Comparative study between nanocrystalline powder and thin film of vanadium dioxide VO₂: electrical and infrared properties

F. Guinneton, L. Sauques, J.C. Valmalette, F. Cros, J.R. Gavarri

Abstract

The reversible metal insulator phase transition of VO₂ (T_c ≈ 68°C) is associated with strong changes in electrical, magnetic and optical properties. Recently, nanopigments were synthesized using the low temperature irreversible structural transformation of the metastable VO₂(B). Thin films were deposited under radio-frequency sputtering conditions. The optical transparency is remarkably increased for these nanosized particles and thin films. The VO₂ transition is characterized in the mid-infrared (MIR) region, using transmittance, reflectance and normal integrated emissivity measurements. Emissivity and reflectance are analyzed from two independent experimental techniques.

1. Introduction

The aim of this work is to compare the thermochromic properties of thin films and nanocrystalline powders of the vanadium dioxide VO₂. The reversible metal insulator phase transition (MIPT) of vanadium dioxide (T_c ≈ 68°C) is associated with strong changes in electrical, magnetic and optical properties.

Cationic and/or anionic substitutions induce modifications of the temperature of transition. The optical contrast of this transition strongly depends on stoichiometry, microstructure and surrounding medium of the oxide. Both scientific investigations and technological applications are of great interest due to the temperature range of this structural transition [1–3]. By the past, thermochromic thin films were extensively studied [4–6]; more recently, several works were focused on applications involving pigments in polymeric matrices [7]. Optical switching materials could be used to modulate IR emissivity, as Hale and Woollam [8] have recently suggested with electrochromism devices applied to space structures.

Previous works [9] investigated the influence of particle sizes on the MID–IR transmittance contrast: the optical contrast was shown to increase when the grain size decreased. Due to the powder synthesis process, the obtained VO₂ grain sizes were broadly submicronic. Such dimensions are similar to the thickness of thin films.

In this study, optical properties of thin films and nanosized powders samples of VO₂ are correlated (transmittance, reflectance, and normal integrated emissivity). For the first time, emissivity measurements are determined on each sample and correlated with the reflectance analyses.

2. Experimental

2.1. Samples

Recently, we have shown that nanosized thermochromic VO₂ (R) pigments could be obtained making use of the structural transformation of metastable VO₂(B) powders [10,11]:

\[ \text{VO}_2 \text{(metastable B form)} \xrightarrow{\Delta} \text{VO}_2 \text{(stable Rutile form)} \]

The VO₂(B) precursor powder was placed in a quartz crucible, heated under inert atmosphere (argon) at 550°C for 2 h, and cooled down to room temperature in the reactor to
prevent oxidation of vanadium dioxide. Due to the synthesis, submicronic powders of VO$_2$ were obtained.

RF reactive sputtering was used to produce thin films of vanadium dioxide. After pumping down to $10^{-7}$ Torr, then performing an adjusted pre-sputtering, thin films were deposited on an amorphous silica substrate using a pure metallic vanadium target (HTC, purity 99.7%). To produce VO$_2$ thin films with high optical and thermo-optical properties, it was necessary to accurately control the oxygen flow and to heat the substrate holder during the sputtering. By this way, VO$_2$ coatings with good switching properties were directly obtained.

2.2. Characterizations

The obtained powder samples were characterized by X-ray diffraction, using a Siemens–Brucker D5000 diffractometer, equipped with a copper X-ray source ($\lambda = 1.540 \text{ Å}$), a secondary monochromator and a rotating sample holder, working in a classical coupled $\theta$–$2\theta$ mode.

Transmission electron microscopy (TEM) experiments were carried out on a Philips EM 400 T microscope to determine grain morphologies and size distributions.

The transition was first investigated using electrical measurements. The electrical resistance of each sample was analysed using a four-points equipment associated with a Hewlett Packard HP 3456A multimeter, and using a Peltier device coupled with an automated control temperature (rate $2^\circ\text{C/min}$).

The reversible changes in optical collimated transmittance T versus temperature of thermochromic materials were made using a FTIR spectrophotometer (Nicolet-Magna 860 IR spectrometer) with an adapted heating controlled cell. Powders were studied after dispersion in a classical KBr pellet (0.1 wt% of VO$_2$), and by coating on a 1-mm thick glass substrate (powder dispersion in solution followed by evaporation). The VO$_2$ powders are just suspended in distilled water (without additive) using an ultrasonic dispersion. A drop of the suspension is deposited at the surface of a glass slide and dried at 50$^\circ\text{C}$. For this sample, using optical microscope observations, the coverage of powder was estimated to be 60%.The initial crystallographic structure is fully preserved. In addition, no texture effect is observed because of the isotropic distribution of particles.

Optical hysteresis curves were deduced from spectral transmittance at a typical wavelength (in this case successively 2.5, 3.5, and 4.0 $\mu$m).

The Nicolet Magna 860 spectrophotometer equipped with Hemispherical Directional Reflectometer (HDR SOC100) extension was used to determine infrared hemispherical directional reflectance. No polarized light was used.

Normal integrated emissivity measurements were carried out, on heating and on cooling in air, in the 8–12 $\mu$m wavelength range, using an HgCdTe infrared sensor (maximum contribution in this range).

![Fig. 1. Crystallite sizes of VO$_2$ nanopowder given by the Scherrer formula (indexation is given in the monoclinic system).](image)

The emissivity data were calibrated by comparing the sample optical response to a black body.

3. Results and discussion

3.1. X-ray diffraction analyses

The powder X-ray diffraction experiments confirm the total transformation of the VO$_2$(B) precursor. The low temperature monoclinic structure ($P_{2_1}/c$) was confirmed. The cell parameters were refined using a classical least mean square method. Twelve Bragg peaks were used to obtain the following results: $a = 5.776(4) \text{ Å}$, $b = 4.547(2) \text{ Å}$, $c = 5.400(4) \text{ Å}$, $\beta = 122.55(4)^\circ$. The diffraction profiles were analysed in the same conditions and compared with the profiles of a standard (Aldrich VO$_2$ sample (Ref. 21,582-1, 99.9%), annealed at 800$^\circ\text{C}$ for 12 h, under neutral atmosphere). Each profile broadening was assumed to result from pure size effects. The crystal sizes were directly deduced from the Full Width at Half Maximum (FWHM) of the observed Bragg peaks. As a first approximation, the mean sizes of crystallites (L) can be calculated using the classical Scherrer formula:

$$L = \frac{0.9\lambda}{\Delta(2\theta) \cos \theta}$$

where $\lambda$ is the wavelength, $\theta$ is the Bragg angle, $\Delta 2\theta$ is the additional broadening due to the size effect.

This broadening can be calculated from:

$$\Delta 2\theta^2 = (\text{FWHM}_{\text{obs}})^2 - \omega^2$$

where $\omega$ is the standard FWHM obtained from the standard VO$_2$ sample. The specific ‘WinPLOTR’ software [12] was used to determine the FWHM.

As a roughly constant value of $L$ was obtained from Fig. 1, it should be admitted that the population of
3.2. Transmission electron microscopy analyses

These results are directly confirmed by the TEM observations. Fig. 2 shows one agglomerate of small particles. In fact, it can be described as a unique grain having the form of a porous holed plate with angular shapes. The observed dimensions of each isolated domains of grain are in good agreement with the values of $L$ calculated from the X-ray diffraction data.

This morphology is a typical consequence of the irreversible phase transformation of plate-like particles VO$_2$(B) into thermochromic ‘rutile’ VO$_3$. The transformation is associated with a strong increase in volumic mass (from 4.03 to 4.67 g cm$^{-3}$) without any chemical composition change.

3.3. Role of dimensions.

In the case of comparative studies between continuous thin films and nano-powdered materials, the sizes of primary particles can play a prominent role in the final properties, because of the diffusive phenomena occurring in the MIR-infrared range [9].

To evaluate the thickness of each film, profilometry measurements were carried out; each film thickness was estimated to be in the range 100–200 nm. Such dimensions are roughly similar to the individual crystal sizes (60 nm for the isolated crystallites observed in porous agglomerates—see Fig. 2). It should be noticed that both materials present dimensions much weaker than the wavelengths of the presently used IR sources. In such circumstances, diffusive
phenomena will be attenuated, as it is the case for materials having sizes smaller than the wavelengths of the incident beam.

3.4. Electrical measurements

Electrical measurements are reported in Fig. 3. The transition temperature \( T_c \) of compacted powders seems to be shifted to a higher value. This can be due to the fact that the samples are heated from the support (below face) and that a significant thermal gradient is probably involved in our experiments.

The measured resistances of the thin film and of the compacted powder sample are highly different. At 20 \( ^\circ \text{C} \), the thin film has a resistance of \( r = 70,000 \) ohms while the compacted sample presents a lower resistance of \( r = 1050 \) ohms. At 140 \( ^\circ \text{C} \), above the transition temperature, the resistances fall to \( r = 2000 \) ohms and \( r = 5 \) ohms, respectively, for the thin film and compacted sample. The ratio \( r(\text{film})/r(\text{powder}) = 34 \) at 20 \( ^\circ \text{C} \) and 40 at 140 \( ^\circ \text{C} \). Correlatively, the slopes \( d(\ln r)/d(1/T) = E_{\text{act}}/k_B \) allow the activation energies for both film and powder samples to be calculated. The values calculated at 20 \( ^\circ \text{C} \) (sufficiently far from the transition, \( T < T_c \)) are 0.162 eV (\( \pm 0.002 \) eV) and 0.129 eV (\( \pm 0.006 \) eV), respectively, for thin film and powder sample. This clearly shows that the thin film is more resistive (semiconductor) than the compacted powder sample. This can be interpreted in terms of improved electrical contacts between grains in the compacted sample.

A simple model can be proposed. If the observed resistance is expressed as \( r = r(\text{VO}_2) + r(\text{interfaces}) \), the electrical contrast at \( T = T_c \) is:

\[
\Delta r(\text{film})(T > T_c) - \Delta r(\text{film})(T < T_c) - r(\text{interfaces})
\]

The values found for the thin film and compacted powder are, respectively, \( \Delta r(\text{film}) = 34 \) and \( \Delta r(\text{powder}) = 209 \). In a first approximation, we have assumed that, due to weak links, the interface resistance should be very large in the thin film and negligible in the compacted powder sample, because of stronger links. Then, making use of the experimental data of Fig. 3, we have evaluated this resistance in the thin film: \( r(\text{interfaces}) = 1675 \) \( \Omega \). This interface resistance is probably at the origin of the higher activation energy observed for the resistance in the thin film.

3.5. Infrared transmittance experiments

The infrared spectroscopy experiments are reported in Figs. 4 and 5. They confirm the strong reversible MIPT modifications, observed in collimated transmittance measurements upon heating and cooling, as well for powders as for thin films. The low temperature \( (T < T_c = 68^\circ \text{C}) \) spectrum shows vibrational bands characteristic of the semiconducting phase in the 400 to 1000 cm\(^{-1}\) wavenumber range. Let us recall that the observed absorption bands are related to the electromagnetic resonance between incident photons (with a specific wavenumber), and the variation of chemical bond polarizations associated with a specific vibrational mode. At low temperature \( (T < T_c) \) the electrons involved in the V–V bonds between \( \text{VO}_6 \) octahedra are localized. In the metal state at \( T > T_c \), these electrons are delocalized: this delocalization involves a screening effect for the incident photons. This screening effect occurs at the surface of the sample. It results that no vibrational absorption band can be observed. In this circumstance, transmittance drastically decreases [13–15].

So, the IR vibrational absorption and the screening effect due to metallic state are two distinct phenomena: they cannot be compared.

To characterize the optical transmission switching efficiency, we have defined a contrast factor \( \tau(\lambda) \) as follows:

\[
\tau(\lambda) = \frac{T_{LT} - T_{HT}}{T_{LT}}
\]

where: \( T_{LT} \) and \( T_{HT} \) are transmittances respectively for \( T < T_c \) and \( T > T_c \), and where \( \lambda \) is the IR wavelength.
Recent works [9] showed the influence on contrasts of the volume fractions of VO₂ inserted in KBr pellets, of the sample elaboration, the morphologies, and the grain sizes (as grain sizes decrease, the transparency and the contrasts simultaneously increase). In the present conditions, the contrast factors \( t \), are 0.85 and 0.99 (at \( \lambda = 2.5 \mu m \) wavelength), respectively, for nanopowders and thin film samples.

For nanoparticles, this contrast is maximum at \( \lambda = 2.5 \mu m \) and slowly decreases in the 2.5–5 \( \mu m \) wavelength range with increasing wavelength, and becomes negligible in the vibrational range (\( \lambda > 10 \mu m \)). In a previous work [9], we have already noticed that, the 995 \( \text{cm}^{-1} \) absorption band, observed on the Fig. 4, and denoted (*), did not disappear upon heating, instead of all the other absorption bands. It is commonly attributed to the partial surface oxidation of VO₂ powders. The red shift of this absorption band, observed in our nanosized samples, could be ascribed to a high specific surface contribution.

Several explanations can be proposed: surface mode contribution (including adsorbed species) or initial step in the oxidation mechanism related to high surface sensitivity of these powders [16].

Fig. 5a represents transmittance spectra first for an amorphous silica substrate at ambient temperature, then, for a thin film at 25 and 80°C, in the 2.5–5 \( \mu m \) wavelength range. Fig. 5b reports the transmittance data of the thin film corrected for substrate absorption. Above \( \lambda = 5 \mu m \), due to the stronger absorption of the substrate, the transmittance is practically equal to zero. For these reasons, the spectra were reported in the 2.5–5 \( \mu m \) range. For wavelengths of about 2.7 and 4.4 \( \mu m \), a substrate effect (denoted * ) influences the response of thermochromic VO₂ in the semiconductor state. Because of the metallic state above the transition temperature, the substrate effects become negligible.

An overview of each material transmittance is reported in Fig. 6. From about \( \lambda = 3.8 \mu m \), transparency is higher for nanopowders than for thin film due to the amorphous silica substrate effect. This can be particularly useful for applications involving pigments in polymeric matrices. Transparency of VO₂ increases with wavelength. So, the performance level of each device will strongly depend on the choice of the substrates or matrices.

The influence of temperature on the collimated transmittance has been studied at three different wavelengths (2.5, 3.5, and 4 \( \mu m \)).

For each sample, a typical optical hysteresis has been observed. Two different optical contrasts are obtained in the mid-IR range (Fig. 7): they are particularly pronounced for the thin film (\( \Delta T = 45\% \), \( \Delta T/T = 99\% \) at 2.5 \( \mu m \)).

To compare the optical responses of the film with the responses of our nanopowder, we have deposited our nanoparticles dispersed in their solvent on a glass substrate. Then, after evaporation of this solvent, we have obtained a granular thin layer.

The contrast is lower than for thin films because of a poorer surface concentration of pigments (Fig. 8). In these conditions, at \( \lambda = 2.5 \mu m \), a jump in transmittance of \( \Delta T = 20\% \) (or \( \Delta T/T = 27\% \)) was obtained for the granular layers while this jump was of \( \Delta T = 45\% \) for the thin film. As the efficient surface of these granular layers is of about 60–70\% of the total surface, these two types of results can be easily interpreted in terms of efficient surfaces. This result can also be correlated with the particularly strong value of the transmittance observed in the metallic state (higher than 50\%).

The arrow in Fig. 7 shows an abnormal feature in the evolution. This behavior is associated with the elaboration process: during the sputtering process, a variation of the temperature should have involved a variation in
stoichiometry, thus involving an additional transition. The study of these modifications is now in progress.

3.6. Reflectance measurements

Reflectance measurements, for a nanopowder pellet and the thin film are presented on Figs. 9 and Figs. 10: the curves have been obtained on heating and at ambient temperature in air. A strong modification is clearly observed for both VO₂ materials.

In the 2.5–5 μm wavelength range, a significant reflectance increase is associated with the MIPT of VO₂. For the thin film, substrate influence can be observed for the low temperature semiconductor phase (between 7 and 10 μm). The reflectance of a nude substrate, reported in Fig. 10, presents strong variations in this range. This phenomenon is due to the great transmittance of the low temperature variety. For temperatures higher than 68°C, VO₂ becomes metallic and, as expected in metallic materials, the reflectivity increases. The transmittance drastically decreases and the substrate influence becomes negligible, as can be observed.

Integrated reflectance values in the 8–12 μm range are reported in Table 1 for nanopowders and thin films. For nanopowders, at 20°C, the integrated reflectance is 20%. At 100°C, higher integrated reflectance values of 56% have been observed. So, the jump of reflectance represents 36% for the 8–12 μm wavelength range.

3.7. Emissivity measurements

For a fixed wavelength, the transmittance $T$, the absorbance and the reflectance $R$ are directly linked through the classical relation:

$$T + R + A = 1$$  \hspace{1cm} (4)
Fig. 6. Collimated transmittance overview of each materials: nanopowder and thin film.

Fig. 7. Transmittance hysteresis for VO₂ thin film.

Fig. 8. Transmittance hysteresis for VO₂ nanopowder deposited on a substrate glass.
When a system is isotherm, on thermal equilibrium, the absorbance is strictly equal to the emissivity $E$. So, it results:

$$A = E$$

This emissivity $E$ was indirectly measured from our HgCdTe-based device.

For opaque samples on thermal equilibrium, transmittance is equal to zero, and the previous relation (1) can be reduced to: $R = 1 - E$.

The $R$ values were obtained from the HDR SOC100 device.

So, from these two different techniques, it is possible to independently determine the $R$ and $E$ values.

Normal integrated emissivity measurements were carried out. Fig. 11 shows the emissivity evolutions of both powder sample and thin film.

Performing a thermal cycle (on heating and on cooling in air), the emissivity measurements for powders were obtained at different temperatures (between 40 and...

---

Table 1

Integrated reflectance values in the 8–12 μm range for nanopowder and thin film samples

<table>
<thead>
<tr>
<th></th>
<th>Nanopowder sample</th>
<th>Thin film sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
<td>100°C</td>
</tr>
<tr>
<td>Integrated reflectance (%)</td>
<td>20</td>
<td>56</td>
</tr>
</tbody>
</table>
The results of Fig. 11 show a hysteresis presenting a large width. This broad hysteresis might be influenced by the existence of a thermal gradient. However, it should be remarked that, in the case of the thin film, a significant contrast is clearly observed. For the nanopowder sample, the jump of emissivity (33%) is weaker than the jump observed for the thin film (47%). Such different values might indicate that the observed optical contrasts should strongly depend on the morphology, the efficient surfaces, the cavities, and of the distribution of sizes. In addition, the existence of surface modes should contribute to degrade the optical contrast.

Normal integrated emissivity values in the 8–12 μm range are reported in Table 2 for nanopowder and thin film samples.

The integrated experimental reflectivity $R$ of the thin film sample was found to be respectively of about $R_{25^\circ C} = 0.20 \pm 0.01$ and $R_{100^\circ C} = 0.72 \pm 0.04$ at 25 and 100°C (see section above). So, an emissivity value of about $E_{25^\circ C} = 1 - R = 0.80$ and $E_{100^\circ C} = 1 - R = 0.28$ should be expected. In fact, from our emissivity measurements, the experimental values are found to be $E_{25^\circ C} = 0.87 \pm 0.10$ and $E_{100^\circ C} = 0.40 \pm 0.05$ at respectively 25 and 100°C. Such small differences might be related to the fact that global emissivity measurements generally depend on both absorption of layer and emission of substrate through the layer.

In the case of the nanopowder sample, the integrated experimental reflectances are $R_{25^\circ C} = 0.20 \pm 0.01$ and $R_{100^\circ C} = 0.56 \pm 0.04$ at respectively 25 and 100°C; thus, the calculated emissivity should be of about $E_{25^\circ C} = 0.80$ and $E_{100^\circ C} = 0.44$. Experimentally, the emissivities $E$ are found to be of $E_{25^\circ C} = 0.78 \pm 0.08$ and $E_{100^\circ C} = 0.45 \pm 0.05$ at respectively 25 and 100°C, which is in good agreement with the reflectance experiments.

From these results, it should be concluded that the two independent techniques could deliver useful complementary measurements of emissivity and reflectance.

### 4. Conclusion

In this work, we have presented a comparative study of the switching properties of thin films and nanoparticles of vanadium dioxide. In Table 3, the main characteristics of these materials are summarized.

We have shown that a high thermochromic contrast could be obtained as well for nanocrystalline powders as for thin films, even if the nanopowders are less efficient than films. High transmittance contrasts in the mid-infrared (MIR) region have been obtained as well for thin films as for nanoparticles.

The major fact resides in the fact that, for the first time, emissivity measurements have been performed and directly correlated with reflectance and transmittance measurements. The contrasts in emissivity are sufficiently high to be promising for IR and thermal detection applications. In

---

**Table 2**

Normal integrated emissivity values in the 8–12 μm range for nanopowder and thin film samples

<table>
<thead>
<tr>
<th></th>
<th>Nanopowder sample</th>
<th>Thin film sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
<td>100°C</td>
</tr>
<tr>
<td>Expected emissivity (%)</td>
<td>80</td>
<td>44</td>
</tr>
<tr>
<td>Experimental emissivity (%)</td>
<td>78 ± 8</td>
<td>45 ± 5</td>
</tr>
</tbody>
</table>
addition, switching emissive materials could now be envisaged. Further studies on composite coatings are planed to investigate the emissivity of new coatings involving nanoparticles embedded in a polymer matrix.

Another prominent feature has been observed from the thin film: the emissivity contrast strongly depends on the nature of the substrate. This fact should lead to new interesting applications.

As an additional observation, we have noticed that modifications in coloration occurs for both nanosized particles and thin films, from bluish-black to brown color. A study of these samples in the visible wavelength range is now in progress.

Acknowledgements

We acknowledge M. Jean Aubry for helping us during emissivity measurements, and the ‘Centre Technique d’Arcueil (Délegation Générale pour l’Armement, DGA)’ for their financial support (under grant: UTV-DGA 12 212).

References