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Optical properties of the Vanadium dioxide

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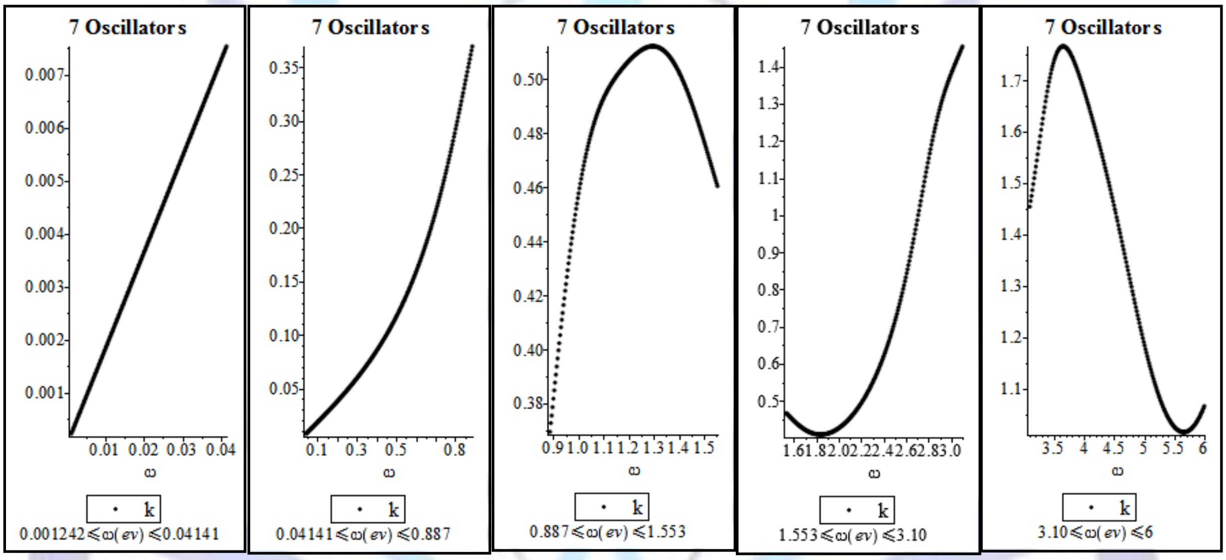
ABSTRACT

The vanadium dioxide is a material thermo chromium which sees its optical properties changing at the time of the transition from the phase of semiconductor state ↔ metal, at a critical temperature of 68°C. The study of the optical properties of a thin layer of VO_2 thickness 82 nm, such as the dielectric function, the index of refraction, the coefficient of extinction, the absorption's coefficient, the reflectivity, the transmittivity, in the photonic spectrum of energy ω located in the interval: 0.001242 ≤ ω (ev) ≤ 6, enables us to control well its practical utility in various applications, like the intelligent panes, the photovoltaic, paintings for increasing energy efficiency in buildings, detectors of infra-red (I.R) or ultra-violet (U.V). We will make simulations with Maple and compare our results with those of the literature.



Curves simulated of the coefficient of extinction K of a thin layer of VO_2 according to the model of the harmonic oscillator deadened in the photonic spectrum in the infra-red, the visible, and in the ultra-violet.

Indexing terms/Keywords

Dioxide of vanadium, Material thermochrome, the dielectric function, the Coefficient of extinction, Index of refraction, the absorption's Coefficient, Transmittivity, Reflectivity, Thin layer, Semiconductor, Metal, Intelligent panes, Energy efficiency, photonic Spectrum, ellipsometric Spectroscopy (SE), Energy of gap E_g.

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SUBJECT CLASSIFICATION

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TYPE (METHOD/APPROACH)

Model of Drude- Lorentz , based simulation and modeling

INTRODUCTION

The vanadium dioxide VO_2 is a relevant material thermo-chrome because of its enormous technological applications into photonic with a gap of 0.7 ev [1,2], detecting ultra-violet [3,4]; optical memory based on its hysteresis loop during this phase transition [5]; intelligent panes [6]. A dramatic change of the optical properties of its thin layers is detected. Several theoretical studies were made to explain the response of the dielectric function for these two phases: semiconductor and metal. Abbate and Mossanek [7] drew the dielectric response from VO_2. Verleur et al. [8] made studies of the dielectric functions of the massive VO_2 by using the reflectivity and transmittivity methods. Actually, Kakiuchida et al. [9] used metric ellipso measurements by (SE) determining constant optics of the thin layers of VO_2.

Methods

By using the model of Drude- Lorentz based on the summation of Lorentz and the oscillators of Drude, we can calculate this constant optics.

$$\varepsilon(\omega) = (n(\omega) + ik(\omega))^2 \qquad (1)$$

$$\varepsilon(\omega) = \varepsilon_1(\omega) - i\varepsilon_2(\omega) \qquad (2)$$

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)\cdot\omega_t^{\,2}}{\omega_t^{\,2} - \omega^2 + i\Gamma_0\cdot\omega} + \sum_{j=1}^{N}\frac{f_j\cdot\omega_{0j}^{\,2}}{\omega_{0j}^{\,2} - \omega^2 + i\gamma_j\cdot\omega} + \frac{\omega_p^{\,2}}{-\omega^2 + i\Gamma_d\cdot\omega} \qquad (3)$$

$$\varepsilon(\omega) = \varepsilon_{SC} = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)\cdot\omega_t^{\,2}}{\omega_t^{\,2} - \omega^2 + i\Gamma_0\cdot\omega} + \sum_{j=1}^{N}\frac{f_j\cdot\omega_{0j}^{\,2}}{\omega_{0j}^{\,2} - \omega^2 + i\gamma_j\cdot\omega} \qquad (4)$$

$$\varepsilon(\omega) = \varepsilon_M = \varepsilon_\infty + \frac{\omega_p^{\,2}}{-\omega^2 + i\Gamma_d\cdot\omega} \qquad (5)$$

ε_{SC} : The permittivity complexes semiconductor state VO_2.

ε_M : The permittivity complexes state VO_2 metal.

ε : The permittivity complexes material.

ε_1 : The real part of the permittivity.

ε_2 : The imaginary part of the permittivity.

T : Transmittivity of a thin layer of VO_2.

R : Reflectivity of a thin layer of VO_2 for the normal incidence.

α : The absorption coefficient of a thin layer of VO_2

n : The index of refraction of material.

k : The coefficient of extinction of material.

ε_∞ : The high frequency permittivity of electronic transition.

ε_s : The static permittivity at null frequency.

ω_t and ω_{0j} (ev) : Frequencies of resonance for the oscillator of energy corresponding to the peak of absorption in electron-volt.

f_j : The oscillator strength j of Lorentz.

γ_j : The widening of each oscillator j knowing damping.

Γ_d : The frequency of collision.

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ω_p : The frequency plasma.

For the semiconductor state of VO_2 we are interested in the contribution of the term: N=7

$$\varepsilon_{SC} = \sum_{j=1}^{N=7} \frac{f_j \cdot \omega_{0j}^2}{\omega_{0j}^2 - \omega^2 + i\gamma_j \cdot \omega} \quad ; \quad \varepsilon_{SC} = \sum_{j=1}^{N=7} a_j - i \cdot \sum_{j=1}^{N=7} b_j = \varepsilon_1(\omega) - i\varepsilon_2(\omega)$$

By using this modeling, we can make a simulation of the optical properties of VO_2 according to the energy of the incidental photon by taking into consideration the parameters of VO_2 film according to the table **[10]** and by taking into account 7 oscillators compared with 4 oscillators in this contribution.

Table. Drude-Lorenz parameter values of VO_2 thin films determined from the simulation of ellipsometric spectra.

	T=30°C							T=85°C			
f_j	0,67	- 0,46	1,11	2,38	1,6	3,4	0,54	0,87	1,76	2,35	-8
ω_{0j}	1,02	1,92	1,39	3,45	4,28	7,57	2,98	2,87	3,46	5,26	0,57
γ_j	0,54	3,02	0,88	1,34	2,24	2,02	0,65	0,77	1,34	2,81	3,7
ω_p								4,47			
Γ_j								0,82			

For the semiconductor state of VO_2 at a temperature of 30 °C:

$$a_1 = 0.697\left(\frac{1.0404 - \omega^2}{(1.0404 - \omega^2)^2 + (0.54 \cdot \omega)^2}\right) \quad ; \quad b_1 = \frac{0.697 \cdot 0.54 \cdot \omega}{(1.0404 - \omega^2)^2 + (0.54 \cdot \omega)^2}$$

$$a_2 = -1.69\left(\frac{3.6864 - \omega^2}{(3.6864 - \omega^2)^2 + (3.02 \cdot \omega)^2}\right) \quad ; \quad b_2 = \frac{-1.69 \cdot 3.02 \cdot \omega}{(3.6864 - \omega^2)^2 + (3.02 \cdot \omega)^2}$$

$$a_3 = 2.144\left(\frac{1.9321 - \omega^2}{(1.9321 - \omega^2)^2 + (0.88 \cdot \omega)^2}\right) \quad ; \quad b_3 = \frac{2.144 \cdot 0.88 \cdot \omega}{(1.9321 - \omega^2)^2 + (0.88 \cdot \omega)^2}$$

$$a_4 = 28.3279\left(\frac{11.9025 - \omega^2}{(11.9025 - \omega^2)^2 + (1.34 \cdot \omega)^2}\right) ; \quad b_4 = \frac{28.3279 \cdot 1.34 \cdot \omega}{(11.9025 - \omega^2)^2 + (1.34 \cdot \omega)^2}$$

$$a_5 = 29.30\left(\frac{18.3184 - \omega^2}{(18.3184 - \omega^2)^2 + (2.24 \cdot \omega)^2}\right) \quad ; \quad b_5 = \frac{29.30 \cdot 0.54 \cdot \omega}{(18.3184 - \omega^2)^2 + (2.24 \cdot \omega)^2}$$

$$a_6 = 194.83\left(\frac{57.3049 - \omega^2}{(57.3049 - \omega^2)^2 + (2.02 \cdot \omega)^2}\right) \quad ; \quad b_6 = \frac{194.83 \cdot 2.02 \cdot \omega}{(57.3049 - \omega^2)^2 + (2.02 \cdot \omega)^2}$$

$$a_7 = 4.95\left(\frac{8.2369 - \omega^2}{(8.2369 - \omega^2)^2 + (0.65 \cdot \omega)^2}\right) \quad ; \quad b_7 = \frac{4.95 \cdot 0.65 \cdot \omega}{(8.2369 - \omega^2)^2 + (0.65 \cdot \omega)^2}$$

$$\varepsilon_1(\omega) = \sum_{j=1}^{N=7} a_j \quad ; \quad \varepsilon_2(\omega) = \sum_{j=1}^{N=7} b_j$$

$$n = \frac{1}{\sqrt{2}}\left(\varepsilon_1 + ({\varepsilon_1}^2 + {\varepsilon_2}^2)^{\frac{1}{2}}\right)^{\frac{1}{2}} \qquad ; \qquad k = \frac{1}{\sqrt{2}}\left(-\varepsilon_1 + ({\varepsilon_1}^2 + {\varepsilon_2}^2)^{\frac{1}{2}}\right)^{\frac{1}{2}}$$

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \qquad ; \qquad \alpha = \frac{4\pi \cdot k \cdot \omega \cdot 10^5}{12.424125} \qquad ; \qquad T = \frac{(1-R)^2 \cdot e^{-\alpha \cdot z}}{1 - R^2 \cdot e^{-2\alpha \cdot z}} \;\; ; \;\; z = 82 \cdot 10^{-7} cm$$

We will simulate by Maple this constant optics in the energetic intervals of the incidental photon in:

The remote I.R	:	$0.001242 \le \omega(ev) \le 0.04141$
Average I.R	:	$0.04141 \le \omega(ev) \le 0.887$
The close I.R	:	$0.887 \le \omega(ev) \le 1.553$
The visible spectrum	:	$1.553 \le \omega(ev) \le 3.10$
The ultra-violet	:	$3.10 \le \omega(ev) \le 6$

Results

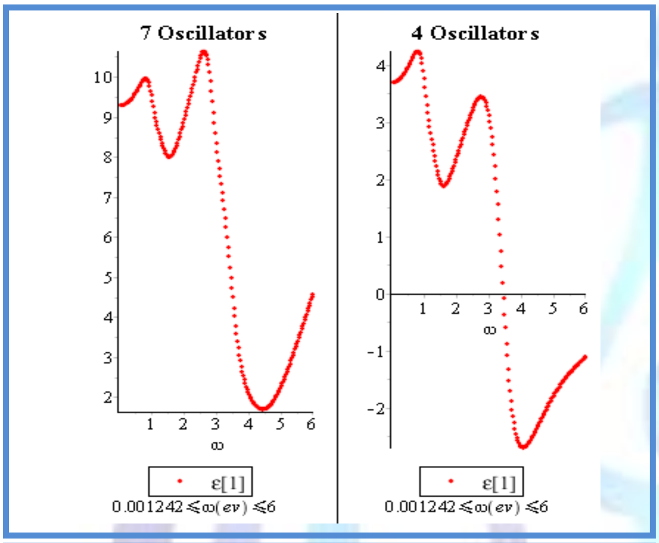

Figure 1. Variation of the real permittivity part ε_1 according to energy of the incidental photon.

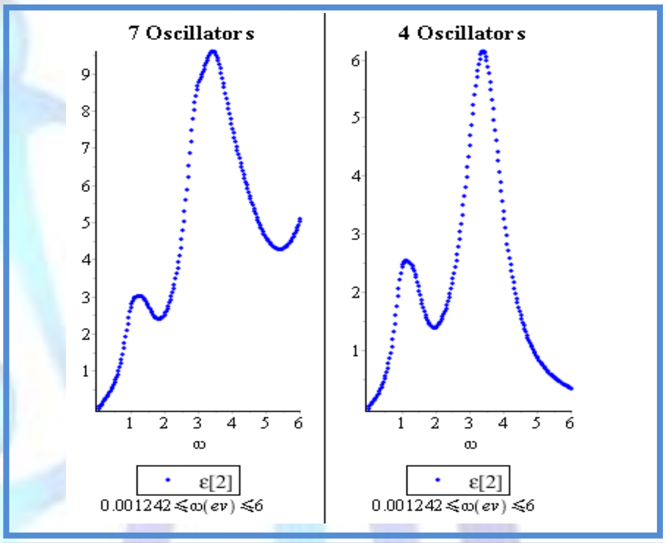

Figure 2. Variation of the imaginary permittivity part ε_2 according to the energy of the incidental photon.

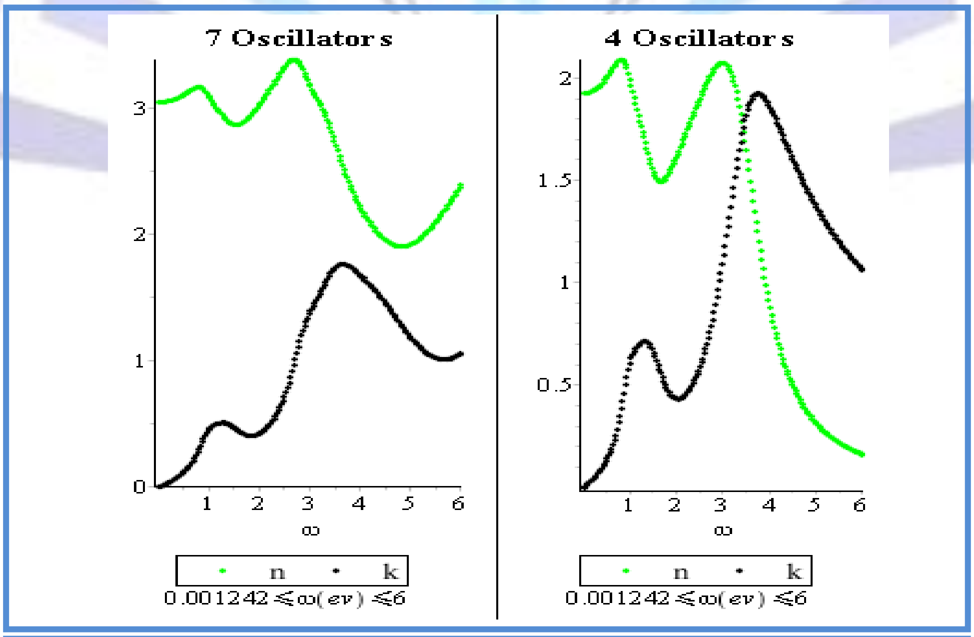

Figure 3. Variation of the index of refraction n and the coefficient of extinction k according to the energy of the incidental photon.

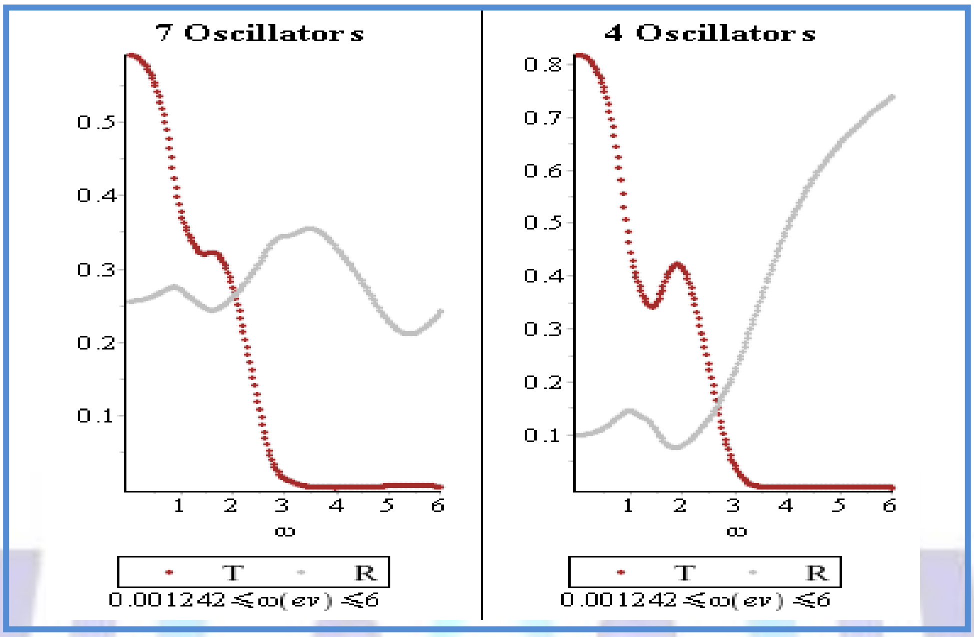

Figure 4. Variation of the transmittivity T and the reflectivity R according to the energy of the incidental photon.

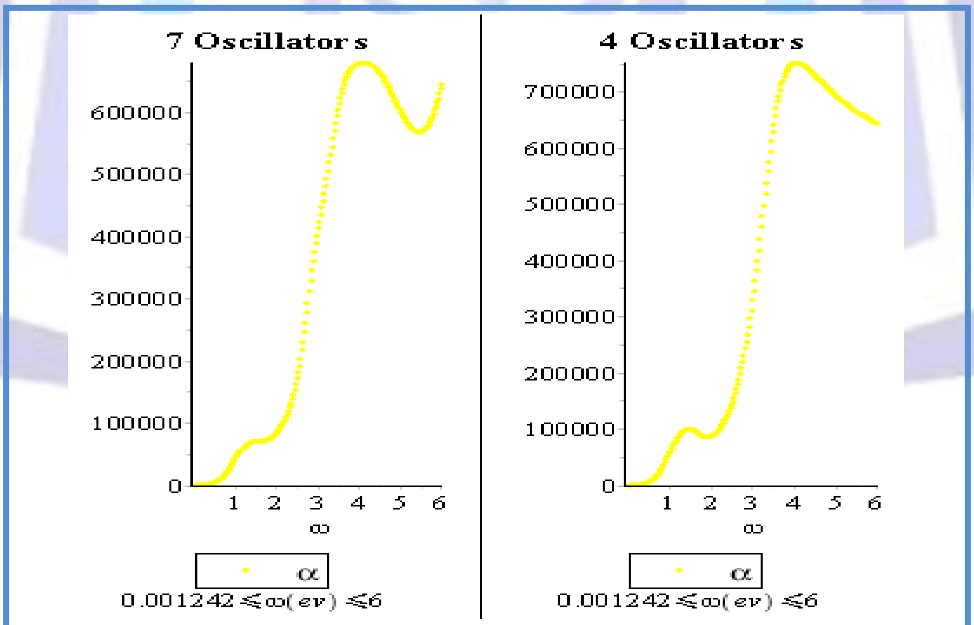

Figure 5. Variation of the absorption's coefficient α according to the energy of the incidental photon.

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Discussion :

In the case of 4 oscillators:

The maxima and minima do not clearly appear in the U.V for T and R . There is only a clear appearance of a maximum and a mini-mum for the transmittivity T. The second maximum and minimum do not appear in this simulation for the index of refraction n and the coefficient of extinction k.The second minimum does not appear in the case of the absorption's coefficient α.

In the case of 7 oscillators:

In the remote I.R, when the energy of the photon increases, T decreases; it continues to decrease in the average I.R and in the close I.R. It reaches a T≅0.30 minimum for ω≅1.4 ev. If ω>1.4 ev, T increases and reaches a T≅0.32 maximum for ω≅1.6 ev in the visible spectrum, then it decreases brutally in the U.V, and becomes minimal and very weak approximately to 0.001 for ω≅4 ev, then reaches its second maximum T≅0.006 for ω≅5.5 ev, it decreases up to 0.003 for ω≅6 ev. In the remote I.R, the reflectivity R grows if ω increases and reaches 0. 25624; in the same way with the average I.R, it reaches a maximum R≅0.275 for ω≅0.8 ev; then it decreases in the close I.R with the increase in the energy of the incidental photon, it grows by reaching a minimum in the visible one, it increases with a maximum of approximately 0.36 for ω≅3.5 ev in the U.V, then it decreases towards a minimum of 0.05 for ω≅5.5 ev and increases towards R≅0.24 for ω≅6 ev. We note a weak absorption in the remote I.R because the energy of the photon ω is very weak in comparison with the energy of the gap E_g of VO_2. If $\omega \cong E_g$, the absorption's coefficient α reaches $1.5 \times 10^4 cm^{-1}$; it grows in the average I.R and reaches an approximate maximum $7.4 \times 10^4 cm^{-1}$ in the close I.R for ω≅1.512 ev; then it increases in the visible spectrum until $4.4 \times 10^4 cm^{-1}$.

In the U.V, the absorption's coefficient reaches a maximum of $6.71 \times 10^5 cm^{-1}$ for ω≅4.1 ev and decreases until the minimum of $5.574 \times 10^5 cm^{-1}$ for ω≅5.4 ev and increases towards $6.425 \times 10^5 cm^{-1}$ for ω≅6 ev. Thus, we note a strong absorption in the U.V. As for the index of refraction, there are two maxima: $n_1 \cong 3.172$ for ω≅0.792 ev and $n_2 \cong 3.384$ for $\omega \cong 2.699$ ev, around which VO_2 material absorbs. During the increase in n with ω, the material transmits the light. When n decreases until the minimum, this material reflects the light; its minimum is approximate to 1.926 for ω≅4.745 ev in the U.V, whereas, it is not visible in the case of 4 oscillators. The first minimum is approximate to 2.876 for ω≅1.629 ev.

By comparing the evolution of the index of refraction n and the coefficient of extinction k of this thin layer, we well note the character thermochrome of vanadium dioxide. The peak, appeared with 3.5ev, is allotted to electronic transition from the band O_{2p} towards the band $V_{\pi*}$. This result is in conformity with the results of Verleur et al, while Drude envisages this peak with 3.15ev. As for the energy of the incidental photon ω>2.5 ev, we have electronic transitions from the band $2d_\pi$ towards the band $3d_\pi$. In the vicinity of the absorption's threshold $\omega \cong E_g = 0.7$ ev there are electronic transitions from the energy band $3d_{/\!/}$ towards $3d_\pi$; for the semiconductor state of VO_2, it is the fundamental absorption.

Comparisons between the results and the model of Cauchy:

For low energies, the variation of the index of refraction n and the coefficient of extinction k and the absorption's coefficient α, according to the energy of the incidental photon ω, is in conformity with the model of Cauchy :

$$n = A + \frac{B}{\lambda^2} + \frac{D}{\lambda^4} = A + B_1\omega^2 + D_1\omega^4$$

A, B, D, B_1, D_1 are the constants, λ is the wavelength of the incidental photon, and ω is the incidental photon energy. In this interval of energy, the material transmits and absorbs the light. The advantage of Lorentz's model: the finite summation of oscillators for the dielectric function, on the one hand, covers an important part of the spectral band of the vanadium dioxide; on the other hand, it enables us to analyze this material with weak energies that makes it possible to observe peaks rising from the transitions related to excitons. The disadvantage of this classic model: it is necessary to take into account a great number of oscillators where there are some oscillators which are strongly deadened by external excitations, like the quantity of heat, the pressure, the electric field, so that there is a convergence of this summation towards values of constant optics that well characterize this material.

Comparisons with results of the literature:

Let us compare our simulated results with those of the reference [11]; according to "Spectral normal transmittance T and near normal reflectance R for 90 nm thick VO_2 film At 22°C"

λ(nm)	500	1000	1500	2000	2500
ω(ev)	2.48	1.242	0.828	0.621	0.497
$T_{exp}[11]$	**0.30**	**0.40**	**0.45**	**0.55**	**0.65**
T (simulated)	**0.15**	**0.34**	**0.45**	**0.52**	**0.56**

T_{exp} [11] **:** Experimental transmittivity of the thin layer considered according to the reference [11].

T (simulated): the transmittivity which we simulated for the thin layer of VO_2 thickness 82 nm at a temperature of 30 ° C.

λ(nm)	500	1000	1500	2000	2500
ω(ev)	2.48	1.242	0.828	0.621	0.497
$\mathbf{R_{exp}[11]}$	**0.20**	**0.40**	**0.35**	**0.30**	**0.25**
R (simulated)	**0.30**	**0.27**	**0.28**	**0.27**	**0.26**

$R_{exp}\,[11]$ **:** Experimental reflectivity of the thin layer considered according to the reference [11].

R (simulated)**:** the reflectivity which we simulated for the thin layer of VO_2 thickness 82 nm at a temperature of 30 ° C.

We notice that $R_{exp}\,[11] \cong R\,(\text{simulated})$ for the interval of the energy ω (ev) of the incidental photon 0.497 ≤ ω(ev) ≤ 2.48. This light difference is due to the thickness z which is of 82 nm during simulation and 90 nm for the experiment [11], and also due to the temperature parameter which is of 22°C according to [11], whereas for our simulation, it is of 30°C. The two parameters influence the reflectivity R and the transmittivity T. We see clearly $T_{exp}\,[11] \cong T\,(\text{simulated})$; this small variation is due to the light difference of the thickness z and to the temperature which remains ambient. Let us compare our simulated results of the refraction index n and the coefficient of extinction k with those of the reference [12] in the energy interval 1.6 ≤ ω (ev) ≤ 2.5

Table.[12]

ω(ev)	**VO_2 semiconductor**	
	n	**k**
1.6	2.81	0.94
1.7	2.76	0.78
1.8	2.74	0.69
1.9	2.77	0.60
2.0	2.81	0.53
2.1	2.86	0.45
2.2	2.97	0.44
2.3	2.98	0.44
2.4	3.05	0.44
2.5	3.11	0.50

Our simulation Results by means of the Maple software are recorded in the following table:

ω(ev)	**VO_2 semiconductor**	
	n	**k**
1.6	2.87	0.44
1.7	2.89	0.42
1.8	2.93	0.41
1.9	2.97	0.41
2.0	3.03	0.43
2.1	3.09	0.46
2.2	3.14	0.51
2.3	3.19	0.56
2.4	3.27	0.63
2.5	3.32	0.71

We see that if ω (ev) increases in our simulation, we have a reduction in the coefficient of extinction k of 0.44 up to 0.41 in the interval 1.6 ≤ ω (ev) ≤ 1.9; then it increases by 0.43 up to 0.71 in interval 2 ≤ ω (ev) ≤ 2.5, whereas for the reference [12], we have only a decrease in k of the value 0.94 up to 0.5 per 1.6 ≤ ω (ev) ≤ 2.5. This difference is due to an error surely made for the distance calculation of the interference rings i in the interference system. There is agreement for ω = 2.1 ev. In our simulation of the refraction index n, we note a growth starting from the value 2.81 up to 3.32 in the interval 1.6 ≤ ω (ev) ≤ 2.5; while the results of the reference [12], we see a growth of n starting from ω = 1.8 ev until ω = 2.5 ev of the value 2.74 to 3.11, which are closer to our simulation, the small dissensions return to precise determination of the distance of the interference rings i [12]. According to table 1 “Major optical properties of VO_2 in both insulating and metallic states from `' Gmelein Handbook of physics and chemistry, 1990” [13], the refraction index n (1.9 ev) ≅2.94; for λ≅648 nm, and for our simulation $\mathrm{n}\ (1.9\ \mathrm{ev}) \cong 2.97$, we see a perfect agreement between the two results. Finally, according to this comparison, our simulated results by using the model of Drude-Lorentz to 7 oscillators are in agreement with those of the literatures experiment [11,12,13] in the interval 0.497 ≤ ω(ev) ≤ 2.5. The simulation curves of the constant optics in our work of this thin layer of the vanadium dioxide in a semiconductor state are in conformity with those of the literature concerning the theoretical studies of the semiconductors.

Conclusion

We showed the evolution of constant optics of the vanadium dioxide on a nanometric scale according to the energy of the incidental photon in the photonic energy spectrum of U.V until the I.R for the semiconductor state at a temperature 30°C close to the room temperature. The model of the approximation of the harmonic oscillator enables us to analyze this material in all energetic range of the considered spectrum: 0.001242 ≤ ω (ev) ≤ 6, from weak energies to visible and great energies; thus, allowing the observation of the peaks rising from the transitions related to excitons. The disturbances generated by the temperature, the pressure and the electric field of the medium are one of the disadvantages which do not facilitate the fact of taking into account the large numbers of oscillators so as to have a good convergence of the values of the two permittivities ε_1 and ε_2 and the other constant optics to better interpret these results rising from a study by means of a spectroscopic ellipsometry.

The interest of this study enables us to see the technological applications aimed at putting this intelligent material in the core of the technological applications' future evolutions.

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