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Direct production of thermochromic VO₂ thin film coatings by pulsed laser ablation

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Abstract

Experimental morphological, electrical and optical properties of VO₂ thermochromic thin films synthesised by excimer pulsed laser ablation are reported. These thermochromic films were elaborated on three different types of substrates from VO₂ bulk target without any substrate heating or atmosphere control during the deposition process. Irrespective of the nature of the substrate, all films showed a large sharp transition close to that given by perfect bulk VO₂ crystals. Irrespective of the nature of the substrate, these laser-ablated films optically switch abruptly from 28% in the metal state to nearly 72% approximately in the semi-conducting state at 3000 nm upon cooling through the transition well centred around 68°C. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

A large number of transition metal oxides and sulphides are semi-conducting and metallic at low temperatures and high temperatures, respectively [1]. In vanadium oxide compounds, this semi-conducting/metal phase transition is a first-order type as in V₂O₃, V₃O₅, V₄O₇, VO₂ [2]. This later dioxide “VO₂” is a material of particular interest for solar technology applications [3–7] as switching infrared smart devices. Indeed, this semi-conducting/metal phase transition, which takes place

at a temperature close to room temperature “ $\approx 68^\circ\text{C}$ ”, is correlated to a sharp optical transition [3,8]. Accurately, this later manifests itself by a large modulation of the optical transmission in the infrared spectral region versus temperature. This so-called thermochromic property offers then the possibility to a self-control of solar radiation heating in architectural building industry and automotive sector [2,3].

For exploitation of this thermochromic effect especially in the two previous technological sectors, VO₂ is needed in most cases in the form of thin film-based coatings. Different thin film techniques have been tested successfully such as sputtering, evaporation, sol-gel processing [3] to obtain thermochromic VO₂ coatings with properties close to that of bulk crystals. Nevertheless, the

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chemical stoichiometry of the obtained films is in general not total and other crystallographic phases are present as well as the VO_2 matrix. Pulsed laser ablation technique offers the possibility to overcome this chemical problem as it is shown in this letter without heating the substrate or controlling the gas atmosphere during the deposition process. Besides this stoichiometric aspect, this emerging thin film technique allows high deposition rates and controlled V/O ratios.

In the present contribution, we present the experimental results of thermochromic VO_2 films synthesised by excimer pulsed laser ablation directly from a VO_2 target with a recourse only to the energy density of the laser beam on the target.

2. Experiments and results

A pressed powder pellet 1.5 cm in diameter and 2 mm thick with nominal composition VO_2 was used as a target. The target was mounted in a small vacuum system with a base pressure of $2.0 \cdot 10^{-6}$ mbar, and irradiated through a KrF excimer laser. A quartz lens was used to vary the energy density in the range $0.5\text{--}2.7 \text{ J/cm}^2$ on the target. Silicon, quartz and sapphire substrates were used. They were mounted at a distance of typically 25 mm from the pellet surface, close to the centre of the laser spot. The laser was fired at a repetition rate of 10 Hz, for a total of 6000 shots. During deposition, the pressure in the vacuum chamber rose to about $1\text{--}2.5 \cdot 10^{-6}$ mbar.

The films synthesised on an average 150 nm thick “2.5 nm/s” and were analysed by Rutherford backscattering, mechanical tencor surface profilometry, atomic force microscopy, X-ray diffraction, VIS-NIR spectro-photometry and electrical resistivity analysis. The optical transmission and electrical resistivity data were taken with the samples held in an optical fixture housed in an evacuated system with a heater for temperature cycling.

The Rutherford backscattering analysis using a 2 MeV He^+ ions beam has shown that the chemical composition of the obtained vanadium oxide films was found to be within $\approx 10\%$ of that of the bulk target “ $0.48 < \text{V/O ratio} < 0.51$ ” for an energy

density of $\approx 1.3 \text{ J/cm}^2$ on the target without heating the substrates or controlling the atmosphere. As to the mechanism of the deposition, the similarity in stoichiometry and, in particular the high oxygen content, between the bulk VO_2 material target and the thin film deposits is due to the highly non-equilibrium nature of the pulsed laser heating. As it is generally admitted, with the excimer laser spots, the heating is confined to a thin surface layer due both to a probably large optical absorption coefficient as well as the poor thermal conductivity of the sintered VO_2 target. This causes a strong overheating of the surface layer and leads to a massive expulsion of the material, on the order of 130 nm per shot, as it will be shown below by atomic force microscopy and indirectly by Tencor mechanical surface profilometry. Therefore, in the current vacuum conditions, the VO_2 material is most likely ejected in the form of fairly large molecular clusters, which may explain the preservation of the stoichiometry in the deposited films irrespective of the nature of substrates. Moreover, the rates of heating and cooling are so fast that phase separation cannot occur in the bulk material.

Fig. 1 shows the atomic force microscopy analysis of VO_2 films deposited onto silicon, quartz and sapphire substrates. Even if the surface characteristics of the three substrates are different, the VO_2 films present fairly the same surface topography. As summarised in Table 1, their surfaces are very rough with a root mean square roughness of the order of 5 nm and approximately the same mean height distribution “ $\approx 22.5 \text{ nm}$ ”. Moreover, irrespective from the nature of the substrate, the films consist of compact quasi-spherical crystallites which are approximately 130 nm in size. This effective non-dependence from the nature of the substrate seems to indicate that the growth mechanism is imposed mainly by the laser–target interaction in the considered deposition conditions.

The crystallographic structure of the films grown on the three different substrates was investigated by X-ray diffractometry using a $\text{Cu } K_{\alpha 1}$ radiation. The emergence of only one VO_2 lines is observed for all substrates, indicating the VO_2 to be a single phase “monoclinic VO_2 ” well oriented

but not epitaxial with (011) direction normal to the substrate surface. This crystallographic growth orientation is observed independently of the na-

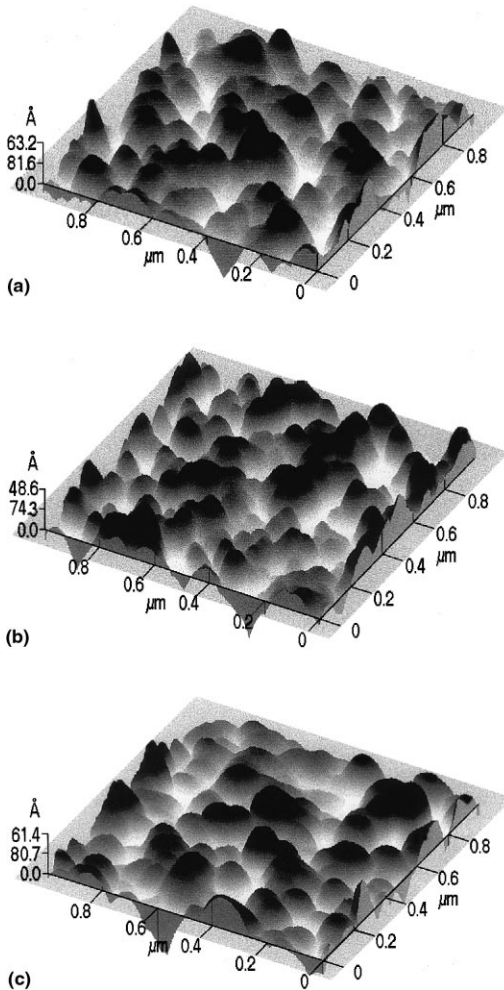


Fig. 1. Atomic force microscopy topography of VO₂ thin films onto the following non-annealed substrates: (a) silicon; (b) quartz; (c) sapphire.

ture of the non-annealed substrates. This particular behaviour may have two reasons. First there is the possibility that the substrate in the growth condition does not influence significantly the coalescence process of the ejected VO₂ micro-clusters as normally it should be [9–13]. On the other hand, it is possible that a larger part of the precipitation on the substrate's surface of these micro-clusters is controlled mainly by the interaction of the laser–VO₂ target interaction.

From an electrical point of view, the three VO₂ coatings exhibit, within the bar error, similar sharp electrical resistance transitions located between 64°C and 72°C. As a typical example, Fig. 2 reports the temperature variation of the electrical resistance per square of VO₂ onto sapphire. The sudden drop of the electrical resistance centred at

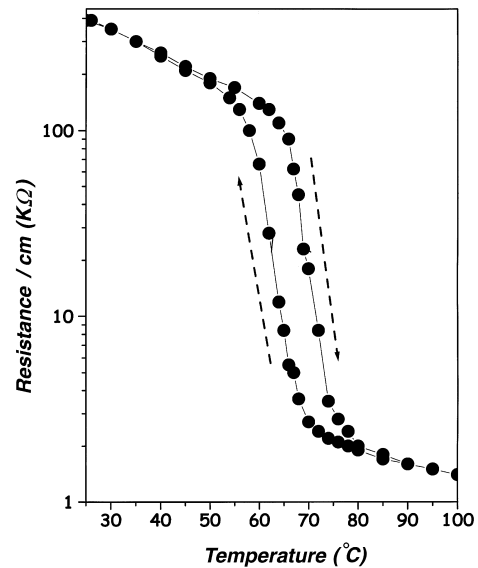


Fig. 2. Temperature–electrical resistance (*R*) hysteresis of VO₂ thin film onto sapphire.

Table 1

Atomic force microscopy experimental surface parameters of VO₂ films deposited onto silicon, quartz and sapphire substrates^a

Sample	σ_{p-v} (nm)	σ_{rms} (nm)	Mean height (nm)	Bearing ratio at 75%	Bearing ratio at 35%
VO ₂ /silicon	38.5	4.5	22.3	19.5	24.0
VO ₂ /quartz	37.5	5.0	21.2	18.1	23.4
VO ₂ /sapphire	4.0	5.7	26.0	21.8	27.8

^a σ_{p-v} and σ_{rms} are the peak to valley and root mean square roughness, respectively.

the critical temperature of 68°C is a signature of the existence of VO₂ phase mainly in the investigated three films. Compared to films obtained by the usual vacuum techniques [2–7], the electrical transition is sharper and characterised by a small hysteresis of approximately 8°C in width. Again irrespective of the nature of the non-annealed substrates, it is noticed that the electrical resistance variation is the same; of the order of three magnitudes for three samples.

The optical measurements were carried out on a Cary double beam spectrophotometer in the spectral range 300–3000 nm at normal incidence. Likewise, as for electrical resistance measurements, the VO₂ films exhibit approximately the same optical transmission and reflection properties in the considered spectral range “only reflection measurements were conducted on VO₂/silicon”. Fig. 3 shows the optical transmittance for six different temperatures “40°, 60°, 65°, 70°, 80° and 100°C” chosen so that they cover the optical response from semi-conducting state to the metallic state. As expected, the optical transmission exhibits a strong dependence with temperature in the infrared region without a significant change in the

visible region as in the case of usually deposited VO₂ films. However, there is a strong and positive advantage of the current pulsed laser-deposited VO₂ films. The change of the optical transmission is very abrupt between 65°C and 70°C, which is not the case for ordinary sputtered, evaporated or sol-gel deposited VO₂ thin films [2–7]. Moreover, as the difference between the optical transmissions at 80°C and 100°C is not significant in the infrared or in the visible ranges, one could argue that the transition to the metal phase is total. Fig. 4 shows the optical transmission switching versus temperature from 30°C to 100°C for the same film for four different wavelengths: two in the visible and two in the near-infrared “500–1000 and 2000–3000 nm”, respectively. As can be observed, the optical switching is smaller than 5% in the visible while in the near-infrared it is larger than 35%; at 3000 nm, especially, the optical modulation is ≈ 45%. The hysteresis loop delineating the cooling and heating cycles is centred exactly at 68°C as in bulk VO₂ crystals. The width of the hysteresis loop is of the order of 8°C which is smaller compared to the values obtained on usually sputtered, evaporated and spin-coated VO₂ thin films [2–7].

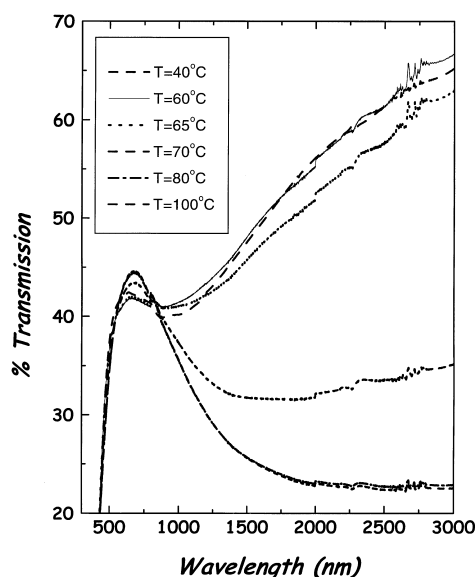


Fig. 3. Optical transmittance (%) versus wavelength for six different temperatures of VO₂ thin film onto sapphire.

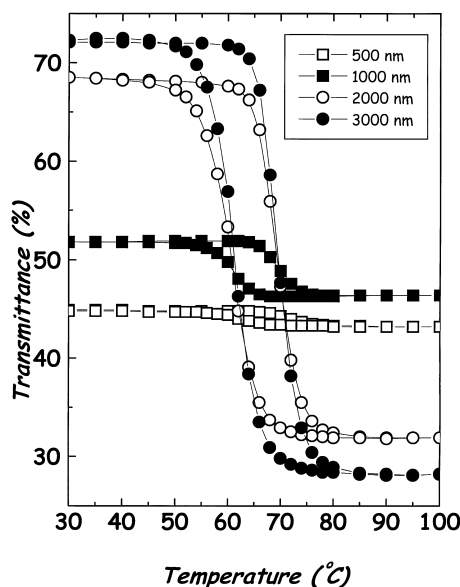


Fig. 4. Temperature-optical transmittance hysteresis of VO₂ thin film onto sapphire carried out at four wavelengths: 500, 1000, 2000 and 3000 nm.

3. Conclusion

VO₂ thermochromic thin films were elaborated by pulsed excimer laser ablation onto silicon, quartz and sapphire substrates. These high stoichiometric films were synthesised from VO₂ target without any substrate heating or atmosphere control, but only by fixing the laser density of the incident beam to $\approx 1.3 \text{ J/cm}^2$ on the target. Their thermochromic properties were found to be close to the bulk VO₂ crystals. In such elaboration conditions, these thermochromic properties were similar irrespective of the nature of the substrate. This may have two reasons. First, the substrate in the growth conditions does not influence at all the coalescence process of the ejected VO₂ micro-clusters. Second, it is possible that a large part of the coalescence on the substrate's surface of these micro-clusters is controlled mainly by the laser–VO₂ target interaction. In order to substantiate this conclusion, it is necessary to conduct a complete investigation which is currently in process.

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