Hysteresis of the metal-insulator transition of VO_2; evidence of the influence of microscopic texturation

Hysteresis of the metal–insulator transition of VO$_2$; evidence of the influence of microscopic texturation

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Abstract. Vanadium dioxide films have been deposited on silicon substrates by reactive RF cathodic sputtering from V$_2$O$_4$ and V$_2$O$_5$ targets. The optical measurements show a good contrast at the semiconductor–metal transition, but exhibit two kinds of hysteresis cycle: a narrow and symmetrical one, and a wider and asymmetrical one. We have mainly studied the microstructure of these samples by means of grazing-incidence x-ray diffraction at the LURE synchrotron radiation facility. We analysed in detail the intensities of the diffraction peak spectra and of the portions of diffraction rings. We found a clear relation between a narrow and symmetrical hysteresis cycle, and a (011) texture of the films. We attribute this result to an improvement in the cooperativity of the transition phenomena.

1. Introduction

VO$_2$ is one of the most studied materials among those which present a thermochromic behaviour, for essentially two reasons. First, its metal–insulator transition occurs at a temperature of $T_c = 68$ °C for a single crystal, which can be decreased down to ambient temperature by light doping, for example with tungsten [1]. This makes it useful for thermal applications like in heat-evacuation-control coatings. Second, it can be deposited as thin films, which is a very convenient aspect as regards the development of highly technological systems. Since its discovery by Morin in 1959 [2], VO$_2$ has been mainly studied in its single-crystal form. It exhibits an important change in its electrical properties at the transition: a five-orders-of-magnitude increase in resistivity from its metallic high-temperature phase to its semiconductor low-temperature phase, which produces a gap of 0.6 eV. Hence there is also an abrupt optical transition in the infrared region from, respectively, an absorbing state to a transparent state [3]. This change is associated with a crystallographic distortion [4]. At high temperature, vanadium dioxide has a rutile-type structure with vanadium atoms equally spaced along the corresponding c_r-axis. At the transition to the low-temperature state, these vanadium atoms pair along the c_r-axis with a slight twist, which leads to a monoclinic symmetry. Although Goodenough [4] proposed an electronic explanation of the transition, fundamental questions still remain, such as that of the nature of the dominant mechanism: a Mott–Hubbard or Peierls scenario [5].

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In the last decade, many people have tried to understand the influence of the thin-film aspect on the transition characteristics [6]. Most of the time, thin films are polycrystalline and exhibit electrical and optical property changes significantly smaller than those of single crystals. Moreover, the width of the transition hysteresis can rise from 1 °C for a single crystal, up to 20–30 °C for a thin film [6, 7]. The polycrystalline nature of the thin-film samples has then strong implications for the properties of the material.

In order to study this influence on the transition, we deposited VO_2 thin films on silicon wafers by RF cathodic sputtering with two kinds of target, V_2O_4 and V_2O_5 powders. The optical measurements indicated differences between the hystereses of the samples, which we tried to explain on the basis of a structural analysis. For that purpose we essentially used x-ray diffraction (XRD) with θ–2θ geometry. Conventional XRD analysis on a standard Philips system did not yield satisfactory results. Therefore we performed grazing-incidence XRD experiments on a synchrotron line at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE) in Orsay.

2. Experimental procedure

2.1. Production of VO_2 thin films

We used reactive RF cathodic sputtering. Previous studies [8, 9] have shown that the use of a vanadium target leads to extremely critical values for the oxygen content in the sputtering gas. Thus we decided to employ V_2O_4 and V_2O_5 targets, made by compression of the respective powders (Johnson–Matthey, ALFA—purity 99.9%), instead of using a pure vanadium target. This allowed us to obtain a stable range for the deposition parameters. The sputtering gas was a mixture of 95% argon and 5% oxygen. Our substrates were (100) silicon wafers fixed on a controlled-heating holder. We focus here on two typical samples: sample 1 deposited with a V_2O_4 target, under 10 mTorr at 350 °C, and sample 2 deposited with a V_2O_5 target, under 15 mTorr at 450 °C. The thicknesses, measured by profilometry and confirmed by Rutherford backscattering analysis, were respectively 50 and 30 nm for samples 1 and 2.

2.2. Characterization techniques

The study of the optical hystereses of the films was performed on a Varian Cary 5 spectro-photometer at a fixed wavelength of 2.5 μm. The temperature was regulated by a Specac accessory for a 1 °C min^{-1} ramping, with a precision of ± 0.5 °C.

The stoichiometry of the samples was controlled by Rutherford backscattering spectro-scopy (RBS) and nuclear reaction analysis (NRA).

The microstructure was analysed by means of x-ray diffraction, at ambient temperature. We first obtained classical x-ray diffraction spectra (XRD) in the θ–2θ geometry, on a Philips X'Pert MPD diffractometer, i.e. with the scattering vector perpendicular to the substrate. We used a 1.54 Å Cu Kα tube with a Ni filter. The measurements were performed with a 0.05° step increment and an accumulation time per point of 30 seconds, which led to a twelve-hour experiment. The angular resolution of the diffractometer is 0.01°.

We then carried out grazing-incidence x-ray diffraction experiments, with the scattering vector almost parallel to the substrate, on the D41B beam line at LURE. A vertical asymmetrically cut Ge(111) monochromator selects a wavelength of 1.381 Å and a slight curvature focuses the beam horizontally with a 1 mrad divergence. The surface of the sample is almost horizontal, and a silica mirror located between the monochromator and the sample deflects the beam at an angle of 2.6 mrad, i.e. less than the surface critical angle. This mirror

is also used to reject the harmonic. Between the mirror and the sample, the beam is collimated through a Hubert slit with a vertical height of 100 μm. A pair of diodes is used to monitor the incident beam. Scattered photons are measured by a vertical circular position-sensitive detector (PSD) with a 550 mm radius which allows one to measure the vertical diffraction up to 11° at each position. The in-plane (horizontal) resolution is determined by a horizontal-gap Soller slit with 2.6 mrad acceptance. The counting time is 30 s/point.

3. Results

The optical hysteresis cycles of samples 1 and 2 are presented in figure 1. Several temperature cycles were performed, and this did not modify them. For the hot and cold states the transmittance levels are the same for the two samples. There is a large change in the optical properties between these two temperature ranges, as expected for VO$_2$. It must be recalled that the transmittance presented includes the transmittance of the silicon substrate ($\sim$50%).
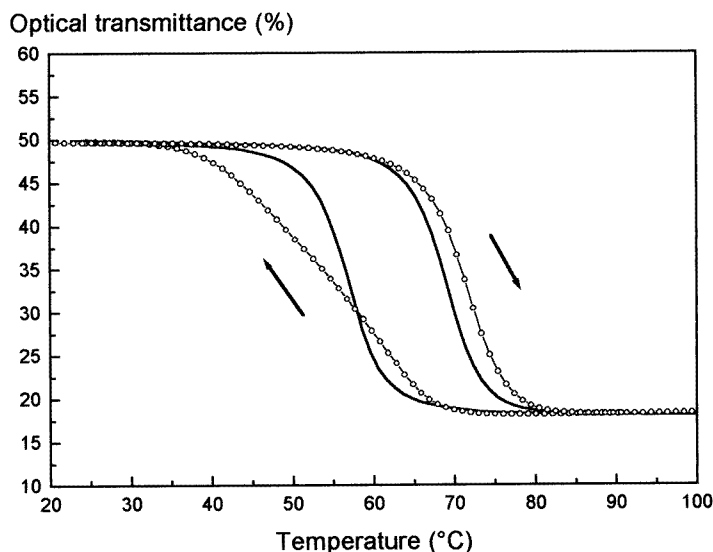

Figure 1. The optical hysteresis (transmittance versus temperature) for sample 1 (black curve) and sample 2 (open circles).

Sample 1 (V$_2$O$_4$ target) has a symmetrical hysteresis cycle, 10 °C wide, centred at 64 °C. Sample 2 (V$_2$O$_5$ target) has a clearly different hysteresis cycle: not only wider (15 °C at half of the transition), but also asymmetrical and centred at about 68 °C.

Classical XRD θ–2θ spectra did not show evidence of differences between the two samples, probably because these samples are too thin for investigation by this technique. That led us to choose a type of analysis better adapted to thin films—that is, grazing-incidence diffraction, carried out at LURE.

The in-plane diffraction scans are presented in figure 2. One clearly observes well-defined diffraction peaks for the two samples. The d-spacing distances of the corresponding crystallographic planes, in the monoclinic system, are summarized in table 1. The measured distances are in good agreement with the international data for powders (JCPDS). In order to compare the two samples, the spectra have been normalized so that we have the same intensities for the principal peak (011) at $2\theta = 24.7°$. It appears that the intensity distribution between
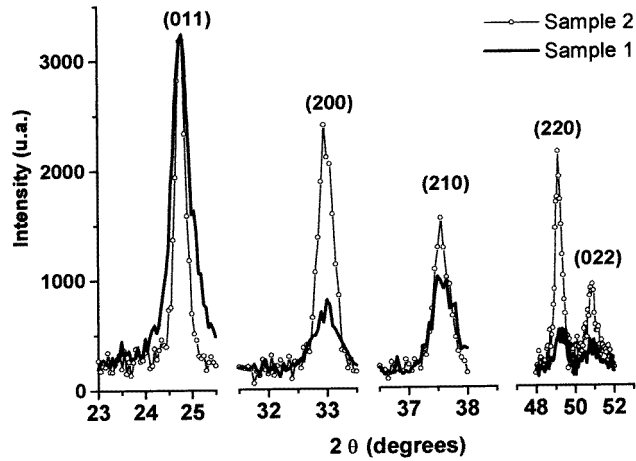
Figure 2. Diffraction peaks in the monoclinic phase, obtained by grazing-incidence x-ray diffraction experiments. The spectra have been normalized so that their intensities are the same for the principal peak (011).

Table 1. Atomic distances and crystallographic planes, deduced from grazing-incidence x-ray analysis, and comparison with the international powder diffraction data (JCPDS). All atomic distances are in Å.

Plane	(011)	(200)	(210)	(220)	(022)
Sample 1	3.2176 ± 0.0007	2.4322 ± 0.0007	2.1430 ± 0.0005	1.6556 ± 0.0006	1.6064 ± 0.0010
Sample 2	3.2203 ± 0.0007	2.4325 ± 0.0002	2.1449 ± 0.0003	1.6597 ± 0.0002	1.6084 ± 0.0005
JCPDS	3.200	2.428	2.141	1.656	1.600

the peaks is different for the two samples. In particular, the (200) and (220) peaks are more intense for sample 2, indicating a difference between the crystallite orientations of the two films.

This assumption is clearly confirmed and augmented by the results shown in figure 3, which presents the intensity distribution measured by the PSD over an 11° out-of-plane range, for each horizontal diffraction peak, i.e. portions of diffraction rings. This figure allows us to understand the difference between the two samples. Our films are polycrystalline. For a sample constituted of perfectly disoriented small crystals, which is equivalent to a powder, one obtains homogeneous diffraction rings. This is the case for sample 2, since all of the portions of the diffraction rings are homogeneous. In contrast, for sample 1 the diffracted intensity is inhomogeneous. The maximum of the intensity occurs in the in-plane orientation for the (011), (210) and (022) rings, and is out of the plane for the (200) and (220) rings. When considering the monoclinic structure of VO_2, one deduced, without any ambiguity, that such a distribution corresponds to a preferred orientation of the crystallites, with their (011) crystallographic planes parallel to the surfaces of the films.

Moreover, the diffraction peaks give us further information. The peak width is linked to the apparent crystallite size by the Scherrer formula:

$$L = K\lambda/(\Delta(2\theta)\cos\theta).$$

K is a form factor, generally taken as equal to 1. λ is the wavelength of the x-ray beam and 2θ the diffraction angle. L, the deduced crystallite size, represents the average size of an elementary homogeneous crystal, along the direction parallel to the substrate. The diffraction
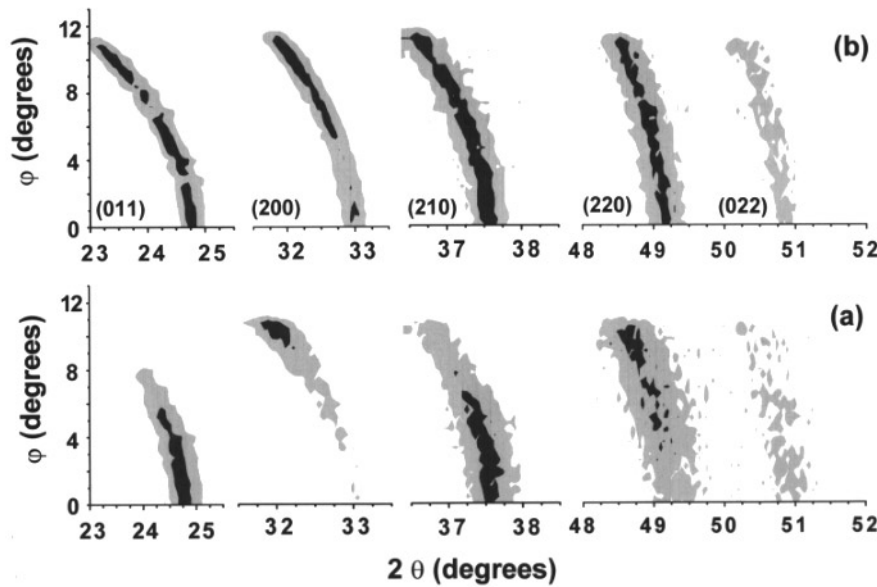
Figure 3. Portions of diffraction rings in the monoclinic phase, obtained in grazing-incidence x-ray diffraction experiments for (a) sample 1 and (b) sample 2. 2θ is the in-plane angle and φ is the out-of-plane angle. Black regions indicate more intense diffraction signals and grey regions indicate less intense diffraction signals.

peak widths for sample 1 are larger than those for sample 2. The average crystallite size is estimated to be 190 Å for sample 1 and 360 Å for sample 2.

4. Discussion

As deduced from the analysis of the θ–2θ scans, the diffraction rings clearly indicate that sample 1, with symmetrical and narrow hysteresis, exhibits a texture. In contrast sample 2, with asymmetrical and larger hysteresis, contains totally disoriented crystallites. In the preferred-orientation case, the (011) crystallographic planes are preferentially parallel to the surface of the thin film. These planes are the ones exhibiting the highest atomic densities in VO$_2$. This result is therefore not surprising, since this orientation usually occurs when a texture will appear without any epitaxial relation with the substrate. The link between the texture and the width of the hysteresis can then be understood. The VO$_2$ crystallographic transition from the monoclinic to the tetragonal structure is due to a slight displacement of the vanadium atoms along the c_r-axis. So there is a preferred direction of atomic displacement, although there is only a very small variation in volume between the two states [10]. In fact, this is a cooperative phenomenon. Hence, we suggest that the presence of a texture induces an increase in the cooperativity of the phenomenon, both from the structural and from the electronic point of view. We think that there is a better dissipation of the internal stress. This is consistent with the fact that single crystals [11] and samples grown by laser ablation, which exhibit perfect epitaxy [12], show only a 1 °C hysteresis width. Therefore the texture certainly influences the origin of the width of the hysteresis, but we still do not understand the asymmetry of the optical hysteresis. Haidinger and Gross [13] have also reported anomalous cooling branches for the hysteresis of samples deposited on glass by CVD. They show symmetrical hysteresis

for samples with (011) texture, as we observed, and asymmetrical hysteresis for samples with an additional (012) texture. We did not find any additional texture in our films. On the other hand, Beteille [14] suggests that the (011) texture, for samples prepared by a sol–gel technique, leads to wider and irregular hysteresis.

We do not think that the crystallite size is a determining parameter of the transition, since we find that sample 1, which exhibits a narrower hysteresis cycle than sample 2, has a smaller average crystallite size. This contradicts the usual observation that the wider the homogeneous regions of the sample are, the closer the sample is to exhibiting the characteristics of a single crystal, i.e. a narrow hysteresis cycle.

5. Conclusions

Thin films of VO_2 have been successfully obtained by reactive RF sputtering, from V_2O_4 and V_2O_5 targets. In order to understand their different optical hystereses, we mainly used grazing-incidence x-ray diffraction results obtained at LURE. We argued that both the width and the symmetry of the hysteresis clearly depend on the microstructure of the films. We found that a (011) texture seems to be favourable for producing a narrow and symmetrical hysteresis, while totally disoriented crystallites lead to wider and asymmetrical hysteresis. The improvement of the hysteresis certainly comes from an increase in the cooperativity of the phenomenon responsible for the transition in textured samples.

Acknowledgments

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