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In-situ characterization of the semiconductor-metal phase transition in vanadium dioxide thin films

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Abstract. Vanadium dioxide (VO_2) exhibits a reversible first-order semiconductor-metal phase transition (SMT) near 68 °C at ambient pressure, consisting in a structural transformation from a low-temperature semiconducting monoclinic phase to a high-temperature metallic rutile phase. This phenomenon is investigated on thin films of VO_2, with thickness ranging from 15 to 300 nm, which are deposited on a silica substrate by magnetron sputtering. The films are systematically characterized at the morphological, structural, and optical level by using Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Grazing Incidence X-ray Diffraction (GIXRD), Raman Spectroscopy, Spectrophotometry, and Spectroscopic Ellipsometry. The SMT is investigated *in-situ* by Optical Spectroscopy in the VIS-NIR spectral range and by Grazing Incidence X-ray Diffraction (GIXRD). Compared to their bulk counterpart, thin films display broader phase transitions upon thermal excitation. This is evidenced by monitoring the temperature-dependent transmittance at specific wavelengths which reveals a hysteretic behaviour, whose thermal width and amplitude depends on the film thicknesses. Additionally, changes in peak positions and intensities in in-situ GIXRD diffraction spectra further elucidate the phase transition dynamics.

1 Introduction

Vanadium dioxide (VO_2) is a strongly correlated material which undergoes a reversible first-order semiconductor-to-metal phase transition (SMT) at about 68 °C at ambient pressure. The transition causes a drastic modification in the electrical conductivity, which increases by several orders of magnitude, as well as in the optical properties, due to the strong change in the dielectric function. This electronic transition is associated to a structural distortion from a low-temperature monoclinic structure to a high-temperature rutile one. In the last decades, an intense investigation has been carried out to identify the mechanism underlying this phase transition, leading to the development of several VO_2-based devices [1, 2].

In the present work, we investigated the broader phase transition and the hysteretic behaviour upon thermal excitation on VO_2 thin films deposited on silica substrates. This phenomenon is studied by monitoring the transmittance variation at a specific wavelength and by analysing the evolution of the GIXRD diffraction spectra in a range of temperatures close to the transition one. The parameters of the obtained hysteretic cycles, like the thermal width and the amplitude, depend on the film thickness, which ranges from 15 to 300 nm. An *in-situ* study of the phase transition provides valuable insights to elucidate the underlying mechanism and explore potential future applications.

2 Results

2.1 Thin film synthesis

The VO_2 thin films are deposited on silica glass (HSQ100 by Heraeus) and silicon by DC magnetron sputtering deposition from a metallic V target. A controlled flow of O_2 is pumped into the chamber together with the Ar gas to promote vanadium oxidation during the deposition. The sputtering time is directly related to the thickness of the layer (t), and the typical deposition rate obtained with this procedure is about 0.4 nm/s. A subsequent annealing treatment is implemented to promote VO_2 crystallization and to finely tune the film stoichiometry. The thickness of the films was varied from t = 15 nm to t = 300 nm.

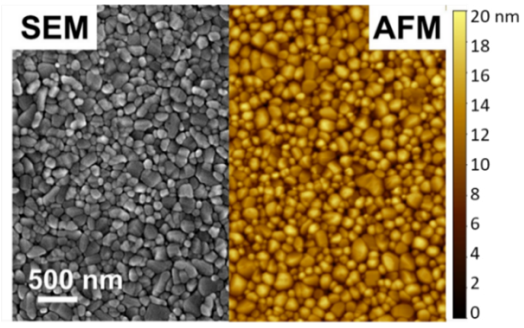

Figure 1. SEM (left) and AFM (right) images in-plane view of the VO_2 thin film (50 nm).

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Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to obtain information on size, shape, and morphology of the thin films. A SEM (left) and AFM (right) images are reported in Fig. 1. The crystal grains are tightly packed and spread over the surface. The average size of the domains is around 50 nm. The surface roughness of the sample was estimated by AFM measurements, ranging from 2 nm and 4 nm depending on the sample thickness.

2.2 In-situ characterization of the phase transition

Grazing Incidence X-ray diffraction (GIXRD) was used to determine the crystalline phases in the deposited and annealed films. By means of an heatable sample holder, two diffraction patterns are acquired: one at room temperature (monoclinic phase), and the another at 90 °C (rutile phase). The insulator-to-metal transition can be clearly identified by the shift of the VO_2 (011) to (110) peak.

Transmittance spectra are acquired in the range from 400 to 2000 nm by varying the film temperature above and below the transition temperature. Additionally, the dielectric functions of the two phases have been determined by Spectroscopic Ellipsometry measurements at room temperature and at 90 °C.

In comparison to bulk VO_2, thin films typically show broader phase transition associated to a thermal hysteresis. This has been investigated by monitoring the evolution of the transmittance with temperature at a specific wavelength, but also considering the modification of the centroid of the main peak in the X-ray diffraction spectra as a function of the sample temperature. These two approaches lead to the hysteresis loops presented in Fig. 2. The blue points represent the transmittance of the VO_2 film at 1540 nm, while the red points represent the position of the main diffraction peak.

The parameters which characterize the hysteretic behaviour, like the width and the position of the transition temperature for the heating and cooling processes, can be extracted by fitting each branch with a Complementary Error Function (cerf) obtaining in this way the characteristic parameters of the hysteresis of the phase transition. The dashed lines in Fig. 2 represent the fitted curves. Table 1 reports the transition temperatures for the heating and the cool process (T_H and T_C, respectively), the width (ΔT_t), and the amplitude (ΔT) of the hysteresis for samples with VO_2 thickness ranging from 60 to 160 nm.

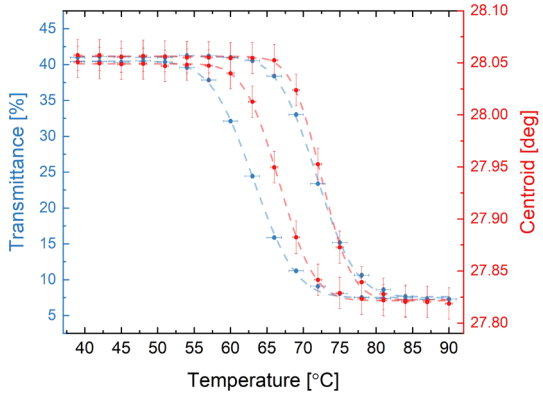

Figure 2. Thermal hysteresis cycle for transmittance at 1540 nm (blue, left axis) for the centroid of the main peak in GIXRD spectrum (red, right axis) for VO_2 thin film (110 nm). The dashed lines represent the fitted curves.

Table 1. Parameters extracted from the fit of the transmittance hysteresis loop at λ = 1540 nm and for samples with VO_2 film thickness of t = 60 nm, t = 110 nm and t = 160 nm; T_H and T_C correspond to the transition temperatures heating and cooling branches, while ΔT_t and ΔT represent the width and the amplitude of the hysteresis loops, respectively.

t [nm]	T_H [°C]	T_C [°C]	ΔT_t [°C]	ΔT [%]
60	72 ± 1	62 ± 1	10 ± 1	31 ± 1
110	71 ± 1	64 ± 1	7 ± 1	34 ± 1
160	70 ± 1	63 ± 1	7 ± 1	40 ± 1

The transition temperature for the heating process is always higher than the values reported for bulk VO_2, and this can be ascribed to the presence of strain in the film due to the lattice mismatch with the substrate [3]. As shown in Fig. 2, the thermal widths extracted with the two techniques are different and this can be explained considering that the diffraction spectrum considers only the crystalline components of the layer, whereas the spectroscopic transmittance accounts also for the amorphous parts. In addition, it is possible that the initial condition is not entirely restored when the temperature is decreased below the transition point, since some grains persists in the rutile phase. Finally, the amplitude and the width of the cycles change with the thickness of the sample, as shown in Table 1 and as reported in some previous works [3].

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