



**HAL**  
open science

## Tailoring thermochromic and optical properties of VO<sub>2</sub> thin films by pulsed laser deposition using different starting routes

Yannick Bleu, Florent Bourquard, Damien Jamon, Anne-Sophie Loir, Florence Garrelie, Christophe Donnet

### ► To cite this version:

Yannick Bleu, Florent Bourquard, Damien Jamon, Anne-Sophie Loir, Florence Garrelie, et al.. Tailoring thermochromic and optical properties of VO<sub>2</sub> thin films by pulsed laser deposition using different starting routes. *Optical Materials*, 2022, 133, pp.113004. 10.1016/j.optmat.2022.113004 . hal-03793783

**HAL Id: hal-03793783**

<https://hal.science/hal-03793783v1>

Submitted on 26 Nov 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

# Tailoring thermochromic and optical properties of VO<sub>2</sub> thin films by pulsed laser deposition using different starting routes

Yannick Bleu, Florent Bourquard, Damien Jamon, Anne-Sophie Loir, Florence Garrelie, Christophe Donnet

Université de Lyon, Université Jean Monnet-Saint-Étienne, CNRS, Institut d'Optique Graduate School, Laboratoire Hubert Curien, UMR 5516, F-42023 Saint-Étienne, France

## Abstract

The insulator to metal transition (IMT) of vanadium dioxide (VO<sub>2</sub>) at about 68 °C enables a variety of optical applications, including switching and modulation, and tuning of optical resonators. However, due to the multivalent nature of vanadium, controlling the synthesis of stoichiometric VO<sub>2</sub> is still a challenge. Moreover, the temperature dependent optical properties are strongly influenced by the microstructure of the VO<sub>2</sub> thin film. In this paper, we report for the first time the effect on the microstructure and optical properties of two different routes implemented using the same PLD process to obtain VO<sub>2</sub> thin films exhibiting an IMT; one route involving ablation of a metallic vanadium (V) target in an oxygen atmosphere, the other ablation of a vanadium oxide V<sub>2</sub>O<sub>5</sub> target in a vacuum, both followed by a similar rapid thermal annealing process. Each route leads to significantly different VO<sub>2</sub> thin films, exhibiting an IMT transition temperature of 69 °C with the V<sub>2</sub>O<sub>5</sub> route, and of 50°C with the V+O<sub>2</sub> route. In addition, VO<sub>2</sub> films obtained from V+O<sub>2</sub> have a narrower hysteresis width, a smoother surface with very low roughness, a slightly higher refractive index, a higher absorption coefficient, and a narrower optical band gap than VO<sub>2</sub> film obtained from V<sub>2</sub>O<sub>5</sub>. The thermochromic and optical properties of both VO<sub>2</sub> are discussed in relation with the nanostructural properties. Our findings highlight the value and versatility of the PLD process in adapting the optical properties of VO<sub>2</sub> films to the application concerned.

## 1. Introduction

Vanadium dioxide (VO<sub>2</sub>) thin films have been of great interest to researchers as they undergo an insulator to metal transition (IMT) at 68 °C. Upon heating, a reversible first order phase transition occurs from the monoclinic to the tetragonal phase involving a decrease in transmittance in the infrared region and electrical resistivity that can be of a few orders in

magnitude [1,2]. Thanks to this transition, many works have been devoted to studying the potential applications of VO<sub>2</sub>, for example, Mott transistors[3], smart window coatings[4], ultra-fast switches and micro bolometers[5], and optical resonant switches [6]. Indeed, pure VO<sub>2</sub> thin film is necessary to obtain a sharp and large hysteresis around 68 °C, and a synthesis of phase. However, achieving the synthesis of the pure VO<sub>2</sub> phase is still a challenge as vanadium has multiple oxidation states. Several methods of obtaining pure VO<sub>2</sub> thin film are reported in the literature, including chemical vapor deposition (CVD)[7], sputtering[8–12], solution based techniques[13–15] and pulsed laser deposition (PLD)[16–18]. Among these methods, VO<sub>2</sub> thin films have long been produced using PLD with a variety of target materials, oxygen gas pressures, laser energies, and other process parameters. Perhaps one of the most intriguing parameters is the target material itself. Several authors have reported on VO<sub>2</sub> thin film deposition using PLD using vanadium metal[19], V<sub>2</sub>O<sub>5</sub> [20], V<sub>2</sub>O<sub>3</sub>[2] and VO<sub>2</sub> [21] as a target material. Among them, V<sub>2</sub>O<sub>5</sub> and pure vanadium metal are the most frequently used. However, no recent reports compare the optical properties of VO<sub>2</sub> thin film obtained using these two vanadium-based targets with the same process. In 1997, Bowman et al.[22] reported the growth of VO<sub>2</sub> using PLD with both targets, and emphasized the effect of the applied strain on the resistance electrical resistivity of the resulting VO<sub>2</sub>, but a systematic comparison of the thermochromic and optical properties of VO<sub>2</sub> thin films obtained using PLD from vanadium metal and V<sub>2</sub>O<sub>5</sub> ceramic is still lacking.

In this paper, we report the synthesis and the optical properties of VO<sub>2</sub> thin films grown by pulsed laser deposition of vanadium metallic and V<sub>2</sub>O<sub>5</sub> ceramic targets, both followed by rapid thermal annealing. Oxygen pressure was introduced during ablation of vanadium, to ensure the formation of vanadium oxide. The rapid thermal annealing process enables precise control of the crystallization of the grown films, with minimum diffusion of impurities from the glass substrate into the films that can be detrimental for the thermochromic properties. We report the results of our investigation of the nanocrystalline structure and morphology of thermochromic properties such as the transmittance commutation from insulating to the metallic phase, the transition temperature, the hysteresis width, and other optical properties including absorbance in the visible ranges, the optical energy gap ( $E_g$ ) and optical conductivity of VO<sub>2</sub> films obtained from both targets. Using the deposited thin films from both targets with the same post annealing process resulted in two VO<sub>2</sub> thin films with different nanostructural and optical properties. Understanding the dependence of any starting

ablated materials on the VO<sub>2</sub> properties can thus help to stabilize VO<sub>2</sub> synthesis with the functional properties desired.

## 2. Experimental details

### *Deposition and annealing of the VO<sub>2</sub> films*

The synthesis route of VO<sub>2</sub> is a two-step process, as depicted in Fig.1. Prior to deposition, the SiO<sub>2</sub> substrates were cleaned using a three-step cleaning process in acetone, ethanol, and deionized water baths for 30 min each.

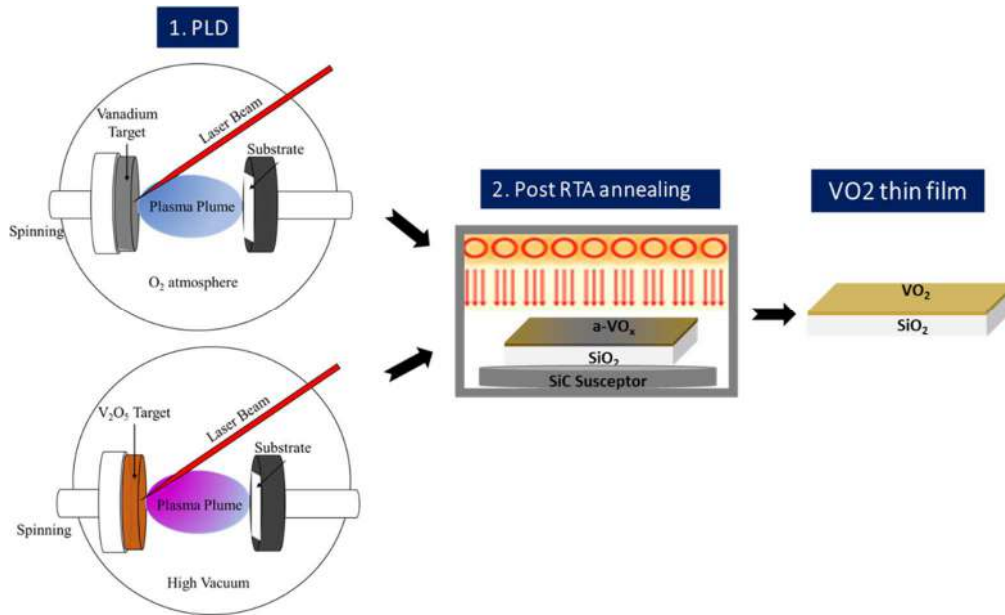


Figure 1: Synthesis steps for VO<sub>2</sub> films obtained by pulsed laser deposition and rapid thermal annealing on SiO<sub>2</sub>.

The first step was the pulsed laser deposition of the target materials. The PLD chamber was evacuated to a background pressure of  $1.7 \times 10^{-7}$  mbar. Two types of targets were used in the investigation: pure metallic vanadium (V) and ceramic V<sub>2</sub>O<sub>5</sub> targets, both with a purity of 99.9%. A KrF excimer laser operating at 248 nm and 10 Hz with a fluence of 13 J/cm<sup>2</sup> was used to ablate the targets. The distance between the target and the substrate was set at 5 cm and the laser beam was placed at an angle of 45° to the target. For the metallic vanadium, the oxygen pressure was  $1 \times 10^{-2}$  mbar (1 Pa) inside the deposition chamber using ultrapure O<sub>2</sub>. The ablation of the V<sub>2</sub>O<sub>5</sub> target was performed without oxygen gas. The substrates were maintained at room temperature and the targets were rotated during the deposition process to ensure uniform ablation of its surface. For both depositions, the average deposition rate was measured using profilometry. The deposition rate for V+O<sub>2</sub> was around 3 nm/min, while the

rate for  $V_2O_5$  was 6 nm/min. The deposition time was then adjusted to obtain 100 nm thin films.

The second step was the rapid thermal annealing process on the as-deposited  $VO_x$  films using a RTP machine (AS-One RTP system from Annealsys, France). This step consisted in heating the samples at 400 °C for 600 s at an oxygen partial pressure of 1 mbar (1 Pa) and a 50 sccm flow, with a heating rate of 5 °C/s and natural cooling. The annealing chamber was evacuated to a  $1 \times 10^{-2}$  mbar pressure before the oxygen was introduced. These conditions were the result of several preliminary optimizations to obtain the best thermochromic behavior of the deposited films. It is worth mentioning that for technical convenience, the  $VO_2$  samples were grown on two different substrates:  $SiO_2$  for Raman and transmittance measurements, Si for ellipsometry, GIXRD, AFM and SEM analysis.

### *Characterization*

The  $VO_2$  thin films were characterized in terms of the surface morphology, micro-structure and optical properties. Raman analysis (Jobin-Yvon ARAMIS) was performed using a 633 nm excitation wavelength, with a laser power of 0.1 mW and a laser beam was focused with a 100x objective, consistent with a laser spot diameter of less than 1 mm. Ellipsometry (HORIBA Jobin Yvon UVISSEL) was performed using a heated sample holder whose temperature was controlled by a thermocouple between 15 and 85 °C. The experimental ellipsometric parameters were fitted with a Tauc-Lorentz formula using three oscillators. Scanning electron microscopy (SEM) (JEOL IT 800 SHL) and atomic force microscopy (AFM) (Icon BRUKER) were used to analyze the morphology and roughness of the films. Grazing-incidence X-ray diffraction (GIXRD) was performed on an AERIS diffractometer (MALVERN PANALYTICAL) with a  $CuK\alpha$  X-ray source (0.1542 nm) of 450W. Data were collected in a  $2\theta$  configuration with an incidence angle  $\omega = 0.4^\circ$ , a  $2\theta$  acquisition range from  $20^\circ$  to  $75^\circ$  and a step size of  $0.04^\circ$ . The  $VO_2$  crystallite size  $D$  was quantified by the Scherrer equation  $D = (0.89 \cdot \lambda / \beta \cdot \cos\theta)$  [23] with  $\lambda$  the X-ray wavelength,  $\beta$  and  $\theta$  respectively the FWHM and diffraction angle of the diffraction peak of  $VO_2$ , using the instrumental peak width deduced from a referenced  $LaB_6$  powder whose diffractogram was recorded in similar conditions to those used for the  $VO_2$  films. Considering the diffraction patterns obtained,  $D$  was calculated as the average value deduced from the four most intense diffraction peaks within the range  $25^\circ$  to  $60^\circ$ . UV-Visible spectroscopy was performed in absorbance mode

within the spectral range 200–900 nm at room temperature. The thermochromic properties of the films were measured by collecting the transmittance between 20-100 °C in the visible and IR wavelength ranges using a fiber optic spectrometer equipped with handmade heating units. For all samples, the integrated luminous transmittance ( $T_{lum}$ , 380–780 nm) and solar modulation efficiency ( $T_{sol}$ , 300–2500 nm) were calculated from the following equation:

$$T_{lum,sol} = \frac{\int \varphi_{lum,sol}(\lambda)T(\lambda)d\lambda}{\int \varphi_{lum,sol}(\lambda)d\lambda} \quad (1)$$

where  $T(\lambda)$  denotes film transmittance at wavelength ( $\lambda$ ),  $\varphi_{lum}(\lambda)$  is the standard luminous efficiency function for the photopic vision of human eye,  $\varphi_{sol}(\lambda)$  is the solar irradiance spectrum for air mass 1.5 corresponding to the sun at an angle of 37° to the horizon[24].  $\Delta T_{sol}$  is obtained from :  $\Delta T_{sol} = T_{sol}(20\text{ °C}) - T_{sol}(90\text{ °C})$  and  $T_{lum} = \frac{1}{2}(T_{lum}(20\text{ °C}) + T_{lum}(90\text{ °C}))$ .

### 3. Results and discussion

#### a. Crystalline structure and surface morphology

Prior to RTA treatments, the as-deposited films a-VO<sub>x</sub> films were analyzed using Raman spectroscopy, as depicted in Fig. 2. According to [25,26], the Raman spectrum of a-VO<sub>x</sub> film obtained from the V<sub>2</sub>O<sub>5</sub> target is dominated by scattering on vanadyl bonds (V=O) centered around 840 cm<sup>-1</sup> (Fig. 2a). It also has another weaker broad feature centered around 400 cm<sup>-1</sup> originating from different complex atomic vibrations. This band is also observed with a very similar feature, on the Raman spectrum of the VO<sub>x</sub> film obtained from the V target with O<sub>2</sub> gas. This film also has a rather low intensity band centered at 705 cm<sup>-1</sup> with the same origin as the band centered at 840 cm<sup>-1</sup>. Indeed, according to these authors, the shift in this band can be attributed to oxygen deficiency in the VO<sub>x</sub> lattice: a lower wavenumber is attributed to an increase in oxygen deficiency. We can therefore state that the as-deposited a-VO<sub>x</sub> from the V target with O<sub>2</sub> gas may contain less oxygen than a-VO<sub>x</sub> deposited using V<sub>2</sub>O<sub>5</sub> target.

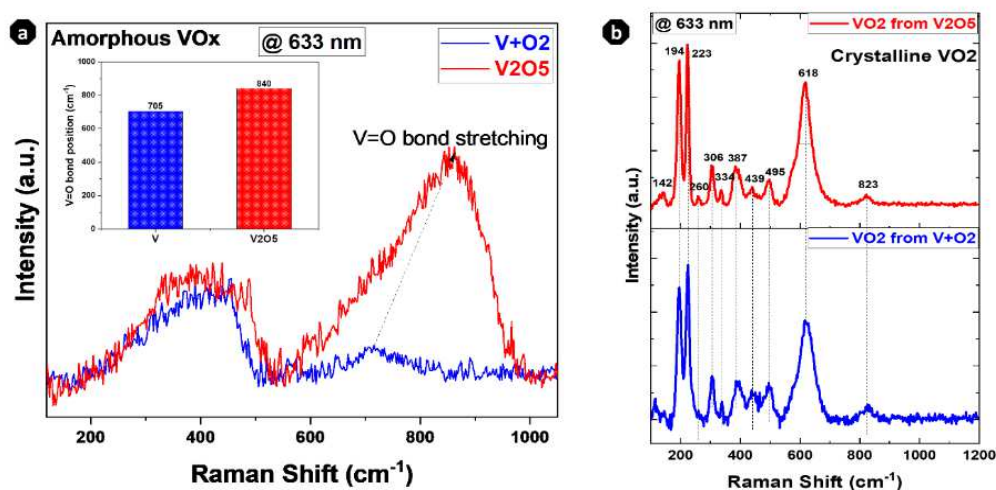


Figure 2: Room-temperature Raman spectra: (a) Raman spectra a-VO<sub>x</sub> samples from both targets: V+O<sub>2</sub> in blue and V<sub>2</sub>O<sub>5</sub> in red; the insert is a bar plot of the position of vanadyl V=O bond for each a-VO<sub>x</sub> deposit; (b) Raman spectra crystalline VO<sub>2</sub> samples from both targets: V+O<sub>2</sub> in blue and V<sub>2</sub>O<sub>5</sub> in red, both after RTA.

Next, after rapid thermal annealing to crystallize both a-VO<sub>x</sub> into a VO<sub>2</sub> phase, Raman spectroscopy was used to check the presence of the monoclinic VO<sub>2</sub> room temperature phase. The narrow peaks in the Raman spectra in Fig. 2b confirm high crystalline quality with the typical Raman signature of monoclinic VO<sub>2</sub> in both kinds of thin film. Indeed, among the 18 Raman-active phonon modes predicted by group theory analysis for all low-temperature phase symmetries of VO<sub>2</sub>, we observed 11 vibrational modes. These different vibrational modes at 142, 194(Ag), 223(Ag), 260(Bg), 306(Ag/Bg), 334(Bg/ Ag), 387(Ag), 439(Bg), 495(Ag), 618(Ag), 823(Bg) cm<sup>-1</sup> are characteristic of pure VO<sub>2</sub>(M1) phase[27,28]. Lower wavenumber phonon modes at 193 and 223 cm<sup>-1</sup> were attributed to V-V vibrations, while the 618 cm<sup>-1</sup> peak corresponds to the stretching mode of V-O bonds[29]. No Raman shifts were identified for other kinds of vanadium oxides or any other types of polymorphs of VO<sub>2</sub> (M2/T)[30]. The peak located around 620 cm<sup>-1</sup> is the most structure-sensitive position for VO<sub>2</sub>. Recently, Maklakov et al.[31] used the FWHM of this peak to discuss the crystallinity of VO<sub>2</sub>. Indeed, the width of a Raman band of a nanocrystalline material is known to decrease with an increase in the size of the crystal, or the defect concentration decreases. A reduction in the Raman linewidth may also be caused by the increasingly uniform size of the nanocrystals [32,33]. Likewise, in our case, the FWHM of the V-O peak located at 618 cm<sup>-1</sup> for VO<sub>2</sub> from V+O<sub>2</sub> was about 45 cm<sup>-1</sup>, while the one for VO<sub>2</sub> obtained from V<sub>2</sub>O<sub>5</sub> was about 54 cm<sup>-1</sup>. This probably means that the VO<sub>2</sub> obtained using V<sub>2</sub>O<sub>5</sub> has either a larger nanocrystalline grain size with fewer defects, or more uniform nanocrystal size than the VO<sub>2</sub> prepared using V+O<sub>2</sub>. This observation was corroborated by the GIXRD and SEM analyses presented next.

Fig. 3 shows the typical GIXRD patterns of the two VO<sub>2</sub> films. According to the ICDD card N°04-003-2035 (COD data base), the peaks detected in both samples can be attributed to a VO<sub>2</sub> monoclinic M1 phase. However, we observed few traces of V<sub>2</sub>O<sub>3</sub>. Most of the peaks were intense and narrow, suggesting that the samples were well crystallized. The (200) peak

dominated the XRD patterns of both VO<sub>2</sub> thin films, indicating a preferred orientation in the (200) direction whatever the synthesis route. Several minor orientations appeared in the patterns, a qualitative indication that both VO<sub>2</sub> were textured. In addition, the average grain sizes deduced from the Scherrer equation of VO<sub>2</sub> films obtained from V+O<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> were estimated to be 14 and 42 nm, respectively.

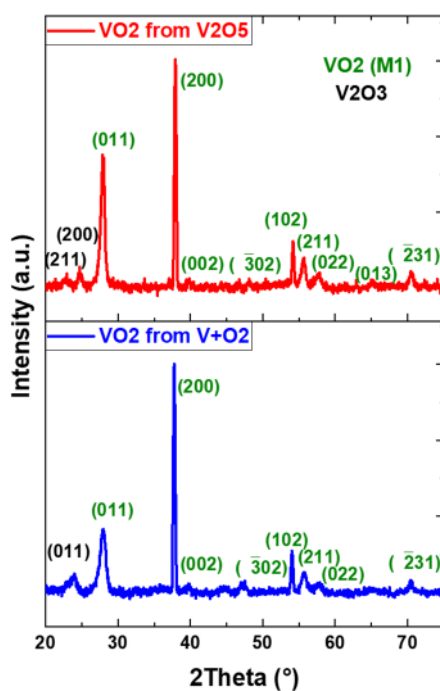


Figure 3: Room-temperature GIXRD patterns: VO<sub>2</sub> films obtained from V+O<sub>2</sub> are shown in blue and those obtained from V<sub>2</sub>O<sub>5</sub> in red.

Fig. 4 shows SEM and AFM images of the surface morphologies of the two VO<sub>2</sub> thin films. The VO<sub>2</sub> obtained from V+O<sub>2</sub> has a smooth surface with only 0.8 nm of roughness (Fig. 4a) with no visible grains, probably because they are too small to be visible, as noted above using GIXRD grain size estimation. Whereas the VO<sub>2</sub> obtained from V<sub>2</sub>O<sub>5</sub> represented the average grain size of around 80 nm, probably inducing the higher surface roughness of 5 nm (Fig. 4b). Indeed, grain size estimated using SEM image processing with ImageJ software was double that estimated using the Scherrer equation in GIXRD. This discrepancy may be due to the processing limit. However, both analyses confirmed that the VO<sub>2</sub> film obtained from V+O<sub>2</sub> has smaller grains than the film obtained from V<sub>2</sub>O<sub>5</sub>. Nevertheless, the roughness of both the films was similar to that of the typical sputtering of VO<sub>2</sub> films obtained by PLD[34,35]. It is also worth noting that the VO<sub>2</sub> film obtained from V<sub>2</sub>O<sub>5</sub> was porous whereas the film obtained



from  $V+O_2$  showed no porosity at our observation scale. Moreover, the thickness of both  $VO_2$  films observed in cross-section SEM analysis was 36-40 nm. This means that the initial film thickness of 100 nm decreased after rapid thermal annealing due to the densification and crystallization of the films. The decrease in thickness was confirmed by ellipsometry, as described next.

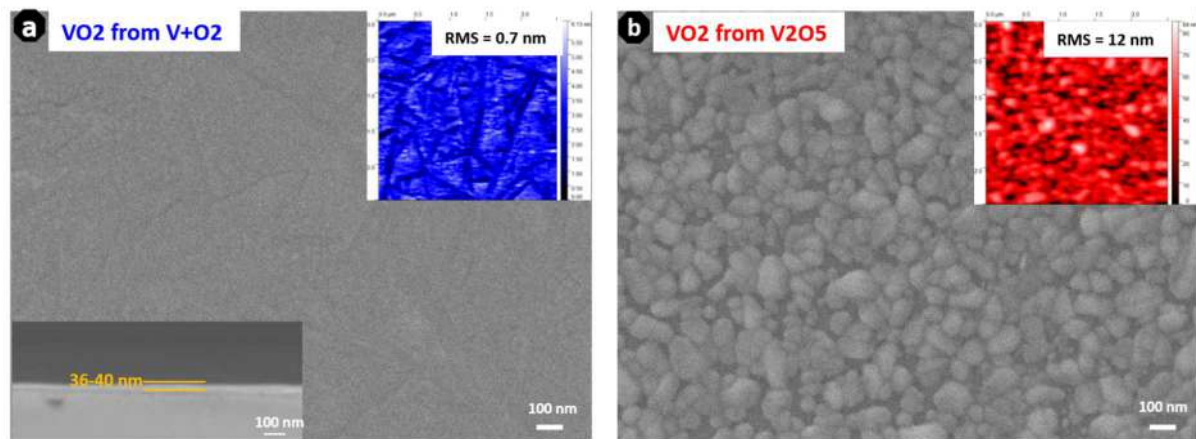


Figure 4: Top-view SEM micrographs of  $VO_2$  thin films: (a) SEM image of  $VO_2$  deposited from  $V+O_2$ , the top blue insert corresponds to the AFM image showing the smooth surface of this thin film, the insert at the bottom left is the cross-section SEM image showing the  $VO_2$  thickness of 36 to 40 nm. (b) SEM image of  $VO_2$  deposited from  $V_2O_5$ , the top red insert corresponds to the AFM image showing a rougher surface. Scale bar = 100 nm.

#### b. Thermochromic and optical properties

To assess the characteristic IMT of grown  $VO_2$  thin films, we measured their transmittance as a function of temperature. Fig. 5a-b illustrate the hysteresis loop at 1550 nm obtained from the optical transmittance  $T_r$  of each sample as a function of temperature, and a plot of  $d(T_r)/d(T)$ . As shown in Fig. 5a, both  $VO_2$  thin films underwent semiconductor IMT when heated from room temperature to higher temperatures, and vice versa. The  $VO_2$  obtained from  $V_2O_5$  underwent a sharper and more abrupt change in transmittance than the  $VO_2$  obtained from  $V+O_2$ . The IMT parameters of both  $VO_2$  thin films were determined by using the first derivative of the transmittance with respect to temperature. The phase transition temperature  $T_t$  is expressed as the average transition temperature between the transition temperatures observed during heating ( $T_h$ ) and cooling ( $T_c$ ), ( $T_t = 1/2 (T_h + T_c)$ ), while the thermal

hysteresis width  $\Delta T$  is defined as the absolute difference in temperature between  $T_h$  and  $T_c$  cycle transition, ( $\Delta T = (T_h - T_c)$ ). The  $\text{VO}_2$  deposited from  $\text{V}_2\text{O}_5$  showed a higher IMT temperature ( $T_i$ ) ( $69^\circ\text{C}$ ) with a larger hysteresis width of  $11^\circ\text{C}$ . In contrast, the  $\text{VO}_2$  obtained from  $\text{V}+\text{O}_2$  showed a reduced  $T_i$  of  $50^\circ\text{C}$  with a narrower hysteresis of  $6^\circ\text{C}$ , as shown in Fig.5c. According to previous reports in the literature[36,37], the oxygen vacancies reduced the critical temperature. Since the ablation of  $\text{V}+\text{O}_2$  results in amorphous  $\text{VO}_x$  with lower oxygen content than its counterpart obtained from  $\text{V}_2\text{O}_5$ , following the same post annealing process to crystallize them, the  $\text{VO}_2$  obtained from  $\text{V}+\text{O}_2$  probably kept less oxygen, resulting in  $\text{VO}_2$  film with oxygen. This may explain the distinct difference in the transition temperature for the two  $\text{VO}_2$  films.

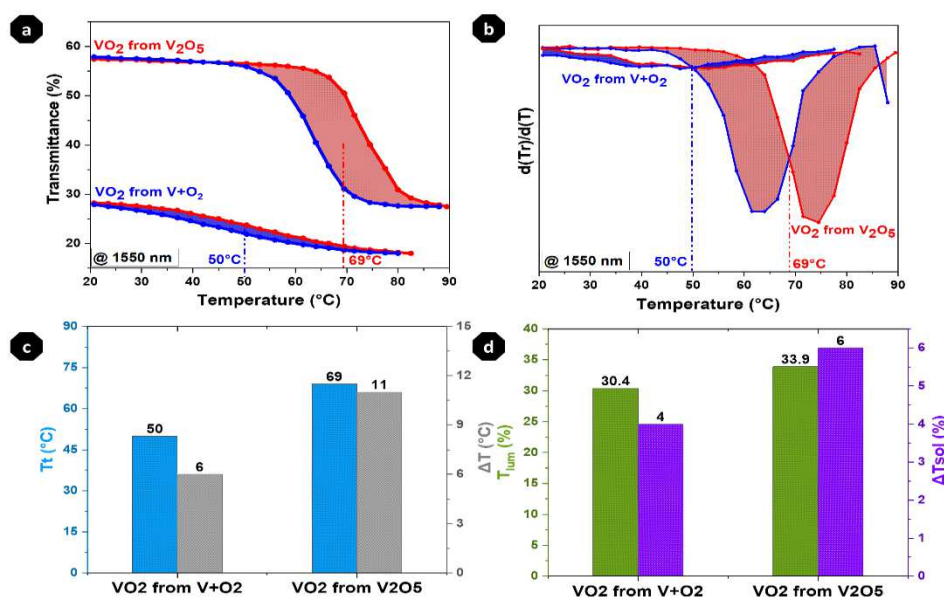


Figure 5: (a) hysteresis loops at 1550 nm, (b) the corresponding  $d(\text{Tr})/d(T)$  vs  $T$  curve for both  $\text{VO}_2$  thin films, (c) the phase transition temperature and the hysteresis width for both  $\text{VO}_2$  films, (d) The calculated optical performance  $T_{\text{lum}}$  and  $\Delta T_{\text{sol}}$ .

The calculated optical performances ( $T_{\text{lum}}$  and  $\Delta T_{\text{sol}}$ ) are plotted in Fig. 5d. The average luminous transmittance was 33.9% for  $\text{VO}_2$  obtained from  $\text{V}_2\text{O}_5$ , which is slightly higher than the luminous transmittance of the  $\text{VO}_2$  film obtained from  $\text{V}+\text{O}_2$ , which was 30.4%. This means that the  $\text{VO}_2$  film obtained from  $\text{V}_2\text{O}_5$  was slightly more transparent in the visible range than the other  $\text{VO}_2$  film. This observation was confirmed by the absorbance measurement of both films. The solar modulation efficiency of the  $\text{VO}_2$  film obtained using  $\text{V}_2\text{O}_5$  was also higher than that of the  $\text{VO}_2$  film obtained from  $\text{V} + \text{O}_2$  gas.

Further, the VO<sub>2</sub> crystallite size and its distribution are assumed to determine the width and shape of the heating-cooling hysteresis loop, whereas the temperature depends on transmittance. More precisely, it has been shown that a high-quality VO<sub>2</sub> crystal and narrow crystallite size distribution resulted in a narrow hysteresis loop and vice versa[38]. However, it has also been shown that the increase in the size of the crystallite due to recrystallization also increased the width of the hysteresis loop[39]. In the present study, the VO<sub>2</sub> film obtained from V<sub>2</sub>O<sub>5</sub> had a bigger hysteresis loop with larger grain size and higher roughness than the VO<sub>2</sub> film obtained from V+O<sub>2</sub> which had a smaller hysteresis loop with lower roughness and probably smaller grain size. Our results are thus consistent with those of the abovementioned studies.

To go further in the optical investigation of synthesized vanadium dioxide, temperature controlled ellipsometry measurements were made of both VO<sub>2</sub> films to obtain the n and k, which respectively represent the refraction ability of the material to incidence light, and the extinction coefficient, indicating the absorption of light. Fig. 6 shows the wavelength dispersions of the refractive index n and the extinction coefficient k of both VO<sub>2</sub> thin films, below (25 °C) and above (85 °C) their transition temperatures. It is clear that both the n or k values are temperature-independent in the visible spectrum, whereas the switching behavior is highly accentuated in the near-infrared region. This significant switching of the optical constants of both VO<sub>2</sub> presents a similar trend as the one reported recently by Zhang et al.[40]. It also confirms the good thermochromic properties of both VO<sub>2</sub>.

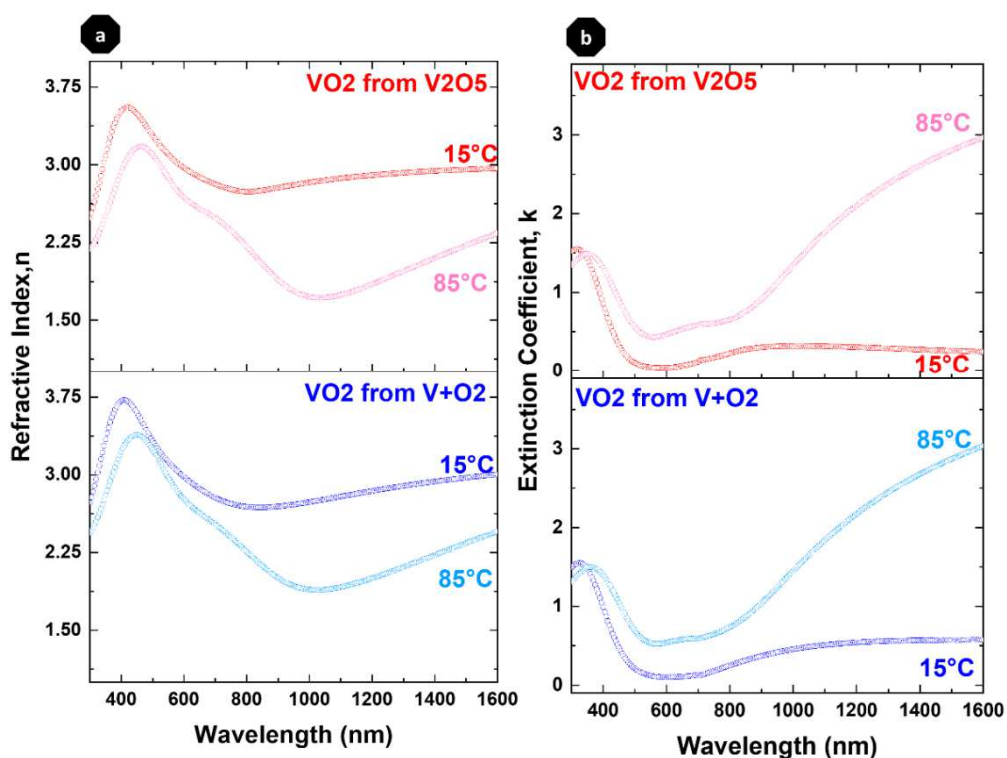


Figure 6. (a) Refractive index,  $n$  and (b) extinction coefficient,  $k$  of both  $\text{VO}_2$  thin films at temperatures below and above the phase transition temperature determined by spectroscopic ellipsometry.

To better observe the difference in the  $n$  and  $k$  values of the two  $\text{VO}_2$  films, we extracted the values at two specific wavelengths in the visible and IR ranges (see results in Table 1). We observed that the  $\text{VO}_2$  obtained from  $\text{V}+\text{O}_2$  presented slightly higher values of  $n$  and  $k$  in both the visible and IR regions. The higher values of  $k$  in the  $\text{VO}_2$  film obtained from  $\text{V}+\text{O}_2$  indicates that this  $\text{VO}_2$  absorbs more than its counterpart obtained from  $\text{V}_2\text{O}_5$ . It is worth mentioning that the values of  $n$  and  $k$  we obtained in our experiment are in good agreement with those reported in the literature for films obtained using other deposition processes [13,40,41].

		$\text{VO}_2$ from $\text{V} + \text{O}_2$		$\text{VO}_2$ from $\text{V}_2\text{O}_5$		$\text{VO}_2$ from $\text{V} + \text{O}_2$		$\text{VO}_2$ from $\text{V}_2\text{O}_5$	
		$n_{15^\circ\text{C}}$	$n_{85^\circ\text{C}}$	$n_{15^\circ\text{C}}$	$n_{85^\circ\text{C}}$	$k_{15^\circ\text{C}}$	$k_{85^\circ\text{C}}$	$k_{15^\circ\text{C}}$	$k_{85^\circ\text{C}}$
550 nm	(most sensitive for human eyes)	3.124	2.976	3.099	2.874	0.119	0.532	0.047	0.434
1550 nm	(Infrared)	2.989	2.399	2.961	2.283	0.574	2.956	0.250	2.888

Table 1: Extracted values of  $n$  and  $k$  at specific wavelengths (550, and 1550 nm) for both  $\text{VO}_2$  films.

In addition, in the optical constant spectra, at a wavelength of 1000 nm,  $n$  decreased and increased strongly with the rise and drop in temperature, and  $k$  increased and decreased respectively. A similar trend has been observed by others [40,42,43]. It was proven by Nagashima et al.[44] that the switching of  $n$  and  $k$  of  $\text{VO}_2$  thin films depends to a large extent on the growing conditions. The optical constant hysteresis behaves in a similar way to the optical transmittance/absorbance hysteresis of  $\text{VO}_2$  thin films. The hysteresis width of about  $11^\circ\text{C}$  and the refractive index with an abrupt variation of  $n$  at  $69^\circ\text{C}$  is similar to that obtained in optical transmittance of polycrystalline sputtered  $\text{VO}_2$  thin films[45]. The extinction coefficient  $k$  also displays excellent phase transition characteristics but only in the near-infrared region.

Absorbance was measured at room temperature in the 300-900 nm range from which the optical band gap and the optical conductivity were deduced. Fig. 7a shows the absorbance measurements for both VO<sub>2</sub> thin films. The results clearly reveal the change in the absorption edge toward the blue region. The absorbance of the VO<sub>2</sub> obtained from V+O<sub>2</sub> was higher than that of the VO<sub>2</sub> obtained from V<sub>2</sub>O<sub>5</sub>. This observation corroborated the fact that this sample had a higher extinction coefficient and lower T<sub>lum</sub>.

The optical band gap was evaluated from the absorption edge of the UV-Vis spectra. The indirect optical band gap was estimated using the Tauc plot:

$$(\alpha h\nu)^{1/2} \propto (E - E_g) \quad (2)$$

and the optical absorption coefficient  $\alpha$  was calculated from the optical absorbance  $A$  using the relation[46]:

$$\alpha h\nu = \frac{2.303 A}{X} \quad (3)$$

where  $X$  is the sample thickness in cm,  $\alpha$  is the absorption coefficient and  $E_g$  is the optical band gap energy. The  $E_g$  value is extrapolated by the linear portion of the plot to  $(\alpha h\nu)^{1/2} = 0$ .

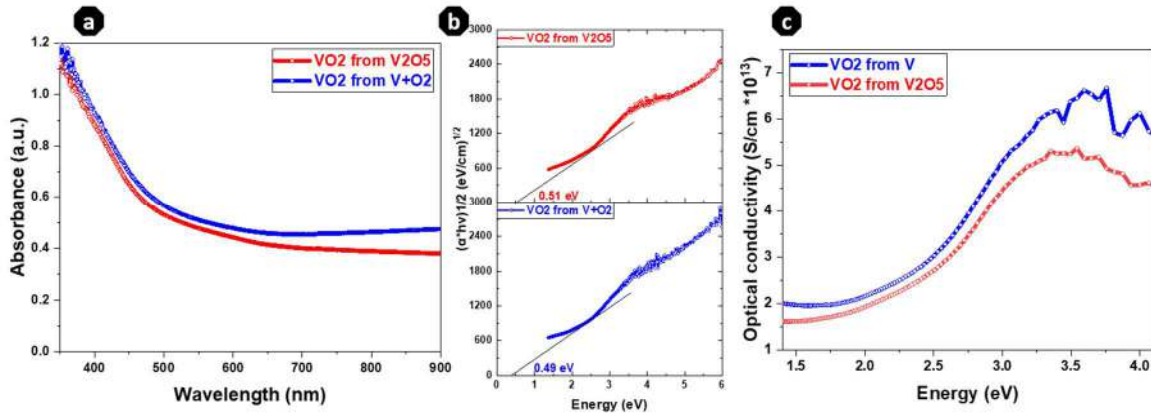


Figure 7. (a) Absorption spectra; (b) Plot of  $(\alpha h\nu)^{1/2}$  versus photon energy ( $h\nu$ ); (c) Variation in optical conductivity as a function of photon energy for both VO<sub>2</sub> thin films.

The optical band gap (0.51 eV) of the VO<sub>2</sub> film obtained from V<sub>2</sub>O<sub>5</sub> was slightly higher than the value (0.49 eV) of the VO<sub>2</sub> film obtained from V+O<sub>2</sub> (Fig. 7b). These values are consistent with recent work on VO<sub>2</sub> film fabricated with V metallic target in argon and oxygen atmosphere using magnetron sputtering reported by Zhang et al.[40]. Indeed, according to previous work, the widening of the optical band gap induces a blue shift and an

enhanced visible transmittance[47]. This can explain the higher visible transmittance of the VO<sub>2</sub> obtained from V<sub>2</sub>O<sub>5</sub>.

Using the absorption coefficient ( $\alpha$ ) and refractive index ( $n$ ) of the material, it is possible to calculate the optical responses of a material in terms of optical conductivity  $\sigma_{opt}$ , which is given by the relation[48] :

$$\sigma_{opt} = \frac{\alpha n c}{4 \pi} \quad (4)$$

where C is the velocity of light.

Fig. 7c shows the variation in the optical conductivity as a function of photon energy for both VO<sub>2</sub> thin films. We observed that the optical conductivity increased with an increase in photon energy. As the VO<sub>2</sub> film deposited from V+O<sub>2</sub> had a higher absorption coefficient and refractive index, logically, it had higher optical conductivity than the VO<sub>2</sub> film obtained from V<sub>2</sub>O<sub>5</sub>. Our results therefore suggest that the optical conductivity of the obtained VO<sub>2</sub> films follows the same trend as the absorption coefficient and refractive index with increasing wavelength.

#### 4. Conclusion

In this work, we demonstrated that the pulsed laser deposition of both vanadium metallic (in the presence of an O<sub>2</sub> atmosphere) and V<sub>2</sub>O<sub>5</sub> ceramic targets, combined with post-rapid thermal annealing, result in the growth of two VO<sub>2</sub> thin films with different nanostructural and optical properties.

- The VO<sub>2</sub> obtained from the pulsed laser deposition of V+O<sub>2</sub> exhibits smaller nanocrystalline grain size with more defects and a smoother surface than the film obtained from V<sub>2</sub>O<sub>5</sub>.
- The VO<sub>2</sub> deposited from V+O<sub>2</sub> shows a lower IMT transition temperature of around 50 °C with a narrower hysteresis of 6 °C and slightly lower solar modulation efficiency with low visible transmittance than the VO<sub>2</sub> obtained from V<sub>2</sub>O<sub>5</sub>. The reduced T<sub>t</sub> value is probably due to the oxygen deficiency in the VO<sub>2</sub> prepared using the PLD of V+O<sub>2</sub>.

- The VO<sub>2</sub> deposited from V+O<sub>2</sub> has a higher absorption coefficient and refractive index, with a slightly lower optical band gap and higher optical conductivity than the VO<sub>2</sub> obtained from V<sub>2</sub>O<sub>5</sub>.

This work highlighted the fact that the thermochromic and optical properties of VO<sub>2</sub> thin film also depends on the target materials. These results provide useful information to define a robust method for adjusting an important PLD parameter such as the target materials to use to produce high quality VO<sub>2</sub> thin films.

## Acknowledgments

This work was supported by the LABEX MANUTECH-SISE (ANR-10-LABX-0075) of University of Lyon, in the program “*Investissements d’Avenir*” (ANR-11-IDEX-0007) run by the French National Research Agency (ANR).

## References

- [1] J.-H. Yu, S.-H. Nam, J.W. Lee, J.-H. Boo, Enhanced Visible Transmittance of Thermochromic VO<sub>2</sub> Thin Films by SiO<sub>2</sub> Passivation Layer and Their Optical Characterization, *Materials*. 9 (2016) 556. <https://doi.org/10.3390/ma9070556>.
- [2] D.H. Kim, H.S. Kwok, Pulsed laser deposition of VO<sub>2</sub> thin films, *Appl. Phys. Lett.* 65 (1994) 3188–3190. <https://doi.org/10.1063/1.112476>.
- [3] S.A. Pauli, R. Herger, P.R. Willmott, E.U. Donev, J.Y. Suh, R.F. Haglund, X-ray diffraction studies of the growth of vanadium dioxide nanoparticles, *Journal of Applied Physics*. 102 (2007) 073527. <https://doi.org/10.1063/1.2786917>.
- [4] Z. Zhang, Y. Gao, Z. Chen, J. Du, C. Cao, L. Kang, H. Luo, Thermochromic VO<sub>2</sub> Thin Films: Solution-Based Processing, Improved Optical Properties, and Lowered Phase Transformation Temperature, *Langmuir*. 26 (2010) 10738–10744. <https://doi.org/10.1021/la100515k>.
- [5] R.T. Rajendra Kumar, B. Karunakaran, D. Mangalaraj, Sa.K. Narayandass, P. Manoravi, M. Joseph, V. Gopal, Pulsed laser deposited vanadium oxide thin films for uncooled infrared detectors, *Sensors and Actuators A: Physical*. 107 (2003) 62–67. [https://doi.org/10.1016/S0924-4247\(03\)00233-4](https://doi.org/10.1016/S0924-4247(03)00233-4).
- [6] E.K. Koussi, I. Verrier, T. Kämpfe, S. Reynaud, F. Bourquard, D. Jamon, H. Bruhier, Y. Jourlin, O. Parriaux, Thermally activated resonant grating using a vanadium dioxide waveguide, *Opt. Mater. Express*, OME. 11 (2021) 1093–1103. <https://doi.org/10.1364/OME.413373>.
- [7] M. B. Sahana, M. S. Dharmaparakash, S. A. Shivashankar, Microstructure and properties of VO<sub>2</sub> thin films deposited by MOCVD from vanadyl acetylacetonate, *Journal of Materials Chemistry*. 12 (2002) 333–338. <https://doi.org/10.1039/B106563G>.

- [8] F. Guinneton, L. Sauques, J.C. Valmalette, F. Cros, J.R. Gavarrri, Comparative study between nanocrystalline powder and thin film of vanadium dioxide VO<sub>2</sub>: electrical and infrared properties, *Journal of Physics and Chemistry of Solids*. 62 (2001) 1229–1238. [https://doi.org/10.1016/S0022-3697\(01\)00013-0](https://doi.org/10.1016/S0022-3697(01)00013-0).
- [9] H.Y. Xu, Y.H. Huang, S. Liu, K.W. Xu, F. Ma, P.K. Chu, Effects of annealing ambient on oxygen vacancies and phase transition temperature of VO<sub>2</sub> thin films, *RSC Adv.* 6 (2016) 79383–79388. <https://doi.org/10.1039/C6RA13189A>.
- [10] A. Dey, M.K. Nayak, M.S. Pradeepkumar, D. Porwal, B. Yougandar, A. Carmel Mary Esther, Studies on Mo doped vanadium oxide film by pulsed RF magnetron sputtering, *Surface and Interface Analysis*. 49 (2017) 805–808. <https://doi.org/10.1002/sia.6226>.
- [11] A.M. Selman, M.J. Kadhim, Fabrication of high sensitivity and fast response IR photodetector based on VO<sub>2</sub> nanocrystalline thin films prepared on the silicon substrate, *Optical Materials*. 131 (2022) 112664. <https://doi.org/10.1016/j.optmat.2022.112664>.
- [12] Z. Xiang, Z. Wu, Y. Shi, C. Li, X. Chen, J. Gou, J. Wang, Y. Zhuang, X. Dong, X. Zheng, Y. Jiang, Optimized thermochromic properties for smart window application of VO<sub>2</sub> films by wet-etching process, *Optical Materials*. 128 (2022) 112359. <https://doi.org/10.1016/j.optmat.2022.112359>.
- [13] J. Zhang, J. Wang, C. Yang, H. Jia, X. Cui, S. Zhao, Y. Xu, Mesoporous SiO<sub>2</sub>/VO<sub>2</sub> double-layer thermochromic coating with improved visible transmittance for smart window, *Solar Energy Materials and Solar Cells*. 162 (2017) 134–141. <https://doi.org/10.1016/j.solmat.2016.12.048>.
- [14] Md.A. Rashid, B.K. Mondal, M.H.K. Rubel, Md.M. Rahman, O.T. Mefford, J. Hossain, Synthesis of Self-Assembled Randomly Oriented VO<sub>2</sub> Nanowires on a Glass Substrate by a Spin Coating Method, *Inorg. Chem.* 59 (2020) 15707–15716. <https://doi.org/10.1021/acs.inorgchem.0c02108>.
- [15] S. Guan, M. Gaudon, A. Rougier, E. Duguet, E. Durand, A. Fargues, O. Viraphong, N. Penin, VO<sub>2</sub> films obtained by V<sub>2</sub>O<sub>5</sub> nanoparticle suspension reduction, *Optical Materials*. 127 (2022) 112117. <https://doi.org/10.1016/j.optmat.2022.112117>.
- [16] D. Bhardwaj, A. Goswami, A.M. Umarji, Synthesis of phase pure vanadium dioxide (VO<sub>2</sub>) thin film by reactive pulsed laser deposition, *Journal of Applied Physics*. 124 (2018) 135301. <https://doi.org/10.1063/1.5046455>.
- [17] S.A. Bukhari, S. Kumar, P. Kumar, S.P. Gumfekar, H.-J. Chung, T. Thundat, A. Goswami, The effect of oxygen flow rate on metal–insulator transition (MIT) characteristics of vanadium dioxide (VO<sub>2</sub>) thin films by pulsed laser deposition (PLD), *Applied Surface Science*. 529 (2020) 146995. <https://doi.org/10.1016/j.apsusc.2020.146995>.
- [18] E.-K. Koussi, F. Bourquard, T. Tite, D. Jamon, F. Garrelie, Y. Jourlin, Synthesis of vanadium oxides by pulsed laser deposition and rapid thermal annealing, *Applied Surface Science*. 521 (2020) 146267. <https://doi.org/10.1016/j.apsusc.2020.146267>.
- [19] R. McGee, A. Goswami, B. Khorshidi, K. McGuire, K. Schofield, T. Thundat, Effect of process parameters on phase stability and metal-insulator transition of vanadium dioxide (VO<sub>2</sub>) thin films by pulsed laser deposition, *Acta Materialia*. 137 (2017) 12–21. <https://doi.org/10.1016/j.actamat.2017.07.025>.
- [20] Y.X. Guo, Y.F. Liu, C.W. Zou, Z.M. Qi, Y.Y. Wang, Y.Q. Xu, X.L. Wang, F. Zhang, R. Zhou, Oxygen pressure induced structure, morphology and phase-transition for VO<sub>2</sub>/c-sapphire films by PLD, *Appl. Phys. A*. 115 (2014) 1245–1250. <https://doi.org/10.1007/s00339-013-7972-0>.
- [21] L.L. Fan, Y.F. Wu, C. Si, C.W. Zou, Z.M. Qi, L.B. Li, G.Q. Pan, Z.Y. Wu, Oxygen pressure dependent VO<sub>2</sub> crystal film preparation and the interfacial epitaxial growth



- study, *Thin Solid Films*. 520 (2012) 6124–6129.  
<https://doi.org/10.1016/j.tsf.2012.05.086>.
- [22] R.M. Bowman, J.M. Gregg, VO<sub>2</sub> thin films: growth and the effect of applied strain on their resistance, (n.d.) 5.
- [23] A.L. Patterson, The Scherrer Formula for X-Ray Particle Size Determination, *Phys. Rev.* 56 (1939) 978–982. <https://doi.org/10.1103/PhysRev.56.978>.
- [24] B. Zhuang, Z. Dai, S. Pang, H. Xu, L. Sun, F. Ma, 3D Ordered Macroporous VO<sub>2</sub> Thin Films with an Efficient Thermochromic Modulation Capability for Advanced Smart Windows, *Advanced Optical Materials*. 7 (2019) 1900600.  
<https://doi.org/10.1002/adom.201900600>.
- [25] P. Shvets, O. Dikaya, K. Maksimova, A. Goikhman, A review of Raman spectroscopy of vanadium oxides, *Journal of Raman Spectroscopy*. 50 (2019) 1226–1244.  
<https://doi.org/10.1002/jrs.5616>.
- [26] P. Shvets, K. Maksimova, A. Goikhman, Correlation between Raman spectra and oxygen content in amorphous vanadium oxides, *Physica B: Condensed Matter*. 613 (2021) 412995. <https://doi.org/10.1016/j.physb.2021.412995>.
- [27] J.C. Parker, Raman scattering from VO<sub>2</sub> single crystals: A study of the effects of surface oxidation, (n.d.) 3.
- [28] P. Schilbe, Raman scattering in VO<sub>2</sub>, *Physica B: Condensed Matter*. 316–317 (2002) 600–602. [https://doi.org/10.1016/S0921-4526\(02\)00584-7](https://doi.org/10.1016/S0921-4526(02)00584-7).
- [29] I.G. Madiba, N. Émond, M. Chaker, F.T. Thema, S.I. Tadadjeu, U. Muller, P. Zolliker, A. Braun, L. Kotsedi, M. Maaza, Effects of gamma irradiations on reactive pulsed laser deposited vanadium dioxide thin films, *Applied Surface Science*. 411 (2017) 271–278.  
<https://doi.org/10.1016/j.apsusc.2017.03.131>.
- [30] J.M. Atkin, S. Berweger, E.K. Chavez, M.B. Raschke, J. Cao, W. Fan, J. Wu, Strain and temperature dependence of the insulating phases of VO<sub>2</sub> near the metal-insulator transition, *Phys. Rev. B*. 85 (2012) 020101.  
<https://doi.org/10.1103/PhysRevB.85.020101>.
- [31] S.S. Maklakov, V.I. Polozov, S.A. Maklakov, A.D. Mishin, I.A. Ryzhikov, A.L. Trigub, V.A. Amelichev, K.I. Maslakov, V.N. Kisel, Post-deposition annealing of thin RF magnetron sputter-deposited VO<sub>2</sub> films above the melting point, *Journal of Alloys and Compounds*. 763 (2018) 558–569. <https://doi.org/10.1016/j.jallcom.2018.06.014>.
- [32] I.H. Campbell, P.M. Fauchet, The effects of microcrystal size and shape on the one phonon Raman spectra of crystalline semiconductors, *Solid State Communications*. 58 (1986) 739–741. [https://doi.org/10.1016/0038-1098\(86\)90513-2](https://doi.org/10.1016/0038-1098(86)90513-2).
- [33] A.K. Arora, M. Rajalakshmi, T.R. Ravindran, V. Sivasubramanian, Raman spectroscopy of optical phonon confinement in nanostructured materials, *Journal of Raman Spectroscopy*. 38 (2007) 604–617. <https://doi.org/10.1002/jrs.1684>.
- [34] D. Fu, K. Liu, T. Tao, K. Lo, C. Cheng, B. Liu, R. Zhang, H.A. Bechtel, J. Wu, Comprehensive study of the metal-insulator transition in pulsed laser deposited epitaxial VO<sub>2</sub> thin films, *Journal of Applied Physics*. 113 (2013) 043707.  
<https://doi.org/10.1063/1.4788804>.
- [35] P. Jin, K. Yoshimura, S. Tanemura, Dependence of microstructure and thermochromism on substrate temperature for sputter-deposited VO<sub>2</sub> epitaxial films, *Journal of Vacuum Science & Technology A*. 15 (1997) 1113–1117. <https://doi.org/10.1116/1.580439>.
- [36] L. Fan, X. Wang, F. Wang, Q. Zhang, L. Zhu, Q. Meng, B. Wang, Z. Zhang, C. Zou, Revealing the role of oxygen vacancies on the phase transition of VO<sub>2</sub> film from the optical-constant measurements, *RSC Advances*. 8 (2018) 19151–19156.  
<https://doi.org/10.1039/C8RA03292K>.

- [37] J. Zhang, Z. Zhao, J. Li, H. Jin, F. Rehman, P. Chen, Y. Jiang, C. Chen, M. Cao, Y. Zhao, Evolution of Structural and Electrical Properties of Oxygen-Deficient VO<sub>2</sub> under Low Temperature Heating Process, *ACS Appl. Mater. Interfaces*. 9 (2017) 27135–27141. <https://doi.org/10.1021/acsami.7b05792>.
- [38] V.A. Klimov, I.O. Timofeeva, S.D. Khanin, E.B. Shadrin, A.V. Ilinskii, F. Silva-Andrade, Hysteresis loop construction for the metal-semiconductor phase transition in vanadium dioxide films, *Tech. Phys.* 47 (2002) 1134–1139. <https://doi.org/10.1134/1.1508078>.
- [39] A.M. Makarevich, I.I. Sadykov, D.I. Sharovarov, V.A. Amelichev, A.A. Adamenkov, D.M. Tsybarenko, A.V. Plokhii, M.N. Esaulkov, P.M. Solyankin, A.R. Kaul, Chemical synthesis of high quality epitaxial vanadium dioxide films with sharp electrical and optical switch properties, *J. Mater. Chem. C*. 3 (2015) 9197–9205. <https://doi.org/10.1039/C5TC01811K>.
- [40] C. Zhang, C. Koughia, O. Güneş, J. Luo, N. Hossain, Y. Li, X. Cui, S.-J. Wen, R. Wong, Q. Yang, S. Kasap, Synthesis, structure and optical properties of high-quality VO<sub>2</sub> thin films grown on silicon, quartz and sapphire substrates by high temperature magnetron sputtering: Properties through the transition temperature, *Journal of Alloys and Compounds*. 848 (2020) 156323. <https://doi.org/10.1016/j.jallcom.2020.156323>.
- [41] M. Currie, M.A. Mastro, V.D. Wheeler, Characterizing the tunable refractive index of vanadium dioxide, *Opt. Mater. Express*, OME. 7 (2017) 1697–1707. <https://doi.org/10.1364/OME.7.001697>.
- [42] H. Kakiuchida, P. Jin, S. Nakao, M. Tazawa, Optical Properties of Vanadium Dioxide Film during Semiconductive–Metallic Phase Transition, *Jpn. J. Appl. Phys.* 46 (2007) L113. <https://doi.org/10.1143/JJAP.46.L113>.
- [43] J.B. Kana Kana, J.M. Ndjaka, G. Vignaud, A. Gibaud, M. Maaza, Thermally tunable optical constants of vanadium dioxide thin films measured by spectroscopic ellipsometry, *Optics Communications*. 284 (2011) 807–812. <https://doi.org/10.1016/j.optcom.2010.10.009>.
- [44] M. Nagashima, H. Wada, Near infrared optical properties of laser ablated VO<sub>2</sub> thin films by ellipsometry, *Thin Solid Films*. 312 (1998) 61–65. [https://doi.org/10.1016/S0040-6090\(97\)00360-X](https://doi.org/10.1016/S0040-6090(97)00360-X).
- [45] J.B. Kana Kana, J.M. Ndjaka, B.D. Ngom, A.Y. Fasasi, O. Nemraoui, R. Nemutudi, D. Knoesen, M. Maaza, High substrate temperature induced anomalous phase transition temperature shift in sputtered VO<sub>2</sub> thin films, *Optical Materials*. 32 (2010) 739–742. <https://doi.org/10.1016/j.optmat.2010.02.005>.
- [46] Sangappa, S. Asha, T. Demappa, G. Sanjeev, P. Parameswara, R. Somashekar, Spectroscopic and thermal studies of 8MeV electron beam irradiated HPMC films, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*. 267 (2009) 2385–2389. <https://doi.org/10.1016/j.nimb.2009.04.007>.
- [47] M. Zhou, J. Bao, M. Tao, R. Zhu, Y. Lin, X. Zhang, Y. Xie, Periodic porous thermochromic VO<sub>2</sub>(M) films with enhanced visible transmittance, *Chem. Commun.* 49 (2013) 6021–6023. <https://doi.org/10.1039/C3CC42112K>.
- [48] N.A. BAKR, A.M. FUNDE, V.S. WAMAN, M.M. KAMBLE, R.R. HAWALDAR, D.P. AMALNERKAR, S.W. GOSAVI, S.R. JADKAR, Determination of the optical parameters of a-Si:H thin films deposited by hot wire–chemical vapour deposition technique using transmission spectrum only, *Pramana - J Phys.* 76 (2011) 519–531. <https://doi.org/10.1007/s12043-011-0024-4>.

