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# A comparative study of the thermochromic performances of VO<sub>2</sub> films obtained by air oxidation of V and VN precursors

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## Abstract

Thanks to its metal-to-insulator transition (MIT) temperature not so far from the ambient one, thermochromic VO<sub>2</sub> exhibits great potentiality in smart coatings devoted to energy purposes. Among the different methods to synthesize thermochromic VO<sub>2</sub> films, reactive sputter deposition remains one of the most suitable for cost-effective industrial-scale production. For a few decades, increasing attention has been paid to a fast and relatively simple approach based on two steps to produce thermochromic VO<sub>2</sub> thin films: synthesis of a vanadium thin film followed by its oxidation at moderate temperatures (often less than 500 °C). Recently, we have revealed that the oxidation of vanadium nitride (VN) thin films also give rise to the formation of thermochromic VO<sub>2</sub>. This work aims to compare the thermochromic properties of VO<sub>2</sub> films achieved after thermal air oxidation of V and VN thin films prepared by sputtering deposition from an elemental vanadium target. For both precursors, short-time air annealing (from 60 to 300 seconds) was performed at 550 °C. X-ray diffraction and Raman spectroscopy depicted that the thermal oxidation domain allowing the formation of the thermochromic VO<sub>2</sub> phase was enlarged for VN compared to V precursor films. These results were confirmed by electrical measurements of the resulting oxides in the temperature region that encompass the MIT of

thermochromic m-VO<sub>2</sub>. Finally, a particular focus was made on the oxides of the VN series in terms of their infrared properties. The results indicate that the oxidation of VN precursor allows the synthesis of monoclinic VO<sub>2</sub> films with high purity displaying good thermochromic performances (IR contrast of 63%, electrical switch of ~ 2 decades) with narrower hysteresis widths (< 9.3 °C) as compared to those obtained by vanadium films oxidation, making VN precursor of particular interest for industrial upscaling.

**Keywords:**

Vanadium nitride, Vanadium dioxide, Thin films, Thermochromism, Optical and electrical properties

## 1. Introduction

Due to its reversible temperature-driven metal-insulator transition (MIT) occurring at  $T_c = 68\text{ }^\circ\text{C}$ , vanadium dioxide ( $\text{VO}_2$ ) is an extensively studied thermochromic material since its discovery in 1959 by Morin [1]. Below  $T_c$ ,  $\text{VO}_2$  crystallizes in a monoclinic structure showing semiconducting properties, with high transmittance in the infrared spectral range and high electrical resistivity. Above  $T_c$ , monoclinic  $\text{VO}_2$  (m- $\text{VO}_2$ ) undergoes a phase transition to a metallic tetragonal rutile phase with high reflectance and low electrical resistivity. It is well documented that during the metal-insulator transition of m- $\text{VO}_2$ , strong changes in resistivity are measured: from 5 orders of magnitude for bulk  $\text{VO}_2$  single crystals [2], up to 4 for epitaxial thin films [3] and often less than 3 for polycrystalline films [4–7]. As a reversible process under thermal cycling, those changes in electrical and optical properties of  $\text{VO}_2$  films follow a hysteresis curve centered around  $T_c$  with amplitude and width that are sensitive to various factors governed by elaboration conditions. Those thermally driven changes in its physical properties make this material suitable for diverse applications in energy, optics and electronics when used as thin films, in smart windows [8–10], smart radiator devices for spacecraft [11–14], thermal solar collectors [15–17], ultrafast electronic devices [18–20]. However, due to the four oxidation states of vanadium atoms (+2, +3, +4 and +5), numerous other intermediate phases belong to the binary V-O system [21,22]. Hence, the synthesis of m- $\text{VO}_2$  films with excellent thermochromic performances appears as a challenging goal which requires stringent control of stoichiometry. Among the various methods to synthesize crystalline m- $\text{VO}_2$  thin films, reactive sputtering of a vanadium target in an Ar- $\text{O}_2$  gas mixture is mainly used. Nevertheless, crystallization of m- $\text{VO}_2$  requires either a substrate heating during the film's growth [3–5,9,11,23–25] and/or a post-annealing of the vanadium oxide film either in air [24,26] or in oxygen [6,27]. Another interesting approach is a two-stage method, consisting, first in the deposition of a vanadium (V) thin film, followed by its oxidation in air [28–32], in oxygen [31,33–35] or even in a  $\text{N}_2$ - $\text{SO}_2$  mixture [36]. On the whole, since an annealing step is mandatory to synthesize crystalline thermochromic m- $\text{VO}_2$  films, the two-steps procedure

appears at the same time as simple and attractive for upscaling VO<sub>2</sub> films on large surfaces (e.g. for thermal solar collectors). However, an accurate control of the coupling temperature/oxidation duration (i.e. thermal oxidation of the vanadium precursor film) represents the most critical issue in the processing development for a given thickness of the initial vanadium layer precursor [29,32,37–40]. Recently, we have demonstrated the possibility to take benefit of this two-stage strategy by air oxidizing sputter-deposited vanadium nitride (VN) thin films to achieve thermochromic VO<sub>2</sub> films [41,42]. A specific emphasis was made for air oxidation at 450 °C of 175 nm-thick VN precursors deposited on silicon substrates, depicting that the VN conversion into m-VO<sub>2</sub> is followed by further oxidation of VO<sub>2</sub> into V<sub>2</sub>O<sub>5</sub>, with subsequent degradation of the thermochromic properties of m-VO<sub>2</sub> [41]. This was also confirmed for VN precursors with the same thickness deposited on aluminum substrates for three sets of temperatures (450, 525 and 550 °C), showing the necessity of an optimal combination of temperature/oxidation duration to reach efficient thermochromic m-VO<sub>2</sub> films [42].

The present work aims to compare the resulting vanadium oxides obtained from air-oxidation of VN precursor films with those obtained from vanadium ones (with precursor thickness kept at 110 nm). To fit within potential scaling-up criteria (i.e. short oxidation process durations), the air-annealing temperature was fixed at 550 °C for different durations up to 300 s. The microstructure of the resulting vanadium oxide films was analyzed by X-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM). Their functional properties were determined with the 4-point probe method, Fourier transform infrared spectroscopy (FTIR) and infrared thermography during thermal cycling in the 25-125 °C range. The results suggest that VN is a better precursor than the traditional V to synthesize m-VO<sub>2</sub> thin films with high phase purity, narrow hysteresis widths and good thermochromic performances.

## 2. Experimental details

### 2.1. Elaboration of the V and VN precursors

Vanadium and vanadium nitride thin films precursors were deposited on undoped (100) silicon substrates and aluminum foils by magnetron sputtering of a vanadium target (2 inches in diameter, 3 mm thick and 99.95% purity) with Ar (flow rate of 30 sccm) for the elaboration of V films, or in a reactive Ar-N<sub>2</sub> gas mixture (30-2.5 sccm) for VN films, respectively. Before their introduction into the sputtering chamber, the substrates were ultrasonically cleaned in acetone and ethanol for 5 minutes each. Prior to the deposition, the substrates cleanliness was guaranteed by a 3 minutes argon ion etching at a voltage bias fixed at -200 V. The base pressure before the sputter-deposition step was less than 10<sup>-3</sup> Pa. For both precursors, the vanadium target was powered by using a pulsed-DC power supply (Pinnacle+, Advanced Energy) operating with a current regulation of 1 A, a DC-pulse frequency of 50 kHz and an off-time of 4 μs. The target-to-substrate distance was fixed at 60 mm and the deposition pressure kept at 1 Pa by adjusting a throttle valve during sputter deposition. Since no intentional heating was used during deposition, the substrate temperature was lower than 60 °C. The rotation of the substrate holder (10 rpm) guaranteed the film's homogeneity. The process duration was adjusted to reach a thickness close to 110 nm, for both V and VN precursors (with deposition rates of 0.79 and 0.35 nm s<sup>-1</sup>, respectively).

### 2.2. Air oxidation of the precursors

The second step of the method consisted of thermal oxidation in ambient air of the vanadium-based films to investigate the formation of their oxides and their functional properties. Within this objective, the as-deposited films of each precursor were quickly introduced for short durations (up to 300 s) in a muffle furnace working in ambient air at 550 °C. The VN-based films were labeled VN\_0 for as-deposited film, and VN\_time for their oxides, according to the oxidation time (in the range 60-300 s). Similarly, as-deposited and oxidized vanadium

precursors were labeled as V\_0 to V\_240. Note that to fulfill industrial transfer potentialities (e.g., minimizing annealing durations), an air oxidation at 550 °C was chosen for this study. On the whole, oxidation durations in literature dealing with this method were ranging between 30 and 45 s for a thick porous vanadium film oxidized at 550 °C [38] to several tens of minutes for thinner vanadium films oxidized at around 475 °C [29,39].

### 2.3. Thin films characterization

The structure of as-deposited and annealed films was studied by X-ray diffraction (XRD) in Bragg-Brentano configuration using a Bruker D8 Advance diffractometer operating with a Cu  $K_{\alpha 1}$  radiation (0.15406 nm). In addition, the phase identification of the vanadium oxides was also performed by micro-Raman spectroscopy (Horiba Jobin-Yvon LabRAM) operating with a 532 nm laser at low power to prevent any further adventitious oxidation of the samples, with a  $\times 100$  objective and a 1200 gr/mm grating. Films morphology was observed by scanning electron microscopy (SEM) with a Philips XL30 S-FEG microscope. The thickness of the as-deposited films was measured by tactile profilometer. Secondary ion mass spectrometry (SIMS) was performed for qualitative elemental depth profiles with a Cameca IMS 7F apparatus. Electrical properties were measured by the four-point probe method equipped with a Linkam HFS600E heating device (Fig. S1) to measure the temperature dependence of the sheet resistance ( $R_{sq}$ ) of the oxidized films. Such measurements were performed between 25 and 125 °C during heating and cooling ramps (2 °C steps). Infrared transmission ( $Tr$ ) measurements of the oxidized films deposited on double-side polished silicon wafers, were performed versus sample temperature by using Fourier transform infrared spectroscopy (FTIR) with a Nicolet 6700 spectrometer in a transmission configuration equipped with the above-mentioned sample heater (hole diameter of 2 mm). For both electrical and optical characterizations, critical temperatures ( $T_c$ ) of the MIT were determined from the minimum of the Gaussian fit of the first derivative curve of  $R_{sq}$  and  $Tr$ , both for heating ( $T_c^{UP}$ ) and cooling ( $T_c^{DW}$ ) ramps. Then,

hysteresis widths ( $\Delta T_c$ ) were calculated by the difference between those later values for each film, as determined in Eq.1.

$$\Delta T_c = T_c^{UP} - T_c^{DW} \quad (1)$$

Furthermore, the properties were ranked considering the quality of the transitions between ambient temperature and 125 °C by calculating the electrical switch  $\Delta R$  as follows (Eq. 2):

$$\Delta R = -\log \left( \frac{R_{Sq}^{125}}{R_{Sq}^{25}} \right) \quad (2)$$

and by determining the difference between infrared transmission signals before and after the MIT (denoted  $\Delta Tr$ ). Finally, an infrared camera FLIR A325sc (7.5-13.0  $\mu\text{m}$  spectral range) was used to follow the thermally-induced emissivity changes of the oxidized VN films deposited on aluminum substrates. This study was performed by measuring the apparent temperature versus sample temperature (also controlled by the Linkam heating cell), taking an arbitrary emissivity value of  $\varepsilon = 1$  for each sample. Within this procedure, emissivity values were calculated from the slope of the linear zones of curves (before and after the MIT). The emissivity switch  $\Delta\varepsilon = \varepsilon_{HT} - \varepsilon_{LT}$  was assessed from the difference between the high-temperature (HT) and low-temperature (LT) domains [11]. The flowchart Fig. S2 in supplementary information depicts an overview of the methodology employed in the framework of this study. Finally, Table S1 lists the principal experimental techniques, their associated measurement range and errors.

### 3. Results and discussion

#### 3.1. Structure of the oxide layer formed by air oxidation of V and VN precursors

X-ray diffractograms of as-deposited precursors deposited on silicon substrates and the subsequent oxides formed after their air oxidation at 550 °C for different durations are presented in Fig. 1a, for vanadium precursor, and in Fig. 1b, for the vanadium nitride series, respectively. As-deposited vanadium films (V\_0), showing a dark-grey metallic color, are poorly crystallized



(Fig. 1a) with only one large and weak diffraction peak located at  $41.3^\circ$  corresponding to (110) planes of the body-centered cubic structure of vanadium (PDF no. 00-22-1058), slightly shifted to lower angles. Except for the silicon substrate peak, no other diffraction peak was observed for vanadium film V\_0. The crystallite size was estimated to be approx. 13 nm by Scherrer's formula. The poor crystallinity of V\_0 film may be due to possible oxygen contamination during its growth [33] (base pressure of approx.  $10^{-3}$  Pa in our case), explaining the slight shift of the diffraction angle to lower diffraction angles. It is noteworthy that by employing the same two-step method to synthesize thermochromic m-VO<sub>2</sub>, Xu *et al.* [28] and more recently Ashok *et al.* [32] started from amorphous vanadium films as feeding material before their subsequent oxidation into thermochromic m-VO<sub>2</sub>. As shown in Fig. 1a, the diffractogram of V\_60 is nearly featureless, except for the silicon substrate peak, the shading of the small vanadium (110) peak and a tiny peak that might correspond to possible traces of V<sub>4</sub>O<sub>9</sub> (PDF no. 04-007-0884). The first evidence of vanadium oxidation is merely detected after 90 s, with the rising of two peaks of m-VO<sub>2</sub> (PDF no. 04-003-2035) at  $27.9^\circ$  and  $37.1^\circ$  corresponding to (011) and (311) planes, respectively. In addition, a weak peak located at  $33.6^\circ$  may be assigned to V<sub>6</sub>O<sub>13</sub> (PDF no. 04-013-9633). Note that for the 90 s oxidation duration, the vanadium layer fully vanished. After 120 s of annealing, peaks of the m-VO<sub>2</sub> phase are detected at  $26.9^\circ$ ,  $37.2^\circ$  and  $39.7^\circ$  in combination with other peaks of different vanadium oxides attributed to V<sub>6</sub>O<sub>13</sub> and V<sub>4</sub>O<sub>9</sub>. Higher air-annealing durations give rise to dramatic changes in the diffractograms of the oxides. Indeed, even though m-VO<sub>2</sub> is still detected for V\_150 (mainly at  $37.2^\circ$ ), there is a steep rise of the V<sub>4</sub>O<sub>9</sub> peak at  $29.2^\circ$ , as well as new other intense peaks of V<sub>4</sub>O<sub>9</sub> at  $13.8^\circ$  and  $24.7^\circ$ . At the same time, numerous other peaks belonging to V<sub>2</sub>O<sub>5</sub> appear, corresponding to the most stable phase orthorhombic  $\alpha$ -V<sub>2</sub>O<sub>5</sub> (PDF no. 00-041-1426) and to a lesser extent, to a metastable monoclinic  $\beta$ -V<sub>2</sub>O<sub>5</sub> phase (PDF no. 00-061-0027) [43]. By contrast, V<sub>6</sub>O<sub>13</sub> peaks seem to be less numerous. By increasing oxidation time up to 180 s, the most significant fact is that the m-VO<sub>2</sub> phase completely disappears, with a critical increase of both V<sub>2</sub>O<sub>5</sub> and V<sub>4</sub>O<sub>9</sub> phases. This is explained by the oxidation of m-VO<sub>2</sub> into over-oxides, mainly V<sub>2</sub>O<sub>5</sub> [31,32]. As a

consequence, an air oxidation of 150 s could be considered as the limit to obtain films containing the thermochromic m-VO<sub>2</sub> phase. After 240 s oxidation, the main phases detected correspond to  $\alpha$ - and  $\beta$ -V<sub>2</sub>O<sub>5</sub> system, while other oxides like V<sub>6</sub>O<sub>13</sub> or V<sub>4</sub>O<sub>9</sub> are hardly detected. This is due to the progressive conversion of those latter over-oxides into the highest oxidation state of vanadium encountered in V<sub>2</sub>O<sub>5</sub> phases (see, for instance, the clear vanishing of the peak at 24.5° that corresponds to V<sub>4</sub>O<sub>9</sub>). It is worth noting that the present oxidation behavior of vanadium films is slightly different from other works operating at approx. 450 °C, where only m-VO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> were evidenced by XRD [28,32,37]. However, similar observations of such traces of other additional vanadium oxides were made by Rampelberg *et al.* [31] within an *in situ* XRD study of the oxidation of ultrathin vanadium films (i.e. lower than 80 nm) for temperature ranging between 430 and 615 °C in diverse atmospheres. Indeed, oxide phases like V<sub>3</sub>O<sub>7</sub>, V<sub>6</sub>O<sub>13</sub> and of course V<sub>2</sub>O<sub>5</sub> emerge when the oxidation temperatures exceed 500 °C (see, for instance, Fig. 1a & Fig. 1b in reference [31]). Moreover, it may be inferred that the presence of high thermal stress during high-temperature oxidation should allow the stabilization of other intermediate phases.

Among the diffractograms presented in Fig.1b, as-deposited VN films (VN\_0), showing a brown-yellowish color [44], exhibit a strong peak located at 37.9° corresponding to (111) planes of the face centered cubic  $\delta$ -VN structure (PDF no. 00-035-0768). Except for the silicon substrate peak at approx. 33°, no other peak is detected. The average crystallite size of VN was estimated to be 37 nm from the full width at half maximum (FWHM) of the VN (111) diffraction peak. As shown in Fig. 1b, marked differences are observed when oxidizing VN films compared to the oxidation of vanadium precursor. First, the oxidation of VN into m-VO<sub>2</sub> takes place even for short oxidation durations. Indeed, VN\_60 film shows an X-ray diffractogram with two peaks at 37.1 and 42.3° attributable to (200) and (210) planes of m-VO<sub>2</sub> in addition to the (111) peak of VN. For further oxidation duration, i.e., 90 s, the main detected peaks are those of m-VO<sub>2</sub> phase, VN and a feeble diffraction peak of V<sub>4</sub>O<sub>9</sub> at 29.5°. VN\_120

depicts two small additional m-VO<sub>2</sub> peaks as compared to VN<sub>90</sub>. In the case of the VN<sub>150</sub>, only two m-VO<sub>2</sub> peaks are detected with the simultaneous decrease of the VN peak. Unlike VN<sub>120</sub> or VN<sub>90</sub>, no trace of V<sub>4</sub>O<sub>9</sub> is noticed here. This means that this phase is doubtless detected as traces for previous lower oxidation durations. Besides, it is worth to note that the VN peaks intensity decreases with oxidation time (corresponding to the gradual consumption of the VN precursor) and is shifted to higher diffraction angles. Indeed, VN(111) peak is located at 37.9° for as-deposited film and at 38.2° and even 38.5° for VN<sub>60</sub> or VN<sub>150</sub>, respectively. This VN(111) peak shift between as-deposited and oxidized films was reported in our previous studies [41,42]. One possible explanation could be a lattice shrinkage explained by a progressive nitrogen depletion during the oxidation of the nitride. This phenomenon may be associated with a possible stress relaxation inside the nitride layer itself. As modeled by Bernstein a few decades ago for oxides scales formed on metals showing a Pilling Bedworth Ratio higher than unity, a planar compressive stress of the oxide is balanced by a tensile stress inside the feeding metal [45]. Herein, since VO<sub>2</sub> exhibits a higher molar volume than VN, an increase of compressive stress in the growing oxide layer is expected. Therefore, this stress balance might produce tensile stress in the residual VN layer, hence a shift of the VN(111) diffraction peak toward higher angles, as observed in Fig. 1b. For an oxidation duration of 180 s, the main diffraction peaks are still attributed to the m-VO<sub>2</sub> phase, even if an additional weak peak is located at 12.2°, which correspond to the metastable β-V<sub>2</sub>O<sub>5</sub> phase. One can notice that oxidizing VN induces the occurrence of (210) diffraction peak of m-VO<sub>2</sub> at 42.3°, which is not encountered in the oxidized vanadium films. A possible reason may arise from the difference between the initial crystal lattice of the precursors (body-centered cubic for V vs. face centered cubic for VN). Moreover, the (111) diffraction peak of VN, though dramatically low, is still detected in VN<sub>180</sub>. With increasing oxidation duration up to 240 s, several other oxides phases appear (such as V<sub>4</sub>O<sub>9</sub> and V<sub>2</sub>O<sub>5</sub>) in combination with m-VO<sub>2</sub>. Interestingly, the evolution of the VN peak in the framework of this experiment indicates that the onset of further oxidation of m-VO<sub>2</sub> to higher oxides occurs after the complete consumption of the VN precursor film and

slightly before the whole transformation of the m-VO<sub>2</sub> phase. Our previous works dealing with the oxidation of slightly thicker VN films at 450 °C (on silicon substrates) [41] and in the 450-550 °C range (on aluminum substrates) [42] converge in this direction. VN<sub>300</sub> displays a diffractogram quite similar to V<sub>240</sub> (Fig. 1a) with the disappearance of the m-VO<sub>2</sub> peaks associated with a huge increase of over oxides peaks of V<sub>2</sub>O<sub>5</sub>. Note that, as observed for vanadium precursor oxidation, the V<sub>4</sub>O<sub>9</sub> peaks tend to decrease in number and intensity as oxidation time increases and V<sub>2</sub>O<sub>5</sub> becomes the predominant phase. As for vanadium (e.g. V<sub>240</sub>), the tendency observed here is a stabilization of the α-V<sub>2</sub>O<sub>5</sub> phase (increase of the peak at 20°) over β-V<sub>2</sub>O<sub>5</sub> phase (with a decrease of the peak located at 15° and 29.6°) [43]. As compared to the V series, no trace of any V<sub>6</sub>O<sub>13</sub> phase was detected for the oxidized VN films.

The crystallite size of the residual VN layer was nearly unchanged during oxidation while those of the monoclinic VO<sub>2</sub> phase, assessed from the main peak (200) at 36.9°, were ranging between 41 and 50 nm, irrespective to the oxidation time. This last tendency is quite different from the work of Xu *et al.* [28] where m-VO<sub>2</sub> grain sizes span from 49 to 86 nm according to the oxidation duration of vanadium films at 470 °C. This result emphasizes the best stability of the crystallite size of m-VO<sub>2</sub> coming from the VN oxidation than the one from the V precursor films. In summary, XRD analyses show that a relatively high-purity m-VO<sub>2</sub> phase is synthesized from VN precursors in an extensive oxidation duration range than for V films at 550 °C. A similar conclusion is drawn from X-ray diffractograms of the films deposited on aluminum substrates and oxidized at 550 °C up to 180 s (Fig. S3 in supplementary information). See for instance, the explicit increase of m-VO<sub>2</sub> peaks vs. oxidation time. From a molar standpoint, similar thicknesses of precursors correspond to 1.32 and 1.03 μmol/cm<sup>2</sup> for V and VN, respectively. Even if the amount of vanadium atoms is 30% lower in VN than in V, the best thermodynamic properties of VN above V yields to a lower global oxidation of the former. Fateh *et al.* observed such difference between VN and V films during tribo-oxidation tests, stating that the oxidation onset differences associated with a best oxidation resistance of VN

above V could be due to the more stable bonding configuration of V in VN compared to the metallic V coating [46]. Fig. 2 displays a schematic summarizing the structural evolution of the diverse oxide phases (and their precursors) detected by XRD for both V and VN series. From this overview, Fig. 2 reveals an evident widening of the m-VO<sub>2</sub> domain of and a best oxidation resistance for VN precursor compared to V one.

To refine structural analyses, Raman spectroscopy has been used as a complementary method to determine the nature of the various vanadium oxides phases formed for both precursors deposited on silicon substrates. Fig. 3 shows room-temperature Raman spectra of V\_150 and VN\_150 up to VN\_300. For each film, the band located at 520 cm<sup>-1</sup> is attributed to the silicon substrate. As previously mentioned [41], the Si band intensity is a powerful method to monitor the oxidation of the VN precursor. The higher the intensity of the silicon band, the greater the thickness of the oxide layer (and therefore the smaller the remaining thickness of the residual VN or V layer). The comparison of this band for V\_150 and the VN\_150 Raman spectra evidences that the oxidation of the V precursor is faster than the VN one. The main features of V\_150 spectra are typical of V<sub>2</sub>O<sub>5</sub> phase with bands located at 102, 145 (intense), 283, 303, 405, 481, 533 (shoulder on the silicon band) and 702 cm<sup>-1</sup> in accordance with literature data [47,48]. However, due to the significant similitude between the Raman spectra of α-V<sub>2</sub>O<sub>5</sub> and V<sub>4</sub>O<sub>9</sub> [48], it seems problematic to accurately index the V<sub>4</sub>O<sub>9</sub> phase in the V\_150 film observed in Fig. 1a. Finally, three additional bands with low intensity, located at 194, 223 and a weak band at 613 cm<sup>-1</sup> are detected, corresponding to the most significant bands of m-VO<sub>2</sub> [47–49]. Therefore, this spectrum confirms the coexistence of m-VO<sub>2</sub> traces with over-oxides (mainly V<sub>2</sub>O<sub>5</sub> phase) in V\_150, as observed by XRD in Fig. 1a.

On the other hand, VN\_150 spectrum presented in Figure 3 shows bands located at 145, 193, 220, 261, 306, 341, 392, 444, 500, 586 and 618 cm<sup>-1</sup> corresponding to m-VO<sub>2</sub> [48,49]. Quite similar spectrum is observed for VN\_180. Note that no trace of any V<sub>2</sub>O<sub>5</sub> phase was detected by Raman in VN\_180. By increasing oxidation time up to 240 s, the vibration bands of m-VO<sub>2</sub>

are still detected at 193, 220, 262  $\text{cm}^{-1}$ , and in a lesser extent at 442 and 500  $\text{cm}^{-1}$ . Additional bands corresponding to  $\text{V}_2\text{O}_5$  phase appear at 102, 143, 280, 301, 405 and 696  $\text{cm}^{-1}$ . Note that a shoulder present at  $\sim 129 \text{ cm}^{-1}$  may be attributable to  $\text{V}_6\text{O}_{13}$  [48] in an amorphous state, since this phase is not noticed by XRD. However, as previously discussed, other over-oxides detected by XRD in VN\_240 (like  $\text{V}_4\text{O}_9$ ) are not evidenced, suggesting a negligible amount of these phases. Finally, VN\_300 exhibits a typical  $\text{V}_2\text{O}_5$  Raman signature, with two other weak bands at 225 and 257  $\text{cm}^{-1}$  that could be ascribed to residual m- $\text{VO}_2$ , though not detected by XRD (Fig. 1b). Hence, Raman spectroscopy confirms that air annealing of VN yields m- $\text{VO}_2$  as the leading compound synthesized during an extended oxidation period than in the case of V films. The m- $\text{VO}_2$  is the principal phase up to 180 s and is still present in combination with  $\text{V}_2\text{O}_5$  for VN\_240. Finally, it nearly vanishes after 300 s. Raman spectra of oxidized VN films deposited onto aluminum substrate in Fig. S4. provide additional support to those conclusions.

### 3.2. Electrical properties of oxides formed using V and VN precursors

Due to the percolative nature of the MIT [50], typical reversible hysteresis loops are observed on the physical properties of m- $\text{VO}_2$  under heating and cooling cycles near its transition temperature ( $T_c = 68 \text{ }^\circ\text{C}$ ). Among these properties, electrical resistivity switches between the semiconducting phase and the metallic one have been successfully used as indicators to rank the quality of thermochromic vanadium dioxide films obtained after different thermal treatments [24,28,29,32,33,35]. Fig. 4 illustrates the temperature dependence of the sheet resistance both for heating and cooling ramps (between 25 and 125  $^\circ\text{C}$ ) for different oxidation duration applied to each precursor films deposited on silicon substrates. Sheet resistance ( $R_{sq}$ ) has been preferred instead of electrical resistivity due to the accuracy lack in assessing the thicknesses of the rough vanadium oxides layers formed after air-oxidation and the remaining thickness of the precursor. In accordance with the previous structural characterizations, oxidized V films (Fig. 4a) were analyzed in the 60 to 180 s range while oxidized VN samples (Fig. 4b) were investigated up to 300 s, i.e., in the oxidation time range allowing the formation

of m-VO<sub>2</sub> up to the threshold corresponding to its vanishing. To estimate the performance of the oxidized films,  $\Delta R$  values, calculated from Eq. (2) are considered. A negligible variation of  $R_{sq}$  is observed in Fig. 4a for V\_60. On the other hand, a weak  $R_{sq}$  change in the V\_90 and V\_120 samples ensures the presence of m-VO<sub>2</sub> in both films. For these two samples,  $\Delta R$  spans from 0.3 to 0.72. By increasing oxidation time up to 150 s, the  $\Delta R$  value raises to 1.62, confirming that the best duration to obtain a thermochromic VO<sub>2</sub> films after V oxidation is fixed at 150 s. This is associated with a large asymmetric hysteresis widening and a global shift to higher sheet resistance values when compared to V\_120. The latter phenomenon may be related to the formation of numerous over-oxides which coexist with the m-VO<sub>2</sub> for V\_150, as evidenced by XRD and Raman spectroscopy. These results are consistent with other works showing how the MIT is affected by increasing over-oxide content in the m-VO<sub>2</sub> films, with V<sub>6</sub>O<sub>13</sub> [35] or V<sub>2</sub>O<sub>5</sub> [24,28,32,37]. With a further oxidation duration up to 180 s, the typical MIT hysteresis disappears, confirming the full conversion of the m-VO<sub>2</sub> phase into other over-oxides in agreement with XRD for V\_180 (Fig. 1a). Here a temperature coefficient of resistance value of this mixed oxide has been assessed to  $\sim -0.011$  /°C close to the value of  $-0.0112$  /°C measured for V<sub>2</sub>O<sub>5</sub> thin films [51].

Fig. 4b displays thermally induced changes of  $R_{sq}$  for oxidized VN precursors. The films oxidized from 60 to 180 s exhibit typical hysteresis loops centered at approx. 70°C with amplitudes ( $\Delta R$ ) rising from 0.11 to 2.03 (Table 1). In agreement with XRD and Raman spectroscopy, this behavior is linked to the high phase purity of m-VO<sub>2</sub> obtained from VN precursors oxidation up to 180 s. On the other hand, VN\_240 reveals a wider hysteresis with a marked decrease of the  $\Delta R$  value to 1.35 and a global offset of its sheet resistance to higher values. This shift is attributable to the mixture of a low proportion of the m-VO<sub>2</sub> phase converted into several other over-oxides (V<sub>4</sub>O<sub>9</sub> and mainly V<sub>2</sub>O<sub>5</sub>). Finally, due to the complete oxidation into the V<sub>2</sub>O<sub>5</sub> phase, VN\_300 does not show MIT anymore. These electrical measurements are in agreement with structural analyses and confirm the high purity of the m-

VO<sub>2</sub> phase obtained up to 180 s for oxidized VN films compared to the V ones. Since the best m-VO<sub>2</sub> (higher electrical switches) synthesis comes from the VN air oxidation, the next part of the present work is focused on this series only.

The MIT temperatures ( $T_c$ ) are determined experimentally from the minimum of  $d(R_{sq})/dT$  both for heating ( $T_c^{UP}$ ) and cooling ( $T_c^{DW}$ ) branches of the hysteresis curve [33]. Thereafter, hysteresis widths  $\Delta T_c$  are calculated from Eq. (1) and tabulated in Table 1. Whatever the oxidation duration to form m-VO<sub>2</sub> from VN films, one can notice similar hysteresis width values ranging between 7.1 and 9.3 °C, with  $T_c^{UP}$  and  $T_c^{DW}$  close to 68-70 °C and 60.0-61.7 °C, respectively. Note a slight shift to higher  $T_c$  for VN<sub>240</sub> showing values of 73.6 °C and 64.7 °C, respectively. The hysteresis width values are close to those obtained in literature for the best MIT after air-oxidation of vanadium films, e.g. 11 °C [33,40] and 15-21 °C [28], or for oxygen annealed films, e.g. 7.4 °C [35] or 9.7 °C [34] but higher than the outstanding 0.4 °C obtained by Xu *et al.* [52]. According to Brassard *et al.*, the width of such hysteresis decreases with the grain size of m-VO<sub>2</sub> [4]. Thereby, one can assume that the unchanged position of the hysteresis curves for all the VN series up to 180 s is caused by the negligible fluctuations of the m-VO<sub>2</sub> grains size (ranging between 41 and 50 nm). Figure 4 indicates that the VN films oxidation provides stable m-VO<sub>2</sub>, due to the best oxidation resistance of the precursor, with superior  $\Delta R$  values (i.e. ~2 decades for VN<sub>180</sub>) than those obtained from oxidation of vanadium precursors. It is significant to note that in our previous work on silicon substrates, a similar limit in the amplitude of the resistivity switch was also observed [41]. Liang *et al.* [40] achieve interesting improvements in  $\Delta R$  by applying two successive annealings (rapid thermal annealing followed by conventional annealing at lower temperature) to increase the grain size of the obtained VO<sub>2</sub> grains.

### 3.3. Performance of VO<sub>2</sub> films formed by air oxidation of VN precursor



Fig. 5 depicts the top view SEM micrographs of the VN series: as-deposited film and samples oxidized for 60, 90, 120, 150 and 180 s. VN<sub>0</sub> film exhibits a smooth and nearly featureless surface (Fig. 5a). Small cracks and first emerging grains appear on the VN<sub>60</sub> film's top surface, corresponding to the early stages of VO<sub>2</sub> formation (Fig. 5b). For VN<sub>90</sub>, the oxide growth is observed around the above-mentioned cracks that are considered excellent pathways for the oxidation of the remaining VN layer (Fig. 5c). After 120 s oxidation (Fig. 5d), the oxide layer agglomerates in a compact packing of grains (< 250 nm in dimension), increasingly covering the residual nitride layer (still observed by XRD up to VN<sub>180</sub> in Fig. 1b). Stacked globular grains of different sizes from 50 to 300 nm are noticed on the top surface of VN<sub>150</sub> sample in Fig. 5e. Beyond this oxidation time, the morphology of the oxide layer of VN<sub>180</sub> evolves into coarse laminated flakes (Fig. 5f) even if the m-VO<sub>2</sub> is still the predominant phase (Fig. 1b).

Fig. 6 presents SIMS depth profiles for VN<sub>0</sub>, VN<sub>90</sub>, VN<sub>120</sub> and VN<sub>180</sub> deposited on aluminum substrates. The initial VN layer exhibits nearly homogenous profiles of V and N with an increase of the oxygen amount mainly at the air/film and film/substrate interfaces (Fig. 6a). Fig. 6b indicates that for an annealing duration of 90 s, the vanadium and nitrogen profiles are not constant along with the film depth anymore. For the inner part of the film, the vanadium and nitrogen intensities are similar to those measured in the as-deposited VN film, corroborating the presence of a residual VN layer. As shown by HRTEM in our previous work [41], no oxynitride phase was detected during the oxidation process in contrast with the observations made by Borgianni *et al.* [53]. Towards the film surface, the nitrogen profile strongly decreases while that of oxygen rises subsequently. As a consequence, a clear demarcation is seen at the top surface of the film (up to 600 s of analysis) with a vanadium and oxygen-rich plateau corresponding to a vanadium oxide layer. With an increase of oxidation time to 120 s, this tendency is confirmed (Fig. 6c) with a progressive oxygen diffusion from the gas phase into the thin film to form vanadium oxide associated with an outwards diffusion of nitrogen from the VN layer. Since this annealing duration is not long enough to induce the whole transformation

of VN into VO<sub>2</sub>, a remaining nitride layer is still evidenced, as confirmed by XRD results (see supplementary information: Fig. S3b for VN\_120). For VN\_180 (Fig. 6d), nitrogen intensity is dramatically reduced in the core layer (by approx. two decades compared to VN\_0 initial intensity), illustrating the nearly complete vanishing of the residual vanadium nitride. Moreover, vanadium and oxygen profiles are relatively constant throughout the entire film thickness, indicating the formation of a single and homogeneous oxide layer.

To check the optical modulation properties in the infrared domain, the series of oxidized VN films deposited on silicon substrates have been characterized by FTIR during heating and cooling ramps from RT up to 120 °C. Fig. 7a features the FTIR transmission spectra of VN\_180 in the 400-1500 cm<sup>-1</sup> range at various temperatures. As expected from electrical measurements, the film transmittance changes from a high-transmitting semiconducting m-VO<sub>2</sub> phase at room temperature to a flat and low transmittance spectrum of the metallic tetragonal VO<sub>2</sub> phase at 120 °C [54]. From a spectroscopic standpoint, at room temperature, intense phonon vibration absorption bands located close to 600 and 508 cm<sup>-1</sup> correspond to the O-V stretching mode in m-VO<sub>2</sub> and V-O-V octahedral bending modes in m-VO<sub>2</sub>, respectively [55]. The MIT transition is evidenced by a progressive decrease of those bands and the overall transmittance level with rising temperature up to 70 °C, followed by nearly featureless spectra corresponding to the metallic rutile phase of VO<sub>2</sub> for temperatures overpassing 72 °C. To illustrate this, Fig. 7b displays the heating and cooling branches of the infrared transmittance signal of VN\_180, determined from the thermally induced spectrum at  $\lambda = 8 \mu\text{m}$ . This wavelength was chosen due to its interest in solar thermal regulation [16]. As for electrical measurements, a typical hysteresis loop of  $Tr(T)$  is observed. At room temperature, the semiconducting phase depicts a good transmittance, close to 66 %. Conversely, beyond the MIT temperature,  $Tr$  decreases strongly to approx. 5 % corresponding to the complete transition of m-VO<sub>2</sub> into the metallic rutile-type VO<sub>2</sub> phase. Fig. S5 shows the infrared transmittance hysteresis curves for VN\_90 to VN\_180. Note that due to the poor oxidation of VN\_60, the resulting film is not transparent in

the IR domain and is not presented here. In addition, the infrared contrast values obtained for this series are summarized in Table 1. The VN<sub>90</sub> film shows a slight thermochromic behavior with a low transmittance contrast (7.8 %), due to the shallow consumption of superficial VN into m-VO<sub>2</sub>. With increasing oxidation duration up to 120 s, a balance between m-VO<sub>2</sub> growth and VN consumption occurs, and  $\Delta Tr$  rises to 42.9 %. Following annealing, samples VN<sub>150</sub> and VN<sub>180</sub> (with almost pure m-VO<sub>2</sub>) exhibit the best thermochromic performance with  $\Delta Tr$  equal to 61.3 and 63.0 %, respectively. For the latter, Fig. 7c depicts the determination of the transition temperatures for the heating and cooling branch from the minimum of the Gaussian fit of the first derivative of the  $Tr$  vs.  $T$  curve [56]. The transition temperatures for heating and cooling ramps during the MIT for VN<sub>180</sub> were assessed to  $T_c^{UP} = 68.3$  °C and  $T_c^{DW} = 61.8$  °C, respectively. The resulting temperatures from VN<sub>90</sub> to VN<sub>180</sub> are shown in Table 1. This Table also depicts that there is a good agreement between  $T_c$  (up and down) measured by infrared transmittance at 8  $\mu\text{m}$  and those determined by the electrical method. Fig. S6 (in supplementary information) reports the determination of the transition temperature for the heating and cooling branches for VN<sub>120</sub> at four different wavelengths (i.e. 4, 8, 12 and 16  $\mu\text{m}$ ). The similar  $T_c$  values undeniably confirm that the transition temperatures obtained by the above-mentioned method are wavelength independent.

The reversible switching properties observed during the MIT for thermochromic VO<sub>2</sub> thin films in the infrared domain are of interest in passive thermal regulation [8,9,11,12,15,16]. This regulation requires positive thermally-induced emittance switching, i.e. from a low emittance ( $\varepsilon$ ) at low temperature (to keep heat in the system) to higher values of  $\varepsilon$  (to dissipate heat excess). Such a positive emittance switch exists when the thermochromic layer is deposited on a highly infrared-reflective material that can be either an intermediate layer (e.g., gold [12]) or directly a metallic substrate (e.g. aluminum [11,16,42]). For this purpose, Fig. 8 represents apparent infrared temperature ( $T_{IR}$ ) of VN<sub>60</sub> and VN<sub>180</sub> samples monitored versus the sample temperature ( $T_S$ ) during both, heating and cooling. The apparent infrared temperature

of an aluminum foil substrate has been also added in Fig.8 as a reference. The VN films oxidized within the 60 – 180 s range exhibit a clear hysteresis loops for the  $T_{IR}$  vs  $T_S$  curves. Emissivity switch ( $\Delta\varepsilon$ ) obtained for the oxidized VN series are represented in Fig. 9a. Those values were determined from the difference between the slopes corresponding to each region before and after the MIT, according to the procedure employed by Benkahoul *et al.* [11]. The values of  $\Delta\varepsilon$  are found to increase with the oxidation duration of VN films, in good agreement with IR-transmittance and electrical measurements (Fig. 9b and 9c). However, the best emissivity contrast obtained for VN\_180 ( $\Delta\varepsilon = 0.19$ ) is relatively low compared to literature for positive thermal regulation purposes. We reported a slightly higher value of 0.21 for m-VO<sub>2</sub> obtained from thicker VN precursors (175 nm) and oxidized at a lower temperature (450 °C) for 30 min [42]. Conversely, for thicker m-VO<sub>2</sub> films deposited on aluminum (~300 nm), Benkahoul *et al.* obtained  $\Delta\varepsilon = 0.26$  [11], Mercks *et al.* obtained  $\Delta\varepsilon = 0.34$  for Al-doped VO<sub>x</sub>/SiO<sub>2</sub> bilayers [16], while a multilayered VO<sub>2</sub>/SiO<sub>2</sub>/Au system deposited on silica by Hendaoui *et al.* reached  $\Delta\varepsilon = 0.49$  [12]. Further enhancements of the emissivity switch properties derived from the oxidation of VN precursor can be expected by modifying the design of our system, by an optimization of the m-VO<sub>2</sub> thickness [37] and/or improving the crystallinity of the resulting m-VO<sub>2</sub>.

#### 4. Conclusion

This study compares the formation and the properties of thermochromic m-VO<sub>2</sub> films synthesized in a two-step procedure after air-oxidation at 550 °C of vanadium and vanadium nitride thin films with similar thickness. X-ray diffraction and Raman spectroscopy revealed that both precursors lead to m-VO<sub>2</sub> followed by complete oxidation into V<sub>2</sub>O<sub>5</sub>. Thanks to its higher oxidation resistance, the use of a VN precursor allows forming nearly pure m-VO<sub>2</sub> in a wider operative window of annealing duration. Moreover, in the timescale allowing the formation of m-VO<sub>2</sub>, electrical measurements showed fluctuations of the hysteresis widths of the V oxidized films, while high stability of the hysteresis is achieved for the m-VO<sub>2</sub> derived

from the VN oxidation. The second part of the present work is dedicated to the infrared properties (transmittance and emissivity) of m-VO<sub>2</sub> obtained from the VN precursors. Typical signatures of m-VO<sub>2</sub> were observed by FTIR and confirmed the relative stability of the hysteresis of the oxides originating from VN. From electrical and infrared transmission thermal cycling measurements, it was shown that the critical temperatures ( $T_c^{UP}$  and  $T_c^{DW}$ ) of the hysteresis curves are similar within the domain allowing the formation of pure m-VO<sub>2</sub>. This work confirms the potential interest in oxidizing VN to synthesize m-VO<sub>2</sub> with good thermochromic performances (e.g., IR contrast of 63% and electrical switch of ~ 2 decades) in a simple procedure.

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## **Declaration of competing 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.

## **CRedit authorship contribution statement**

**D. Pilloud:** Writing, Original draft, Investigation. **A.C. García-Wong:** Investigation, Review & Editing. **D. Mangin:** Investigation. **F. Capon:** Review, Funding acquisition. **J.F. Pierson:** Writing - Review & Editing, Supervision.

## **Appendix A. Supplementary data**

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