, *et al.*, Dynamical singlets and correlation-assisted peierls transition in  $\text{VO}_2$ , *Phys. Rev. Lett.*, 2005, **94**(2), 026404.

54 C. Kang, *et al.*, Transformation of crystalline structure and photoelectric properties in  $\text{VO}_2/\text{glass}$  thin films by inserting  $\text{TiO}_2$  buffer layers, *Appl. Surf. Sci.*, 2019, **463**, 704–712.

55 C. W. Jo, H. J. Kim and J. W. Yoo, Thermochromic Properties of W-Mo Co-Doped VO(M) Nanoparticles According to Reaction Parameters, *J. Nanosci. Nanotechnol.*, 2017, **17**(5), 2923–2928.

56 Y. Xue and S. Yin, Element doping: a marvelous strategy for pioneering the smart applications of  $\text{VO}_2$ , *Nanoscale*, 2022, **14**(31), 11054–11097.

57 L. Fan, *et al.*, Modulation of  $\text{VO}_2$  metal-insulator transition by co-doping of hydrogen and oxygen vacancy, *Sol. Energy Mater. Sol. Cells*, 2020, **212**, 110562.

58 M. A. Abozeid, *et al.*, Development of nano- $\text{WO}_3$  doped with  $\text{NiO}$  for wireless gas sensors, *Arabian J. Sci. Eng.*, 2019, **44**(1), 647–654.

59 M. Zhou, *et al.*, Periodic porous thermochromic  $\text{VO}_2$  (M) films with enhanced visible transmittance, *Chem. Commun.*, 2013, **49**(54), 6021–6023.

