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Optimized infrared switching properties in thermochromic vanadium dioxide thin films: role of deposition process and microstructure

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Abstract

This work deals with high efficient optical switching properties at 68 °C of thermochromic vanadium dioxide (VO_2) thin films deposited on amorphous silica substrates. VO_2 thin films were deposited by radio frequency reactive sputtering process. Conditions of deposition were optimized making use of parameters such as film thickness, gas ratio and substrate temperature. Process was optimized adjusting the distance between target and substrate, and dimensions of target and substrates, to obtain a good uniformity and reproducibility of the layers. X-Ray diffraction patterns and scanning electron microscopy convincingly illustrated that VO_2 thin films could grow on amorphous silica substrates with a specific preferential crystal orientation: the $[001]_M$ crystallographic direction of oxygen octahedral chains is parallel to the substrate plane and corresponds with vanadium–vanadium links (insulating state) or with a maximum of electron delocalization (metal state). Optical switching properties in the mid-infrared range are discussed: transmittance, reflectance and emissivity values are strongly modified at the thermochromic transition temperature ($Tc = 68$ °C). A maximum of optical transmittance contrast is observed for a thickness of 120-nm, then interpreted in terms of absorption law. Using a specific software, the n and k optical indices are determined and used to simulate the variation of transmittance vs. film thickness.

Keywords: Vanadium oxide; Coatings; Optical properties; Infrared spectroscopy

1. Introduction

The general aim of this study was to better control the infrared switching properties of thermochromic thin films of VO_2 vanadium dioxides. The doped $V_{1-x}M_xO_2$ vanadium dioxides, in which M is an electron-doping element, are well known for their interesting insulator–metal transition associated with strong variations of infrared optical properties [1]. The doping by M^{n+} cations has two types of consequences: a modification of the transition temperature ($Tc = 68$ °C for pure VO_2) and a modification of the optical contrast. In addition, when thin films are deposited on specific substrates, the optical transmittance, reflectance and emissivity are generally conditioned by texture effects, film continuity, density, porosity, grain boundaries, defects and finally film thickness. Presently, we will focus our attention on two main parameters: the film thickness and the final microstructural orientation of deposited films.

To establish correlations between these parameters, thermochromic vanadium dioxide thin films were elaborated by radio frequency sputtering deposition on amorphous silica substrate. Pure vanadium dioxide VO_2 exhibits a reversible metal–insulator phase transition (MIPT) at 68 °C.

Using specific chemical substitutions for vanadium cation, this transition temperature can be lowered: for instance, in the case of $V_{1-x}W_xO_2$ [2], W^{6+} stable cations are formed through the local reaction $W^{4+} \rightarrow W^{6+} + 2e^-$; $2e^- + 2V^{4+} \rightarrow 2V^{3+}$ in which the W^{4+} cations should behave as electron donors for vanadium

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V^{4+}. This doping effect is at the origin of the electrical, magnetic and optical modifications. A lot of studies were previously published, essentially on the infrared transmittance potentialities. Several applications such as smart windows for thermal regulation could be envisaged. During the past years, numerous optical applications were envisaged such as smart windows for thermal regulation of buildings (transmittance contrast) [2–7], accordable IR mirror for LASER applications (reflectance contrast) [8–11], optical storage media [12], uncooled microbolometer [13,14]. Various authors tried to optimize the transmittance properties in thin films of VO_2 [15–19]. Recently, we have compared the optical properties of nanosized polycrystalline samples with those of thin films and we have obtained experimental correlations between transmittance, reflectance and emissivity [20,21].

Using chemical substitution or doping, the transition temperature can be modified. Many authors showed that the optical contrast ineluctably decreases as the fraction of doping elements (anionic and/or cationic substitutions) increases [22,23]. The first aim of this study is to determine the most prominent parameters allowing obtaining good switching films in the mid-infrared range. The second aim of this study will be to propose a modeling of switching properties.

2. Experimental section

Thin films were made by radio-frequency cathodic sputtering technique (PVD process). Starting from a pure vanadium target (HTC purity 99.99%) and an adjusted gas mixture Ar/O_2, VO_2 coatings were deposited on an amorphous silica substrate. In the mixture Ar/O_2 reactive environment, the percentage of oxygen O_2 ranged between 0.5 and 2%. The total chamber pressure ranged from 5 to 30 mTorr. The temperature of the substrates was carefully controlled: the deposition processes were performed between 380 and 470 °C. The deposition rate was very stable, linear and reproducible, with a mean value 2.1 ± 0.1 nm/min. So, the film thickness could be directly related to the sputtering time.

Spectroscopic experiments in the mid infrared wavelength range were carried out to determine the thermo-optic performances of the as-prepared VO_2 films. Transmittance spectra were measured using a Nicolet Magna 860, equipped with a thermo-regulated environmental cell. Hemispherical directional reflectometer (HDR SOC100 extension) was used to determine the infrared hemispherical directional reflectance. Hence, a blackbody heated at 600 °C was used. Diffuse and specular components can be determined simultaneously. To perform these studies, emissivity equipment developed in our laboratory was carried out for the normal integrated emissivity factors vs. temperature. A classical HgCdTe infrared sensor (maximum contribution in the 8–12-μm wavelength range) was employed. The emissivity values were directly determined by calculating the luminance ratio between the sample and a blackbody material at the same temperature. X-Ray diffraction experiments were performed using a Siemens–Brucker D5000 diffractometer, equipped with a copper source, Soller slides, a secondary monochromator and a rotating sample holder. Scanning electron microscopy (SEM) experiments were performed on a Philips XL30 microscope to determine coating morphologies and grain size distributions. To evaluate thickness of each film, profilometry measurements were carried out using a Tencor P1 profilometer equipment (film thickness is determined with approx. ±5 nm precision).

Table 1
Influence of the substrate temperature on the color of the sample

Sample references	Substrate temperature (°C)	Color
V1	380	Dark blue
V2	395	Blue
V3	410	Blue
V4	425	Bronze
V5	440	Bronze
V6	455	Bronze
V7	470	Bronze

3. Results and discussion

In this study, the influence of two independent parameters was considered: the substrate temperature during the deposition process and the thickness of the layer. From preliminary studies, we established that the deposition rate was 2.1 nm/min at the deposition temperature of 440 °C. The thickness was initially fixed to a mean value of approximately 120 nm corresponding to the predicted range of 30–220 nm.

3.1. Influence of the deposition temperature

The thickness of each film being fixed to 120 nm, the substrate temperature, as a unique parameter, was increased from 380 to 470 °C. Modifications of color aspect were observed. Table 1 shows the correlations between the experimental conditions used to prepare the various samples and the resulting colors. Such a color variation corresponds with two different varieties of vanadium dioxide: the $VO_2(B)$ phase that is not thermochromic, obtained for substrate temperatures lower than 420 °C and the thermochromic VO_2 phase, obtained for substrate temperatures higher than 420 °C. The same feature was observed for pigments elaborated from thermal treatment of ammonium hexavanadate [5].

3.1.1. Optical transmittance analyses

The optical variation $\Delta Tr = Tr(LT) - Tr(HT)$, is defined as being the difference between the low tem-

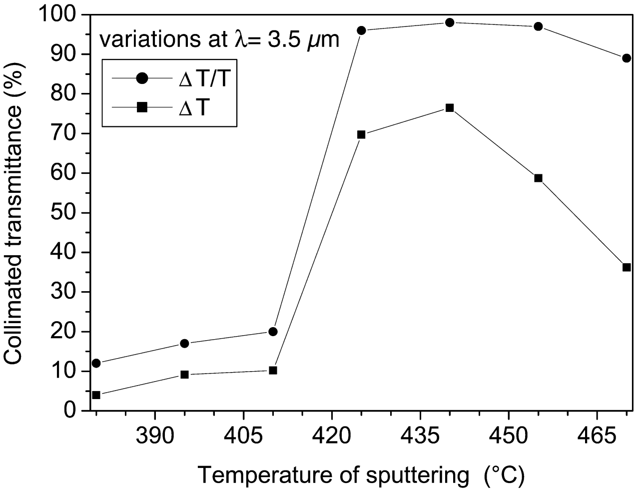

Fig. 1. Influence of the temperature of deposition on the collimated transmittance variations.

perature Transmittance, noted $Tr(LT)$ and the high temperature Transmittance, noted $Tr(HT)$. $Tr(HT)$ and $Tr(HT)$ experiments were carried out at, respectively, 25 °C and 90 °C, making room atmosphere as references for the measurements. $Tr(CT)$ and $Tr(HT)$ experiments clearly show that infrared contrast drastically increases in the case of films deposited at a temperature of 425 °C. ΔTr is maximum for a deposition temperature of Approximately 440 °C. Above this temperature, it slowly decreases (Fig. 1). The infrared spectrum of a thin film deposited at 440 °C, in the 2.5–5-μm wavelength range, is reported on Fig. 2. In the semiconductor state at $T < Tc$, a high transmittance is observed for wavelengths ranging between 2.5 and 3.75 μm. Above 3.75 μm, the transmittance strongly decreases: this absorption effect is directly related to the optical absorption of the substrate (the substrate transmittance is reported on the figure). In the metallic state ($T > Tc$), the transmittance strongly decreases in the full wavelength range and the film becomes opaque. A collimated transmittance hysteresis cycle was obtained, as reported on Fig. 3, for a fixed wavelength ($\lambda = 3.5$ μm) vs. temperature. The width of the hysteresis cycle is quite narrow (<10 °C at the full width at half maximum ($\Delta Tr/2$)). The transition jump occurs with a strong contrast, in a very tight temperature range: a switching property of $\Delta Tr =$ 76% is observed for a temperature variation of only 4 °C.

3.1.2. Reflectance analyses

Reflectance measurements were carried out on the same samples. The optical contrast is found to be maximum for the films elaborated at 440 °C. Fig. 4 presents the reflectance variations for a film occurring on phase transition occurs. In the semiconductor state for $T < Tc$ (transparent state), the influence of the substrate is clearly visible in the 8–10-μm wavelength range. The reflectance values are weak in this semiconductor state, however, they strongly increase in the metallic state for $T > Tc$ (the ΔR variation values are found to range from 70 to 75%). No substrate reflection is observed. For temperatures higher than $Tc = 68$ °C, electrons are delocalized and a screening effect appears for the incident photons. For the film deposited at 440 °C, the infrared contrast was Approximately $\Delta R = 65\%$ for several wavelength, and, as for transmittance, the contrast associated with the switching effect is higher (Fig. 5). The reflection data were obtained by adding diffuse and specular components of reflectance, making use of a specular gold reference having a very low diffusion contribution. Ours results are in good agreement with reflectance values obtained by Hanlon et al.

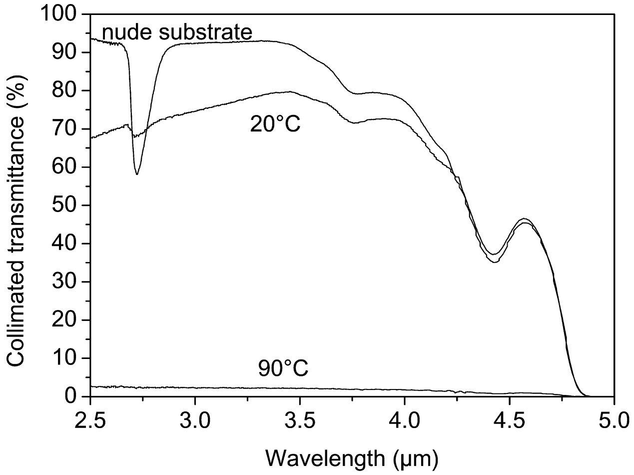

Fig. 2. Fourier transform Infrared collimated transmittance spectrum for VO_2 thin film deposited on amorphous silica at 440 °C in the 2.5–5-μm wavelength range.

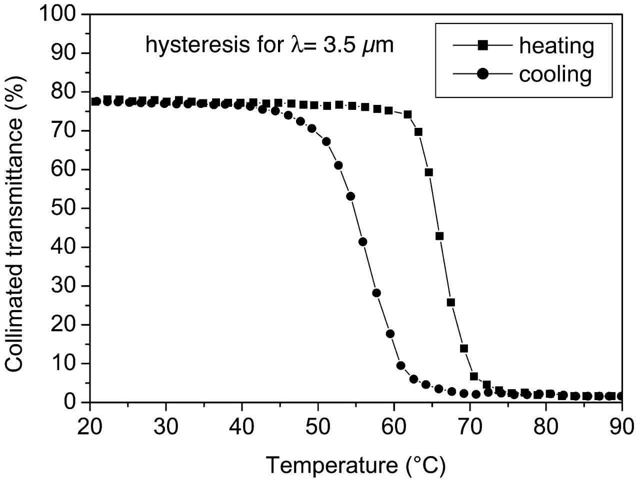

Fig. 3. Transmittance hysteresis at $\lambda = 3.5$ μm for a VO_2 thin film deposited on amorphous substrate at 440 °C.

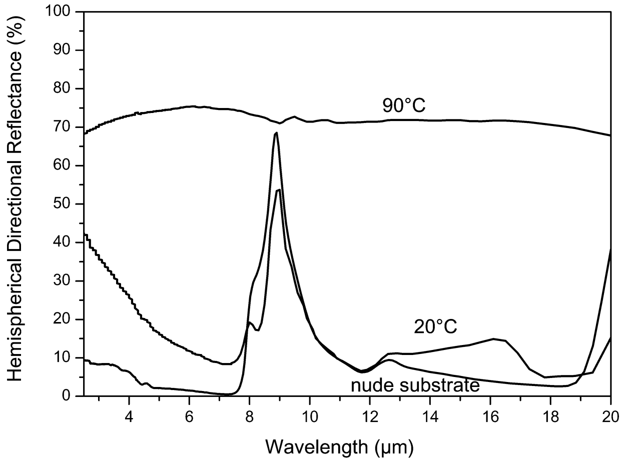

Fig. 4. Hemispherical directional reflectance of VO_2 thin film deposited on amorphous substrate at 440 °C.

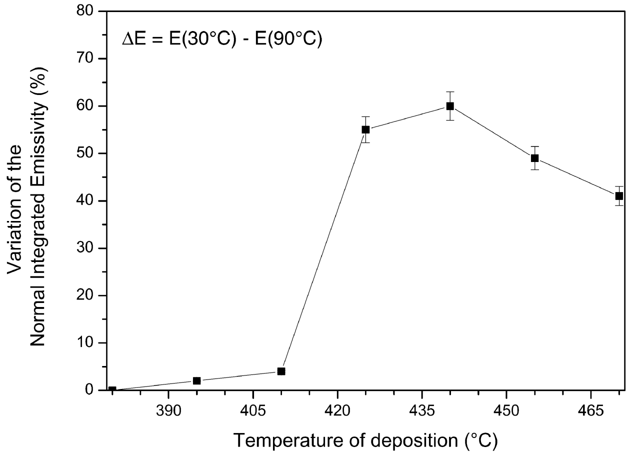

Fig. 6. Influence of the deposition temperature on the emissivity contrast of V5 thin film.

[24]. Our V5 film exhibits 60% change in reflectance in the infrared range, as these authors. Reflectance values depend on the substrate temperature involved in the process, as observed in Fig. 5. In their film, Dillon et al. [25] present a ~60% change in reflectance, with values noticeably higher than our own values. This can be easily interpreted by the fact that their experimental conditions strongly differ from ours: they used a crystallized silicon substrate heated at 550 °C.

3.1.3. Emissivity measurements

The results concerning the normal integrated emissivity measurements have been reported on Fig. 6. Emissivity values (E) were directly integrated in the 8–12 μm range corresponding to the HgCdTe infrared sensor. Emissivity decreases when temperature becomes higher than $Tc = 68$ °C. The contrast in emissivity determined from the difference of the measured values $|\Delta E| = E(30\ °C) - E(90\ °C)$ was maximum for the V5 film deposited at 440 °C. The $|\Delta E|$ variation was of approximately 60%. This result is in good agreement with the reflectance and transmittance results discussed in previous sections. Using the relations $E + R + Tr = 1$ (or from variation form $\Delta E + \Delta R + \Delta T = 0$), we can verify, from specific numerical values at fixed wavelengths (see Figs. 2–6), that the reflectance and emissivity measurements obtained from two types of independent techniques are fully correlated.

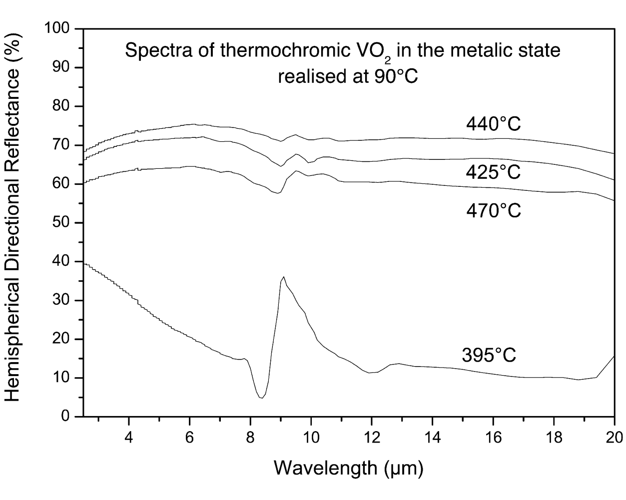

Fig. 5. Influence of the temperature of deposition on the hemispherical directional reflectance of VO_2 thin film (data were obtained at 90 °C).

3.2. Influence of the thickness

After optimization of the deposition temperature, the influence of the film thickness on the optical switching properties was then studied. The deposition temperature was fixed at the optimal temperature of 440 °C, as suggested in the previous section. Using various deposition times with a particularly stabilized depositing rate (approx. 2.1 nm deposited per min), variable film thicknesses measured from profilometry technique were obtained in the range 30 (±3)–220 (±18) nm. A linear correlation was observed between deposition time and thickness (Table 2).

Table 2
Influence of the sputtering duration on the film thickness

Sample reference	Sputtering duration (min)	Mean thickness (nm)
V8	15	31
V9	30	62
V10	45	92
V5	60	125
V11	75	155
V12	90	189
V13	105	217

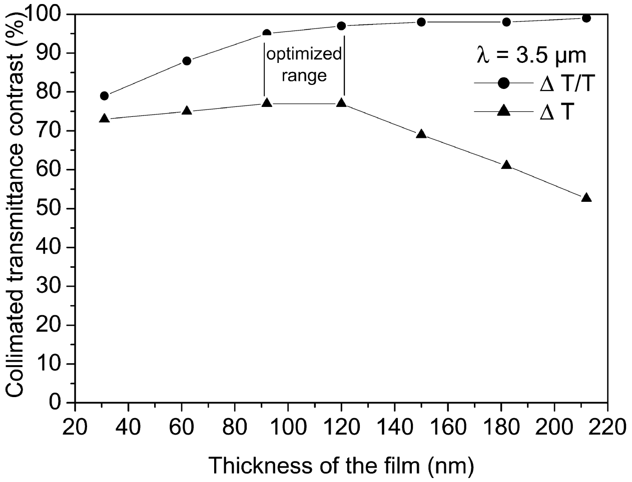

Fig. 7. Influence of the thickness on the contrast in collimated transmittance at $\lambda = 3.5$ µm.

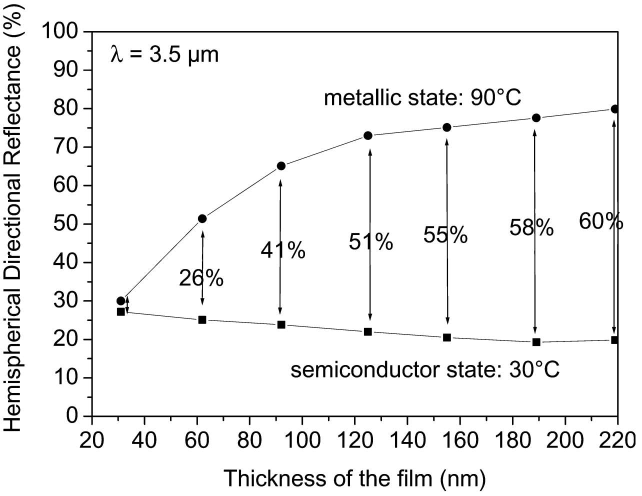

Fig. 8. Influence of the thickness on the contrast of hemispherical directional reflectance.

Infrared contrast values for collimated transmittance experiments are reported on Fig. 7. It can be noticed that, for thickness between 90 and 120 nm, a satisfactory compromise could be obtained for applications such as reversible switching smart windows. The 120-nm thick film presents a ΔTr variation of 75% and $\Delta Tr/Tr = 98\%$.

Alternatively, no optimal thickness was observed in the case of reflectance and emissivity measurements, which was expected. In fact, the amplitude of variations increases when film thickness increases, as it can be seen on Figs. 8 and 9. In the metallic state, thin films are opaque (Tr is approximately equals to zero), no back side effect or substrate effect can be observed, and then, reflectance (denoted R) and emissivity (denoted E) measurements can be correlated through the derived Kirchoff relation [26]:

$$R+E=1$$

This relation is derived from the classical relation of the conservation of energy from reflection (R), absorption (A) and transmission (Tr):

$$R+A+Tr=1$$

in which $A=E$ for samples studied at the thermal equilibrium and $Tr=0$ for opaque systems. This relation integrates the scattered component in the reflection and transmission terms. Our measurements permit us to include the scattered contribution. So, a good agreement between integrated hemispherical directional reflectance and normal integrated emissivity values is observed.

3.3. Microstructure

X-Ray diffraction patterns were recorded at room temperature (Fig. 10). The Bragg peaks (with Miller indices noted $(h,k,l)_M$ or $(h,k,l)_R$, respectively, for monoclinic or rutile representations) were analyzed and compared with the data corresponding to No 44-0252 JCPDS card [27] (thermochromic VO_2 phase). All films deposited on the amorphous silica substrate at a temperature higher than 410 °C are crystallized and present a preferential orientation, parallel to the $(011)_M$ plane of the monoclinic system (or $(110)_R$ in the tetragonal rutile system). Lying in this $(011)_M$ (or $(110)_R$) plane, the $[001]_R$ rutile axis of the structure can be found: this direction corresponds with the V–V linked pairs that are formed in the low temperature state and with the maximum electron delocalization in the high temperature metallic state [2]. Generally, such an electrical anisotropy might be associated with a corresponding aniso-

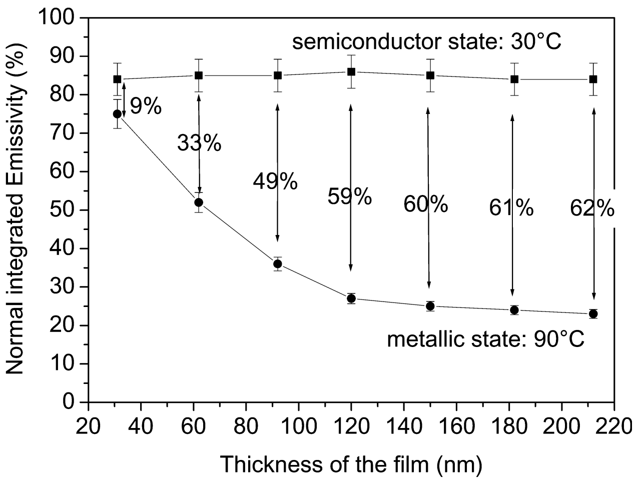

Fig. 9. Influence of the thickness on the contrast of normal integrated emissivity.

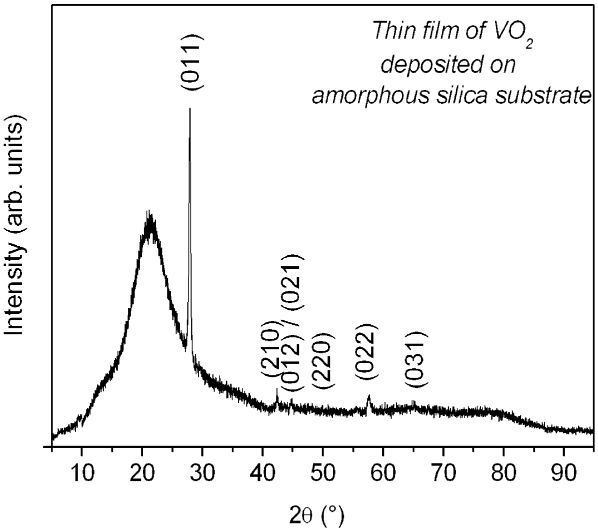

Fig. 10. X-Ray diffraction pattern of the of VO_2 oriented thin film. Indexation is given in the monoclinic system.

tropy in optical properties. This is a reason why we expect improved contrast behaviors in such VO_2 films.

On the secondary electron image (Fig. 11), the film appears as being continuous with a grain microstructure composed of primary particles having sizes of 50–100 nm. The surface is characterized by a relative roughness. Using AFM analysis, a roughness parameter $R_{ms}=12$ nm was obtained. This confirms the fact that the film is dense with no crack, nor fissure.

4. Modeling of the infrared properties

In this section, we propose a simple interpretation of the optimal thickness observed in our experiments, then we make use of a specific software well adapted to the calculation of optical indices of thin films deposited on a substrate.

The existence of optimal properties in layered systems can be easily justified through the elemental expression describing the transmittance in bi-layered systems [28]:

$$Tr=(1-R)^2\ (1-R_0)^2\ \exp-[\alpha(\lambda,T)\cdot x+\alpha_0(\lambda,T)\cdot x_0]/\\ [1-R^2\cdot\exp(-2\alpha\cdot x)][1-R_0^2\cdot\exp(-2\alpha_0\cdot x_0)]$$

In this expression R and R_0, $\alpha(\lambda,T)$ and $\alpha_0(\lambda,T)$ are the reflectance and linear absorption coefficients of the VO_2 film and substrate. The thicknesses are, respectively, x and x_0. When the optical transition occurs, the R and $\alpha(\lambda,T)$ coefficients of VO_2 strongly vary, while the substrate coefficients are assumed quasi constant. Taking into account the fact that the denominator $[1-R^2\ \exp(-2\alpha\cdot x)]$ is close to unity and slowly varies, we can simplify the expression as follows:

$$Tr=K\cdot(1-R)^2\ \exp-[\alpha(\lambda,T)\cdot x+\alpha_0(\lambda,T)\cdot x_0]$$

with $K=(1-R_0)^2/[1-R_0^2\ \exp(-2\alpha_0\cdot x_0)]$ (let us recall that this K term results from an approximation).

In this simplified expression, the term $K\cdot(1-R)^2$ represents the global reflectance of the bi-layered system. These reflectance and absorbance characteristics $K\cdot(1-R)^2$ and $\alpha(\lambda,T)$ strongly vary with temperature close to the transition; they depend on substrate thickness x_0, but generally they do not depend on VO_2 film thickness x.

The variation of transmittance $\Delta Tr=Tr(LT)-Tr(HT)$ in which LT and HT designate the low temperature and high temperature states, can be expressed as follows:

$$\begin{aligned}\Delta Tr&=K\cdot\{(1-R_{LT})^2\cdot\exp[-\alpha_{LT}(\lambda,T)\cdot x-\alpha_0(\lambda,T)\cdot x_0]\\&\quad-(1-R_{HT})^2\cdot\exp[-\alpha_{HT}(\lambda,T)\cdot x-\alpha_0(\lambda,T)\cdot x_0]\}\\&=\Delta Tr\\&=\Phi_{LT}\cdot\exp[-\alpha_{LT}(\lambda,T)\cdot x]\\&\quad-\Phi_{HT}.\exp[-\alpha_{HT}(\lambda,T)\cdot x]\end{aligned}$$

with

$$\Phi=K\cdot(1-R)^2\ \exp[-\alpha_0(\lambda,T)\ x_0]$$

Calculating the zero of the derivative $\partial\Delta Tr/\partial x$, assuming that the reflectances R do not vary with material thickness x in a significant way, a maximum of contrast in transmittance is obtained with the resulting relation:

$$x_{opt}=[1/(\alpha_{HT}-\alpha_{LT})]\cdot\mathrm{Ln}\ \ (\alpha_{HT}\Phi_{HT}/\alpha_{LT}\Phi_{LT})$$

If all α and Φ values were known, then this relation could deliver the optimized thickness x_{opt}. In fact, these α and Φ values cannot be strictly determined because they depend on surface quality (cavities, irregularities, grain boundaries ...).

This relation shows that, depending on the strongly different absorption coefficients of the semi conducting and metallic VO_2 phases, the thermochromic contrast of

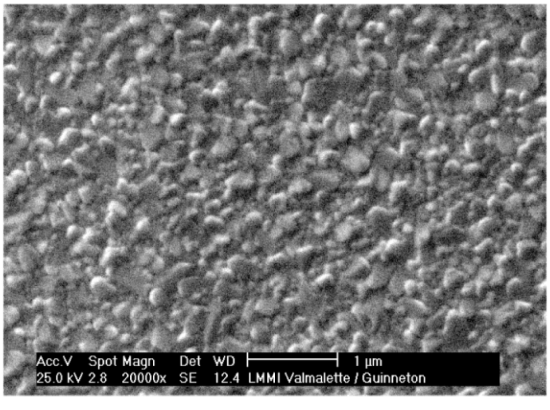

Fig. 11. SEM micrograph of the V5 thin film.

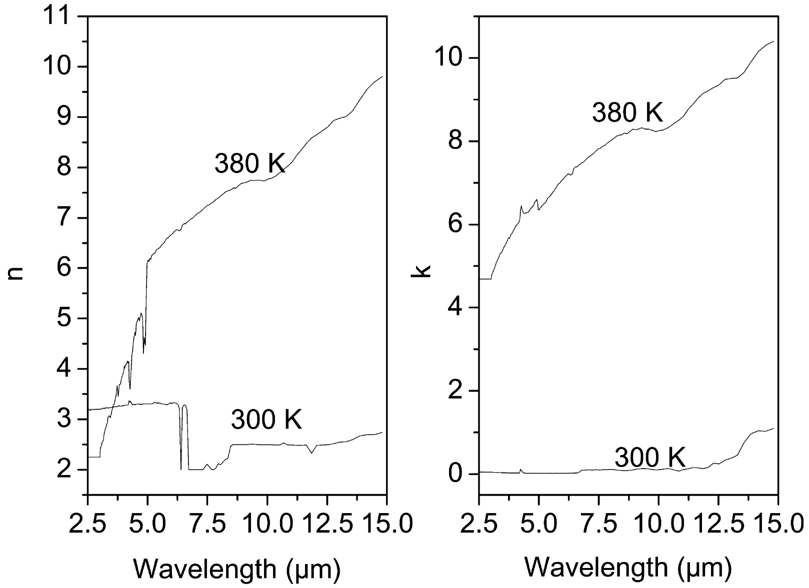

Fig. 12. Optical indices of the V5 thermochromic VO_2 for $T<Tc$ and $T>Tc$, determined from thickness measurement, transmittance and reflectance experiments.

thin films can be optimized by controlling deposition time or film thickness. If all optical factors (absorption, reflectance) could be well determined for the as prepared films, then the film thickness could be optimized and predictions of deposition times could be proposed, which should be of high industrial interest.

4.1. Simulation of optical indices

For each wavelength, from thickness, transmittance and reflectance measurements, optical indices (n,k) could be determined. As the V5 film presents the best emissivity contrast, we have selected this film to perform the modeling calculation of optical indices.

Film Wizard software was used to determine the (n,k) indices. In this software, Fresnel relations allow fitting the (n,k) indices directly associated with the VO_2 layers as deposited on amorphous silica substrates. Global optimization of calculations allows avoiding local minima and delivers the best solution. In addition, a constrained optimization option is provided, in such a way that any user can input maximum and minimum bounds for any variable that has to be optimized.

4.2. Principle of the calculations

Optical n and k indices are fitted to experimental data (reflectances and transmittances) making use of classical optical model. The approximations give rise to the simplified relations:

- Linear absorption coefficient: $\alpha=(4\pi/\lambda)\cdot k$
- Reflectance (semitransparent approximation): $R=[(n-1)^2+k^2]/[(n+1)^2+k^2]$

The code implements double precision calculations for greater accuracy and control of round off errors in large designs.

To perform such a calculation, it was necessary first to determine the optical indices of the SiO_2 substrate and then to compare these indices with data from the literature [29].

Finally, the n and k values of the VO_2 film are determined from the global film-substrate data, taking into account the previously calculated substrate indices. The results are reported on Fig. 12.

Ours (n,k) indices are in good agreement with the indices obtained for VO_2 films deposited on sapphire and silicon substrates [19,30], in the 2.5–15 μm range. Our calculated curves present similar evolutions: however, in the metallic state, our resulting n and k values sensibly differ from the values obtained by these authors. This might be attributed to the lower transmittance in this state, which should involve difficulties for optical simulations. In the semiconductor state, (n,k) indices are practically constant, however, they increase with the wavelength, in the metallic state.

Using the optical indices of this 'V5' VO_2 film, we have achieved the simulation of transmittance and reflectance functions as a function of thickness, for a fixed wavelength of $\lambda=3.5$ μm. The results are shown on Fig. 13. A good agreement between calculated and observed curves is obtained for the different films.

4.3. Prediction of optimized thickness

Making use of the n and k simulated values, we have calculated specific α and R values for the HT and LT

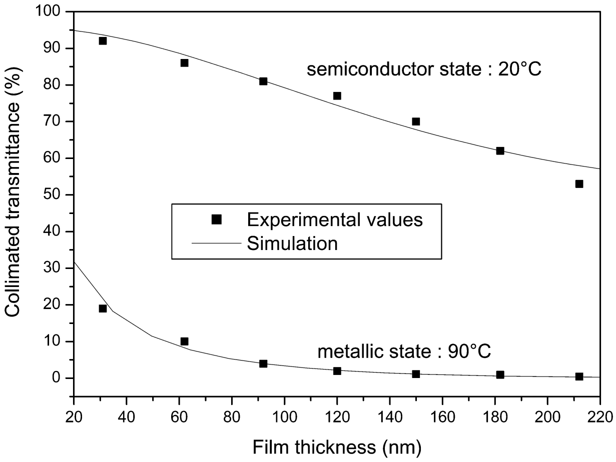

Fig. 13. Measured and calculated transmittance from (n,k) indices at $\lambda = 3.5$ μm.

VO_2 phases (using: $\alpha = (4\pi/\lambda)\cdot k$ and $R = [(n-1)^2 + k^2]/[(n+1)^2 + k^2]$). For a wavelength of 2.5 μm, we have obtained:

$$R_{HT} = 0.71,\ R_{LT} = 0.25;\ \alpha_{HT} = 23.5\ \mu m^{-1} \text{ and } \alpha_{LT} = 0.25\ \mu m^{-1}.$$

It results (in nm):

$$x_{opt} = [1/(\alpha_{HT} - \alpha_{LT})].\mathrm{Ln}\ (\alpha_{HT}\Phi_{HT}/\alpha_{LT}\Phi_{LT}) = 113 \text{ nm}$$

Taking into account all our approximations, such a value is in quite good agreement with the present observations (120 nm).

5. Conclusion

Thin films of thermochromic vanadium dioxide were successfully deposited on amorphous silica substrate. The films present a preferential crystal orientation with a maximum of electron delocalization (V–V links) in a direction parallel to the substrate plane. As the domain of existence of thermochromic VO_2 in the V–O phase diagram is very slight, a fine optimization of the sputtering process was necessary. Excellent contrasts in infrared transmittance, reflectance and emissivity were obtained. An overview of the optical performances is reported on Table 3.

Table 3
Optical contrasts of a 120-nm thickness VO_2 thin film deposited at 440 °C on an amorphous silica substrate

Sample V5	30 °C	90 °C	Variation
Collimated transmittance ($\lambda = 3.5$ μm)	77%	2%	75%
Hemispherical directional reflectance (*)	22%	73%	51%
Normal integrated emissivity (*)	86%	27%	59%

(*) integrated in the 8–12-μm wavelength.

The optimization of transmittance as a function of thickness was first interpreted from the classical Beer–Lambert absorption law. Then a computer simulation of optical properties delivered the optical (n,k) indices was given.

It can be emphasized that these high optical contrasts directly result from high film densities, low particle sizes (lower than incident light wavelength).

Applications such as smart windows based on transmittance properties, IR thermal detection or switched modulations of the emissivity of space structure could be now envisaged.

Acknowledgments

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