A guide for achieving multiple VO_2/Si heterostructures for thermally tunable Near- and Mid-Infrared optics and electronics

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Abstract: This work reports on the thermochemical reaction in air of layers between 110 and 285 nm of vanadium zigzag oblique columns on silicon. A gradual oxygen diffusion results in different linear velocity growth of the formed VO_2-based overlayers depending on the initial V thickness. The study can be used as a practical operational guide for choice since it reveals a reference chart of multiple thermochromism, microstructure, composition, thickness and color features for many products achieved in different situations of reactivity evolution, that can be technologically attractive at one or another stage. For the conditions allowing larger VO_2 yields, outstanding optical responses for films up to 500 nm (over 95% of relative MIR and NIR transmittance modulation with temperature) are achieved, which is relevant for IR filtering or shuttering applications. However, the wavelengths for which this near-absolute optical blockage works, vary and can expand to a wide spectral window of 2 to 9 µm for a thickness of about 250 nm even tolerating the presence of incipient V_2O_5. For every thickness series, depending on the oxidation extent till V is consumed, the maximum NIR-MIR transmittances and the ranges of resistivities of the electric hysteresis can be adjusted with temperature, from more transparent to more opaque, and from more similar to a metal to more similar to an insulator, respectively, that may be useful in thermo-optic and thermo-resistive tunable applications.

Keywords: Vanadium oxidation; vanadium dioxide synthesis; glancing angle deposition; flash lamp annealing; Raman spectroscopy; Vis-NIR-MIR spectrophotometry; thermochromism; NIR-MIR thermo-optics; thermo-resistivity; smart coatings.

1. Introduction

Monoclinic vanadium dioxide (VO_2) is receiving an increasing attention due to its thermochromic characteristics implying a semiconductor-to-metal reversible phase transition (SMT) at heating to the tetragonal dioxide, accompanied by abrupt changes not only at the structural level but also on its optical, thermal, mechanical and electrical performances. A great effort have been focused on integrating VO_2 on glass for smart windows applications, with interesting achivements[1,2]. There is a vast know-how on the industrial manufacture of silicon as a large-scale substrate and, in many cases, its electronics or photonics characteristics can give additional advantages to VO_2/Si devices. Some recent examples of applications of monoclinic VO_2 layers on Si platforms are optical memories[3], smart radiators[4], electrical switches and sensors[5–9], optical modulators, limiters or switches[10,11] or infrared photodetectors[12].

Due to the complex chemistry of V, mainly promoted by its numerous available valences, there are multiple stoichiometries and/or polymorphs that are thermodynamically more favorable than the dioxide. Therefore, only a limited combination of reaction parameters allows achieving pure monoclinic VO_2 by different strategies, which comprise the reduction of V_2O_5, the oxidation of V, or the direct deposition of this dioxide, often combined with further annealing in vacuum or in other controlled atmospheres. The challenging approaches to reach high-quality VO_2 coatings mostly involve complex or expensive methods (hydrothermal or chemical synthesis routes, sol-gel process, electron-beam evaporation, pulsed-laser or chemical-vapor depositions…) that employ very low pressures, special reagents, multiple steps with long processing times, very small substrates, etc. Besides the wafer-scale growth of VO_2 on sapphire[13], there is a lack of methods to reach large-scale VO_2 surfaces on silicon, and we believe that physical vapor deposition of vanadium combined with ex-situ oxidation is a feasible, relatively simple, and low-cost way to reach industrial scalability. In this context, our group has been developing and improving an original and effective two-step approach to attain VO_2(M)/Si structures. In a first step, porous films of V nanostructures were sputtered by GLancing Angle Deposition (GLAD), and later on they were submitted to a fast but finely controlled thermal treatment in air atmosphere[14]. Based on this patented methodology of oxidation to achieve VO_2 in open tube reactors, using either free-standing V powders[15] or thin films of slanted V columns on Si[16] or glass[17], we were recently successful to treat highly porous boomerang-like 100 nm V films in a continuous flow of air using heating lamps, in order to attain high-quality uniform VO_2 coatings[18]. We have now extended this knowledge to anneal larger areas of multiple thicker zig-zag V layers, using a smoother air flow than before, and a larger reaction chamber heated by IR lamps, winning reproducibility and scalability. Moreover, this work makes prospecting on the practical uses of these Si/VO_2-based heterosystems, for thermochromic and thermos-resistive devices.

2. Materials and Methods

110, 175, 220 and 285 nm layers of GLAD vanadium nanocolumns (one zigzag period) were deposited in a home-made magnetron sputtering chamber at angles of 85º on Si, with the same conditions to those reported elsewhere[14,16]. A RPT-100 rapid thermal annealing system (from UniTemp GmbH), an inner constant lower flow of 1 L/min of compressed air, and similar heating (40ºC/s) and cooling (-10ºC/s) ramps than those used for our previous trials on silicon, were chosen to oxidize, at a moderate temperature of 475ºC, groups of the described zigzag V-GLAD (zz-V) samples. Note that the twisted geometry provides a more balanced gradient of porosity to the zz-V film by compensating the directional preferred shadowing effects of nanocolumns, making them also more homogeneous in thickness; that 18 infrared lamps (20 kW) combined with a graphite susceptor, allow to automatize the needed high heating rates that were formerly manually achieved by trained operators in resistance furnaces at the same time while ensuring a uniform reaction surface for a single wafer up to 100 mm (4") or 100 mm x 100 mm substrate size; and that the smooth continuous air overpressure finely stabilized by a mass flow controller, avoids the exhaustion of O_2 in the surrounding oxidative atmosphere, which might happen in calm air atmosphere inside open tubes or even for fluxes managed by ball flowmeters. The specimens are named "#nm/#s" hereafter, according to their initial thickness in nanometers and the time in seconds they were oxidized in the plateau of higher temperature.

The samples were studied by Scanning Electron Microscopy (SEM) in a FEI NanoSEM 450 equipment. Raman spectra were acquired in a LabRAM HR Evolution (Horiba Scientific) spectrometer, using a 532 nm excitation laser source, 20 s of integration time, 10 averaged spectra, 2 mW power, 50x objective lens and a measurement wavenumber interval of 100–900 cm^{-1}. The thermochromic optical behaviors of the prepared VO_2-based films were determined by transmittance in a FTIR spectrometer from Bruker (Alpha-II model) measuring the difference between ambient temperature and heated specimens, and in UV/Vis/NIR spectrometers using a PerkinElmer Lambda 900 equipped with a THMS600 Linkam stage for temperature control, or a Cary 5000 system from Agilent Technologies having a Microptik MHCS120-XY heating and cooling stage. UV-Vis-NIR and MIR spectra were recorded in the wavelength ranges of 180–3300 nm and 3 to 25 µm, respectively, at 25ºC, and in many cases at 100ºC. DC electrical resistivity *vs.* temperature measurements of selected films were performed in a custom-made chamber covered to have a dark environment, using the four-probe van der Pauw geometry in the temperature range of 25−100 °C with a ramp of 1 °C min^{-1} and then back to 25 °C with the same negative ramp. Humidity and cleanness were considered as constant. The error associated to all resistivity measurements was always below 1%, and the quality of the contacts was checked prior to every run (I/V correlation close to 1) to ensure that ohmic contacts were attained (use of gold-coated tips).

3. Results and discussion

As we have demonstrated recently[18], despite using different reaction systems (i.e. flash lamp radiative or resistance convection heating), the oxidation progresses from the surface of the coating towards the interface with the substrate. The evolution of the nanostructures on these systems can be well tracked by observing the relative intensity of specific VO_2 to V_2O_5 Raman bands. In fact, the first appearance of pentoxide signatures coming from the films' surfaces in reacted 100 nm zz-V was an indication of the unavailability of V:O amorphous mixes and the maximum quantity of formed polycrystalline VO_2. This event has a reflect in the surface look by optical microscopy, with the appearance of pentoxide droplets over the films, that on the other hand change their background colorings depending on their original thickness. This is confirmed by a rapid sight of **Figures 1, 2 and 3**, showing surface images and Raman spectra (with the exclusive VO_2 band at about 222 cm^{-1} normalized to 1) for the 110, 175 and 285 nm zz-V samples series, respectively. Note that the band at 145 cm^{-1} is very sensitive to the V_2O_5 presence, and that a height of this band smaller than 2-3 units indicates a still incipient pentoxide presence. Moreover, for the wider scanned range of wavenumbers, only Si, VO_2 or V_2O_5 signatures are found (V does not give any signal by its metallic bonding), excluding a novel feature in the more oxidized samples of the 285 nm series, where a V_3O_7 band appears at about 165 cm^{-1}, indicating the sudden presence of this phase[19]. This is certainly a cleaner scenario than the progress of freestanding or supported V nanostructures reactions in open-tube calmed air[15,20], which demonstrated the appearance of additional phases different to VO_2 and V_2O_5 (i. e. $V_{16}O_3$, VO, V_2O_3, V_6O_{13}), and even a competence of oxidative and reductive effects for the nanoparticles. The general trends are synchronized with the rising of V_2O_5 droplets in the optical images (their composition confirmed by Raman spectra not shown here are proper of pure pentoxide), looking as freckles at a mid-magnification, with a clear semispherical shape, as shown in **Figure 3** in the zoomed picture in plain view, or in the SEM cross-section micrograph. There are different trends with additive oxidation in the background colors variations, with a red-grey-blue-green gradient in the 110 nm series, a blue-green-yellow-red one for the 175 nm series, and going from a brighter to a darker brownish shade in the 285 nm group. **Figure 2** contains an inset in the Raman plot with a picture of a 25 mm x 25 mm specimen demonstrating the uniformness in almost the entire surface after oxidation, with lateral stripes showing bare Si because these positions are covered from the V downfall in the sputtering chamber with necessary holder clamps. This is an optimum sample in terms of increased VO_2 and minimized V_2O_5, but samples that are more oxidized, as for example 110nm/270s, 175nm/420s, or 285nm/1980s, show a similar non-heterogeneous aspect at a macroscopic scale, since these pentoxide droplets are not visible to the eye. Based on the present work and previous experiences, **Figure 4** presents a scheme proposal for the evolution of the vanadium oxide heterostructures in these series.

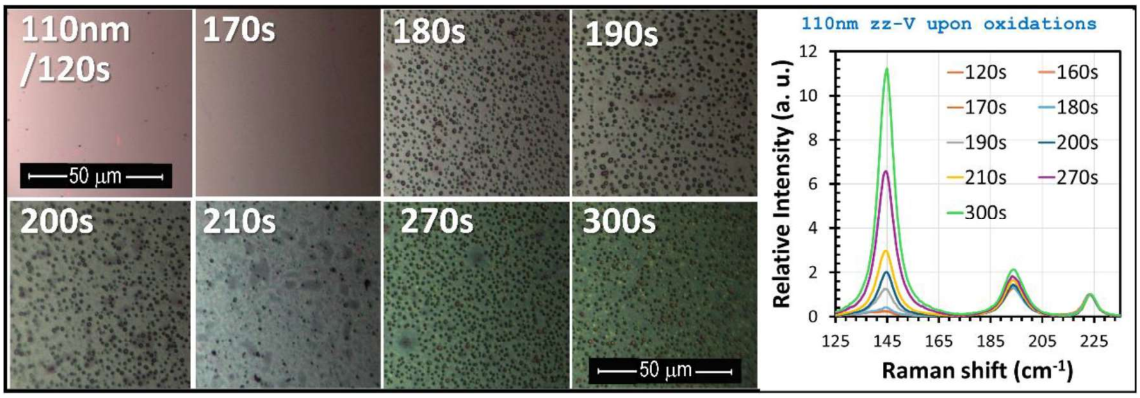

Figure 1. Optical micrographs and Raman spectra of the 110nm/#s series.

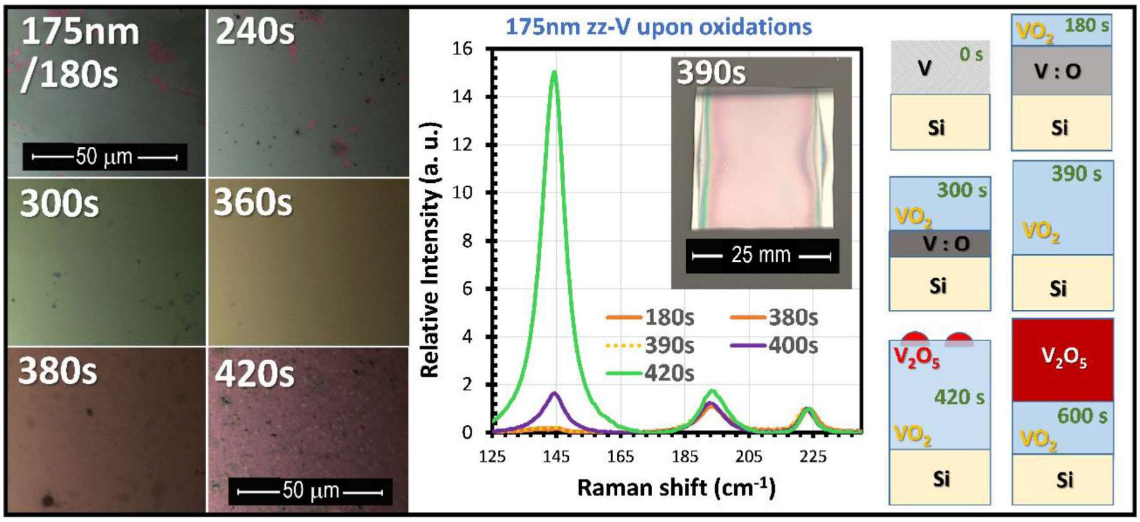

Figure 2. Optical micrographs and Raman spectra of the 175nm/#s series, and evolution scheme.

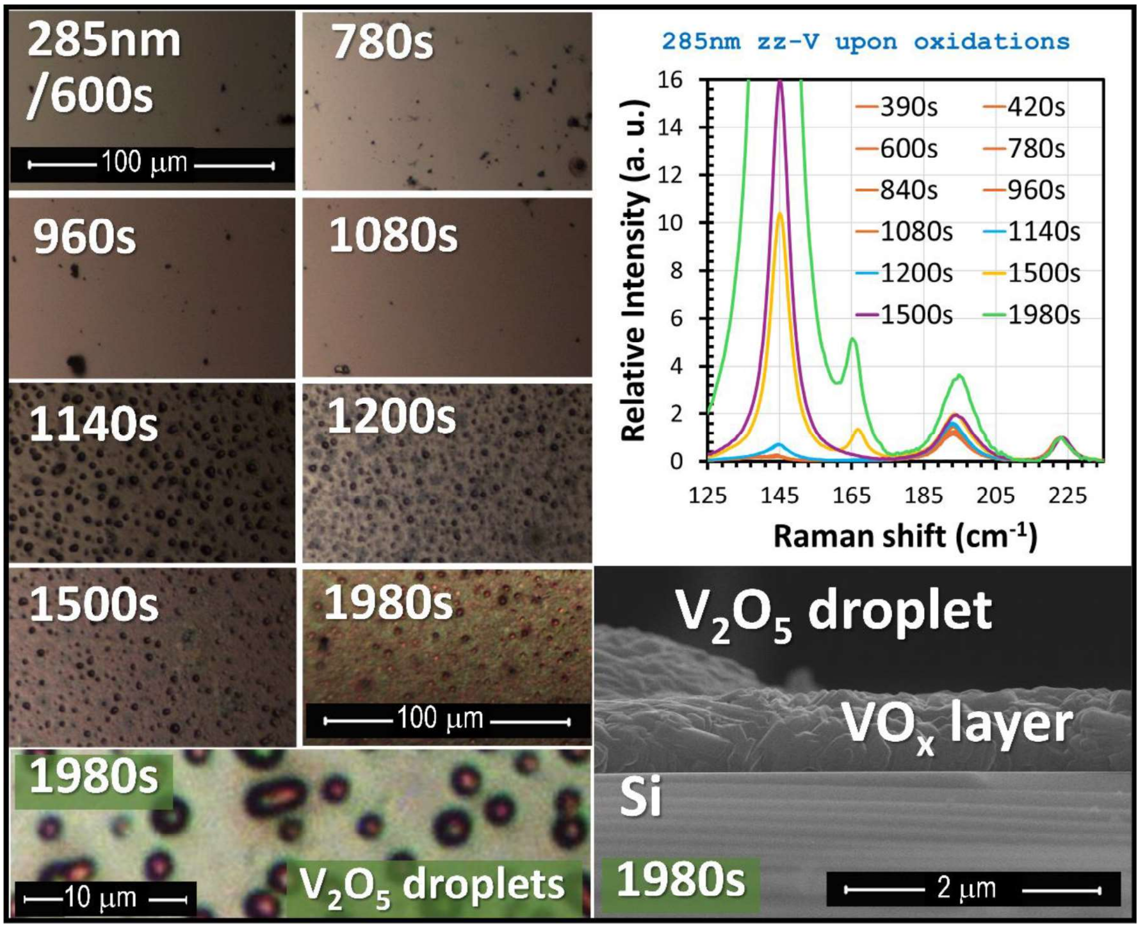

Figure 3. Optical micrographs and Raman spectra of the 285nm/#s series, with SEM detail.

As remarked in the abstract, a gradual oxygen diffusion results in different linear velocity rates of VO_2-based overlayers formation depending on the initial V thickness. This agrees with previous studies that claim that oxidation of V follows linear or parabolic trends and that VO_2 and V_2O_5 are the dominant developed phases[21]. This has been proved by the measurement in cross-section of the thicknesses of many overlayers in all series, from SEM micrographs as those presented for the 220 nm series in **Figure 4**. This figure also shows a plot (**Fig.4(a)**) with this parameter, with respect to the oxidation time for a same initial zz-V layer thickness, which can be fitted linearly leading to correlations of $R^2 > 0.95$; the data marker values are averaged from at least 6 measurements, and in some cases, deviations of widths till ±20 nm were found within the same sample. Moreover, as the SEM images of unreacted (**Fig.4(b)**) and reacted (**Fig.4(c)**) layers show, these systems have homogenous coatings with regular thicknesses. However, the growth rate diminishes dramatically with thickness. Because as the films are thicker, the forming VO_2 top sublayer blocks more effectively the O_2 in-diffusion to the V:O unreacted buried sublayer. Thus, for example, to double its initial thickness and reach the early formation of V_2O_5 on the thicker series (285 to 490 nm in 1980s), a time which is more than one order of magnitude shorter, is needed for the thinner sample to undergo the same occurrence (110 to 220 nm in 150 s). The vanadium oxide thickness marker at this point before the pentoxide rises is painted in red for every series, and an exponential fitting was possible for them, meaning that the curved plot in **Fig.4(a)** can be used as a convenient orientation for getting the optimum (oxidation time and thickness of the VO_2 layer) from any initial zz-V thickness oxidized at 475°C with 1 liter per minute of compressed air, and indeed, the 220 nm optimization needed much less trials since we already used the presented roadmap.

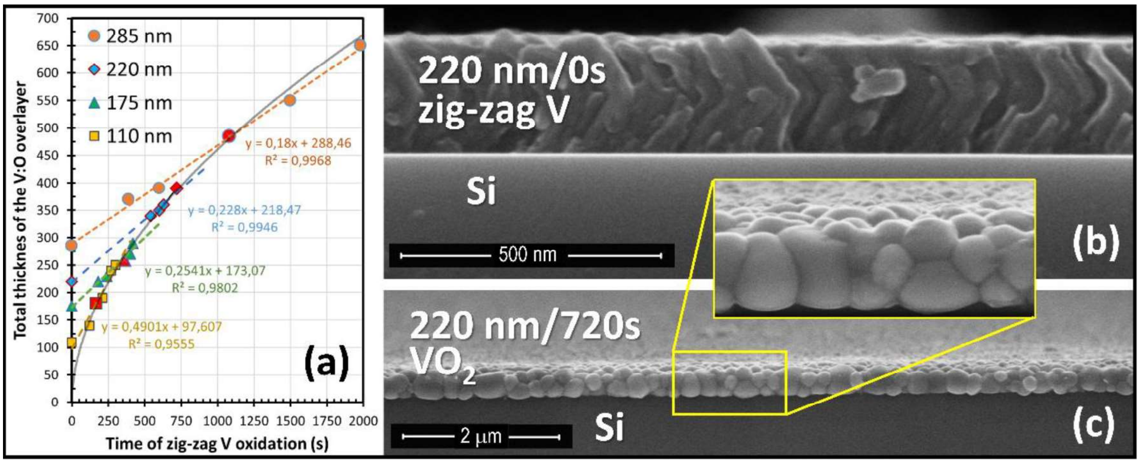

Figure 4. Plot of linear regressions of thickness vs reaction time data (a), and SEM micrographs illustrative of one unreacted zz-V layer (b), and its optimized counterpart after oxidation (c).

However, we cannot anticipate as a universal rule that the pentoxide appearance coincides with the finish of V:O and the maximum yield of VO_2, till the thermo-optical behavior is analyzed. On this purpose, cool (ambient temperature, about 25ºC) and hot (marked as H in the graphs, meaning 100ºC) temperature NIR and MIR transmittance spectrometry measurements for every series were performed and most of these results are shown in **Figures 5, 6, and 7**. The facts that the 110nm/190s and the 175nm/390s are the optimal specimens for IR switching purposes can be concluded since (i) the previous samples of every series (as they are less oxidized) transmit less and less at ambient temperature while keeping their minimum possible transmittance in their hot states; and (ii) the next ones (more oxidized) in each series, for example 110nm/200s and 175nm/400s, are the first to separate from the near-zero transmittances in hot state. Compared to the transmittances of the 285nm/1080s specimen, 285nm/1200s and 285nm/1500s overpass its value at ambient temperature, but they only slightly elevate their transmittances at high temperatures. One hypothesis to explain this, is that while pentoxide is forming, the dioxide underlayer is also thickening, finding the system in this way the best balance of increased transparency at ambient temperature by the antireflective texture of the V_2O_5 shell, and an enhanced thermochromism by having enlarged VO_2 volumes.

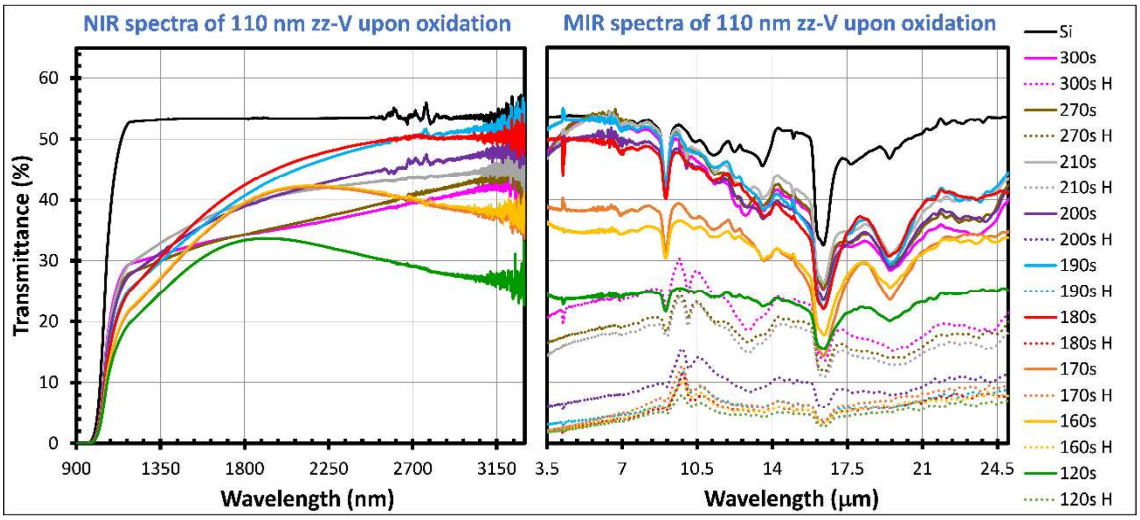

Figure 5. NIR and MIR optical measurements performed on 110nm/#s samples and silicon, with transmittance spectra recorded at 25ºC (solid lines) and for MIR at 100ºC (dotted lines).

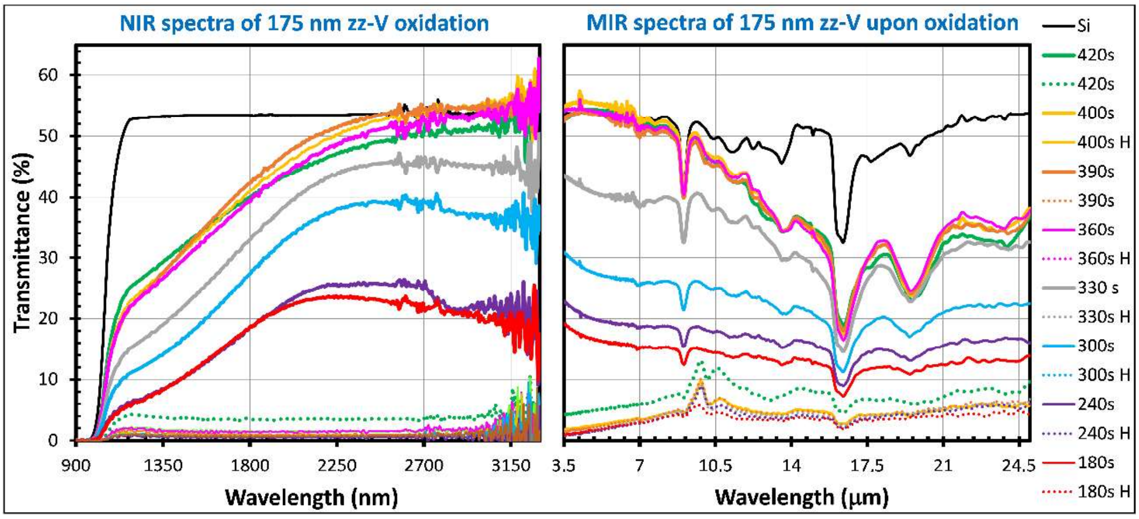

Figure 6. NIR and MIR optical measurements performed on 175nm/#s samples and silicon, with transmittance spectra recorded at 25ºC (solid lines) and 100ºC (dotted lines).

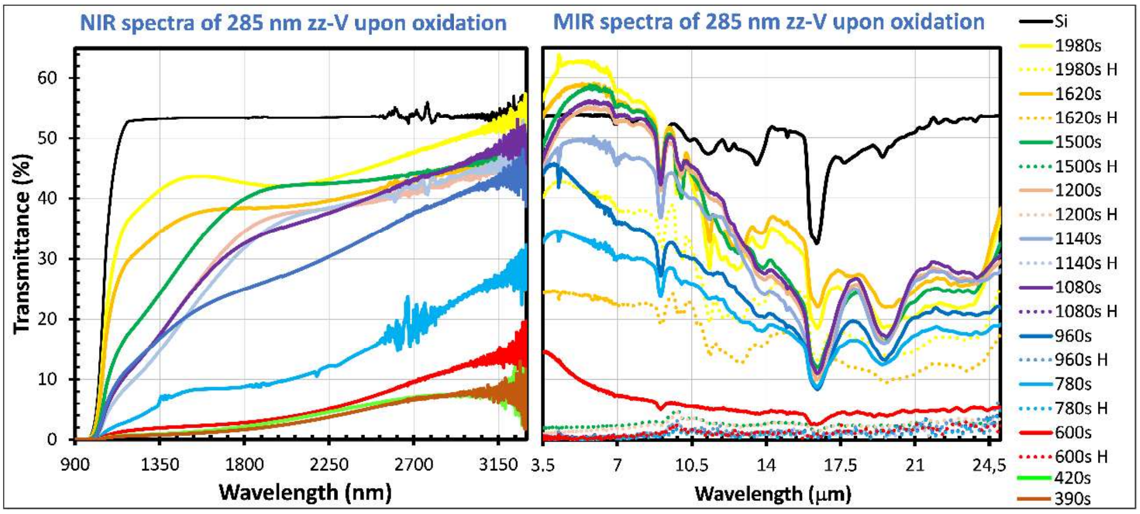

Figure 7. NIR and MIR optical measurements performed on 285nm/#s samples and silicon, with transmittance spectra recorded at 25ºC (solid lines) and for MIR at 100ºC (dotted lines).

Other observations on these results are worth to be mentioned. Firstly, from 1 to 2.5 μm wavelengths, the samples are suddenly more transmissive in the cool state showing a smaller slope till its maximum transmittance value as they are thinner. Moreover, while in the NIR region, the hot transmittances are quasi-null in all series, the MIR blockage turns slightly in the 3 to 25 μm course from ~2 to ~9% in the 110nm/ series, from ~1 to ~6% in the 175nm/ series, and from ~0 to ~2% in the 285nm/ group. This means that a thicker coating, while reducing the effective blockage range, can be more efficient in a restricted region, and for example, at λ=6 μm, the specimen 285nm/1500s has shown an absolute ΔT_{IR} of 56%, meaning a relative transmittance with respect to silicon of 106% while having a low transmittance of ~2% in hot state. Secondly, considering that the substrate itself blocks NIR and MIR an average of 53% at 1.2-8.2 μm wavelengths, the fact that many samples, while preserving their opacities at high temperatures overpass the Si transmittances in fragments of this range positioning their maximum in different values, means that their VO_2 films behave as perfect infrared stoppers, since removing the Si contribution, they can modulate sometimes absolute ΔT_{IR} values over 100%. For some applications, the presence of a thin shell of V_2O_5 can be useful, when gives the system a higher chemical stability and does not hinder the optical modulation. The cause of this transmittance intensification over that of bare Si can be associated with the combined effect of the higher intrinsic transparency of the pentoxide phase compared to that of the VO_2(R) one, as well as the antireflective effect that the V_2O_5, and even the VO_2, textures can stimulate on the Si surface. For example in the pentoxide this happens due to the particular plate-like and open (voided) structures formed on these latter samples promoting a high overall porosity[22]. Thus, the developed coatings can be useful as thermal barrier coatings of Si-based electronic devices exposed to hot sources to avoid their overheating (passive radiative cooling), for lenses that make IR gradual filtering modulated by thermostats, or for contactless IR thermal sensing or vision by adjusting the film thickness to the range of expected measurements.

Let us discuss deeper some potentials of VO_2/Si heterostrucutres for uses as IR shutters. Many optical systems are adapted to work in the atmospheric 3-5 μm and 8-12 μm transmission windows, since they allow an adequate signal-to-noise ratio and, thus, long range vision. There are military laser applications designed to work against detectors active in these ranges, and the integration of the developed layers can be a solution to protect them. Instead of placing expensive IR lenses or slow mechanic shutters, the VO_2 stoppers can activate quickly by Joule heating, provide a sufficiently low transmittance in the closed mode, while letting pass as much radiation as possible in the open mode. On this way, VO_2 films on Al_2O_3 were used to develop 3-5 μm laser shutters having achieved 55% of transmittance in the open mode, 0.1 % in the closed mode, and switching times down to 15 ms[23]. We believe that our heterostructures are more effective and versatile on this purpose, firstly because they have achieved better performances for a less transmissive support: A wafer of sapphire transmits 85% from UV but suddenly blocks IR after 5 μm. In contrast, a cheaper and more available Si wafer transmit 50-55% on the entire NIR and MIR regions and only decay to about 30% in the 16-17 μm range. A study focused on VO_2/Si have shown meritorious results comparable to ours in certain cases for 150 nm films achieved by a process consisting in VO_2 nanoparticles seeding by ultrasonic or spin coating, plus insertion of these templates in a PVD chamber applying 2h of V plus O sputtering at 650ºC[24]. Unfortunately, that work lacks of optical inspection in the MIR region and in contrast to our procedure, the use methodology needs longer processing times and higher temperatures. These authors expanded similar studies to achieve 140-185 nm films on more types of substrates[25], with similar results of maximum transmittances on Si (T_{max}~55%) and lower NIR transmittances on Al_2O_3 (T_{max}~50%) and SiO_2 (T_{max}~40%). They later confirmed that for progressively diminishing the substrate temperatures from 650ºC till 500ºC, the NIR modulation is dramatically lowered[26].

Thermo-optic modulators are widely used in optical communication, photonic circuits, data encoding, and optical metrology and spectroscopy, and their performance are closely related to the efficiency of optical devices. Some works are starting to explore the potential of VO_2 as a non-volatile phase-transition material, in combination with other switchable volatile phase-change materials, to develop thermally regulated MIR modulators[27,28]. A recent pioneering work has demonstrated an electrically controlled vanadium dioxide–metal metasurface that simultaneously works as a tunable optical switch, an optical limiter with a tunable limiting threshold and a nonlinear optical insulator with a tunable operating range, with major modulations similar to those achieved in the present work. Unfortunately, as for sapphire, the used TiO_2 substrate limits their uses in a broadband range, and they are active only in a very limited fringe of the mid-wave infrared regime (4-5 μm)[29]. The prospective of the presented heterostructures in this work is to implement them to emulate these devices, and this is planned to be the matter of our future research.

On the other hand, for any thickness series, up to the moment that V is consumed, the VO_2 volumes are additive, meaning that while fixing the near-zero transmittances in hot state, this parameter can be tuned for ambient temperature depending on the oxidation time, so this modulation gap can be adjusted on demand for potential uses. For example, a single set of VO_2/V:O/Si heterostructures with different VO_2/V:O thickness ratios can be ideal apertures of different power limiting levels in a laser optical bench, with the possibility of modulate multiple types of laser wavelengths since, as demonstrated, it is active a wide range of this parameter.

Another example where this oxidative modulation can have a practical impact, is the tuning of the electrical characteristic of the VO_2/V:O/Si system. With the aim of measuring electronic properties, samples of the 175nm/# series were replicated but on glass substrates this time, given that tip-contact measurements are more stable on these insulating platforms because Si promotes electron leakages that often ruin the experiments. Eventually, the Vis-NIR-MIR transmittances for a more transparent substrate than Si (from UV till 5 μm) indicate that the optical quality of each VO_2 layer on glass is lower than its counterpart on Si (best modulations on the order of 15% absolute). We believe that, as it has been previously observed, the reaction of V+O with an alkali-containing silica has formed non-thermochromic mixed oxides as sodium vanadate, that compete with the VO_2 growth and systematically diminish the quantity of dioxide. However, in this lower transmittance scenario, the optimum sample in optical terms, and the general trends on this property, are basically the same as on silicon, and the transmittance spectra of **Figure 8** demonstrate this. In this figure, the electrical measurements for VO_2-containing layers of the same layers are shown. A relevant effect has been observed: The range of resistivity variations for every sample changes to average higher values as they are more oxidized. So it is possible to have different electrical switches activated by temperature that cover the about 4 orders of magnitude that are between a metallic behavior and an insulator one. In this way, the electrical measurements graph also shows the results for a 175 nm zz-V sample 60s oxidized at 550ºC and 5 lpm of air (A) that has been over oxidized on purpose to get higher concentrations of V_2O_5 than those which are typical in the studied series. The consequence of this is that the hysteresis vanishes and the values are more similar to those of a less-conductive non-thermochromic material. On the other side, the measurements on a 175 nm compact V layer oxidized at 475ºC with 1 lpm of air for 90s (B) show almost the same resistivity of pure V with temperature. This means that the formed vanadium oxide overlayer is not predominant with respect to the remaining unaffected metallic amorphous vanadium. It was also possible, after some trials, to measure the optimized 175nm/390s sample on Si (C), and in this case, given that the volume of thermochromic VO_2 is larger and with a higher quality, the extension of the smaller to bigger resistivity is wider, extending over 2 orders of magnitude. This drop is more than twice these reported in our previous studies for similar layer thicknesses on Si, coming from the oxidation of one period V oblique nanocolums[14], meaning a clear improvement in VO_2-yields and/or crystalline quality. Note that for all films, the temperature of phase transitions presented small variations without a clear tendency, but all values laid on the typical of pure monoclinic vanadium dioxide, with transitions at 65-70ºC for heating and 55-60ºC for cooling.

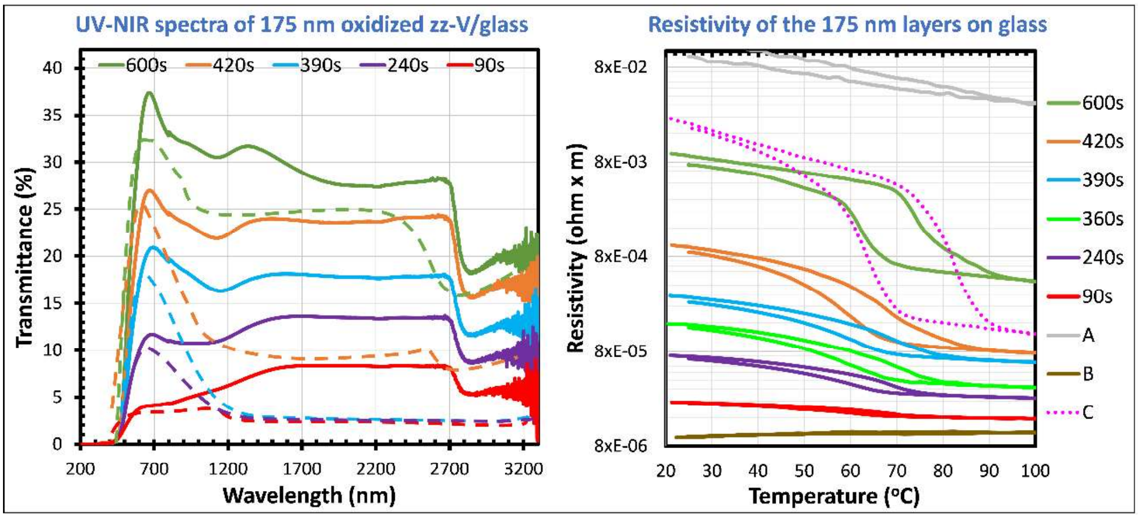

Figure 8. Left: UV-NIR transmittances of oxidized 175 nm zz-V layers on glass at ambient temperature (solid lines) and at 100ºC (dashed lines). Right: Resistivity versus temperature for these samples, a sample 60 s oxidized at 550ºC and 5 lpm of air (A), a sample with a 175 nm compact V layer oxidized for 190s (B), and an optimized sample on Si: 175nm/390s (C).

4. Conclusions

An original and simple method is proposed to achieve thermochormic VO_2-based layers on Si in a wide range of thicknesses bellow 1 micron. It consists in the deposition of zig-zag vanadium columnar nanostructures by sputtering followed, under a flux of 1 lpm of air, by rapid heating till 475ºC and further maintenance of this temperature for a period. Multiple scenarios are tracked and described, with examples of optical transmittances, Raman spectra, or films colors or thicknesses. Consequently, the use of a reference plot is recommended in order to choose the initial V width and the right oxidation time for the linear growth of VO_2-containing layers with target thicknesses and required performances. For pure dioxide films of all thicknesses, the VO_2/Si systems are able to pass from transmit to block a broadband of NIR and MIR wavelengths (from 2 to 9 μm) similarly or even better than the bare Si at ambient temperature. Given that the systems transmit with record numbers in open mode, even withstanding residual amounts of V_2O_5, and that they transmit near-zero in closed mode, in addition to the fact that studies of the behavior at MIR are very scarce, the attained structures are envisaged as ideal infrared shutters and other uses for acting in interesting wavelength windows. Last but not least, and subject of other potential devices, depending on the degree of V reaction, one can thermally tune (i) the optical switching gap from near-zero to the desired NIR-MIR transmittance, and (ii) the level of the resistivity average and interval values associated to the electrical thermochromic hysteresis, from more to less insulating.

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Data availability statement

Data will be made available on request.

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.

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