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SUBSTRATE EFFECT ON STRUCTURAL, MICROSTRUCTURAL AND ELEMENTAL MICROCOMPOSITION OF VANADIUM DIOXIDE THIN FILM

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ABSTRACT

Vanadium dioxide (VO2) is a phase change material with a metal-insulator transition (MIT), occurring around 68°C with several order of change in its electrical resistance. In this work, structural and microstructural studies have been carried out in order to understand the substrate effect on VO2 crystallographic growth properties as well as on transition quality. VO2 thin films were deposited by pulsed laser deposition (PLD) technique on a 2 µm thick oxide SiO2 buffer layer for the first sample (VO2/SiO2/Si) and on a 200 nm thick gold buffer layer for the second sample (VO2/Au). Microstructural and microcomposition analysis were performed using scanning electron microscopy and related energy dispersive X-ray analyses (SEM-EDX). Results show a variation in VO2 grain shape depending on the substrate type. "Trapezoid-like" shape grains are covering the surface of gold (Au) thin layer, and elongated shape "nanoplatelets-like crystals" are covering the (VO2/SiO2/Si) surface due to a preferential 2D layered growth. In addition, the structural characterizations show that VO2 deposits promote a preferential growth direction of (011). The substrate type strongly affects the VO2 growth rate. This work could help the optimization of metal-insulator transition (MIT) materials quality that have many applications ranging from sensor devices that need sharp transition slope to storage devices requiring a large hysteresis width.

KEY WORDS

- Microstructure,
- Vanadium dioxide,
- SEM,
- EDX.

I. INTRODUCTION

Vanadium dioxide (VO_2) has recently interested many researchers around the world for both the scientific challenge to understand the complex mechanisms behind its ultrafast phase transition and the development of potential applications using VO_2 for innovative coatings, sensors, and devices [1-4]. VO_2 has a unique sharp resistivity change, with reversible temperature-driven insulator-to-metal transition (referred as MIT) occurring at moderate temperatures around 68°C [5-8]. This characteristic of sharp resistivity change at low temperature has made VO_2 a good candidate for resistive switching devices based on phase change [9-13]. Controlling the epitaxial quality, microstructures of vanadium dioxide thin films and understanding the metal-insulator transition behaviors are critical to novel device development [14-17]. In this paper, structural and microstructural studies on various substrates have been carried out in order to appreciate the effect of substrate on VO_2 growth properties as well as on transition quality and how to optimize this quality of MIT at the development stage.

II. EXPERIMENTAL

Our VO_2 thin films have been grown by Pulsed laser deposition (PLD) technique. This deposition method gives us the possibility to monitor several parameters such as temperature and pressure to obtain a good stochiometric quality of the deposited thin films [18-20]. Our interests focus on the substrate effect on both structural and microstructural properties of VO_2 thin films and the appreciation of elemental microcomposition.

To perform this study, we have deposited VO_2 on a substrate of silicon wafer Si (100) on which is deposited a layer of Au (111) with a titanium (Ti) adhesion layer and another silicon substrate with 2 µm thickness of oxide SiO_2 (Fig. 1). The silicon (Si) substrate is chosen based on its compatibility with CMOS technology. Concerning the gold (Au) substrate which is not compatible with the CMOS technology, we used it in order to show that with a metallic base the conductivity change and maybe other transition can occurs at lower temperatures "Mott-transition" compared with the other structure. The structural and microstructural characteristics of the films were studied by

X-ray diffraction (XRD) with a Bruker D8 Advance X-ray diffractometer using a Cu Kα (λ = 0,154 nm) radiation source, which determines the crystal orientation of the layer, and the grain size calculated from the full-width at half-height (FWHM) from the peak corresponding to the preferential orientation.

Microcomposition of the films were investigated by high-performance scanning electron microscope and energy dispersive X-ray (EDX)analysis with resolution of 133 eV to Mn Kα using an FEI Quanta 650 scanning electron microscope. Using the spectral EDX analysis, we investigated the composition of the thin films, and we have found the approximate concentration of each element. The thickness of the deposited VO_2 thin films was also measured by SEM FEI Quanta 650 where granular structure of the film was taken into account.

Fig. 1 : Schematic of the deposited VO_2 thin films.

III. RESULTS AND DISCUSSIONS

1. Structural characterizations

a. SEM Analysis

Figure 2 shows a granular aspect of the surface morphology with a grain size around 70-80 nm with an apparent trapezoid-like shape of the grain for the VO_2 growth on gold (Au).

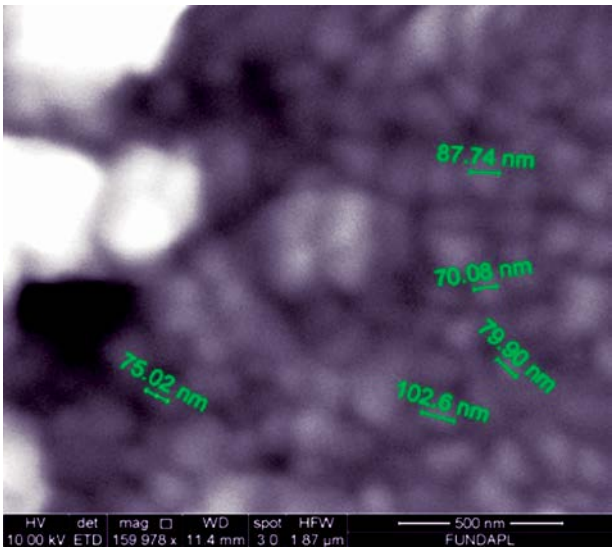

Fig. 2 : Morphological aspect by SEM (VO_2/Au) sample.

On the other hand, there is a difference in the shape of VO_2 grain growth on Si (see Fig. 3), the shape is rather elongated compared to VO_2/Au grains [20]. The monocrystalline appearance on Si affects the microstructure by promoting 2D growth [20].

In our case of textured layers, this gives rather nanoplatelets-like crystals grains in the preferential direction of growth with a grain size approximately around 70-90 nm in width and around 500 nm in length [20, 21].

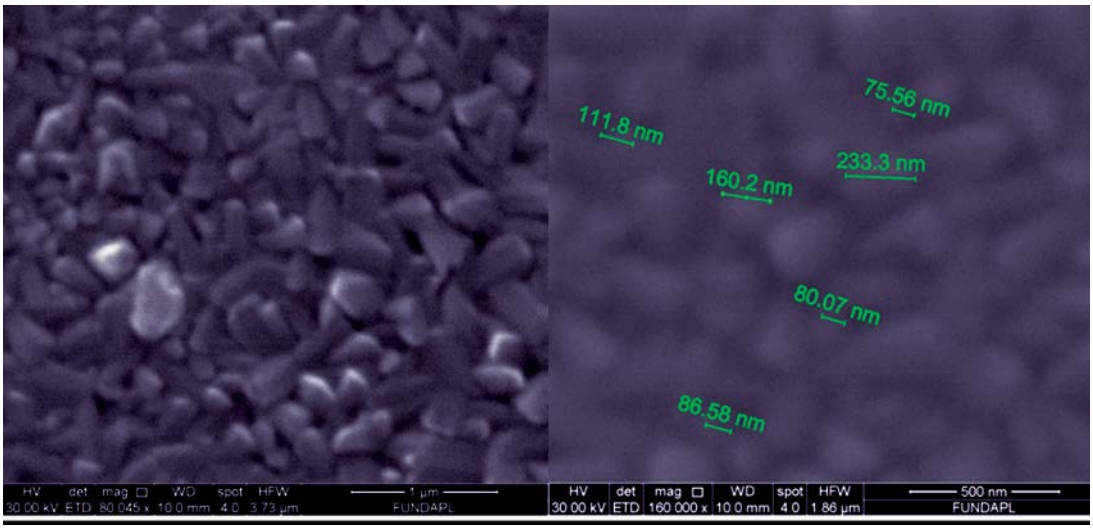

Fig. 3 : Morphological aspect by SEM (VO_2/SiO_2/Si) sample.

b. XRD Analysis

For both samples (VO_2/Au) and (VO_2/SiO_2/Si), X-ray diffraction (XRD) was performed to determine whether our deposits corresponds to pure vanadium dioxide VO_2 phase and to appreciate the quality of growth. Fig. 4 shows XRD pattern performed on the (VO_2/Au) sample.

This sample has a most apparent peak at about 2θ = 28,008° and a width (Full Width at Half Maximum) of about $W_{h/2}$ = 0,326° which is attributed to the monoclinic phase of VO2 corresponding to the orientation (011) [22]. It is important to note that the position of the peak is slightly different from that of the «theoretical» one which is positioned at 27,878°. This shift is probably caused by the lattice mismatch between the VO_2 films and the substrates. Also, the interplanar distances vary.

This causes a change in the position of the peaks. By measuring the displacements of the peaks, deformation of the lattice can be deduced, therefore also the residual stress in the material. For the samples grown on Silicon Si (100) with a 2 µm thickness of oxide (SiO_2) (see Fig. 5), we find that the most dominant peak is approximately around 2θ = 28,043° which is also attributed to the monoclinic

phase of VO_2 corresponding to the (011) orientation [22]. The value of 2θ is also shifted.

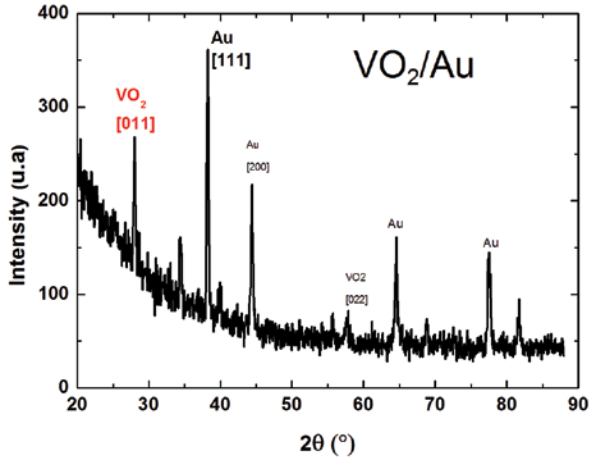

Fig. 4 : XRD patterns of (VO2/Au) deposited film.

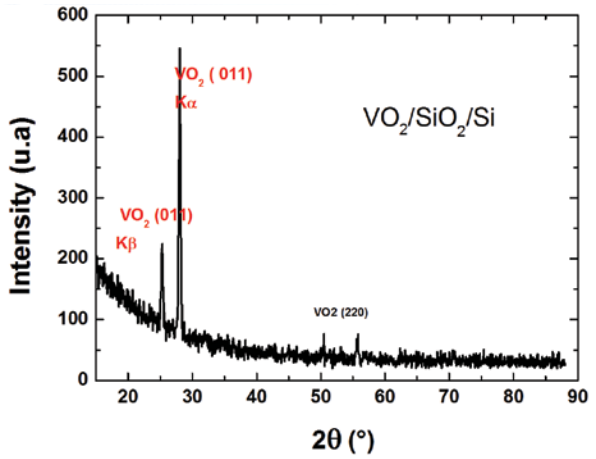

Fig. 5 : XRD patterns of (VO2/SiO2/Si) deposited film.

In order to evaluate the average size of the crystallites D, we used the Scherrer formula [23] :

$$D = \frac{0,9\lambda}{w\cos\theta}$$

Where w is full width at half maximum, (FWHM) of the diffraction line which is calculated by an interpolation around $2\theta = 28,007°$ using a pseudo-Voigt1 function by ORIGIN (see Fig. 6). λ is the wavelength $Cu_{K\alpha}$ equal to 1,5406 Å and θ The Bragg angle corresponding to the peak (011) of VO_2.

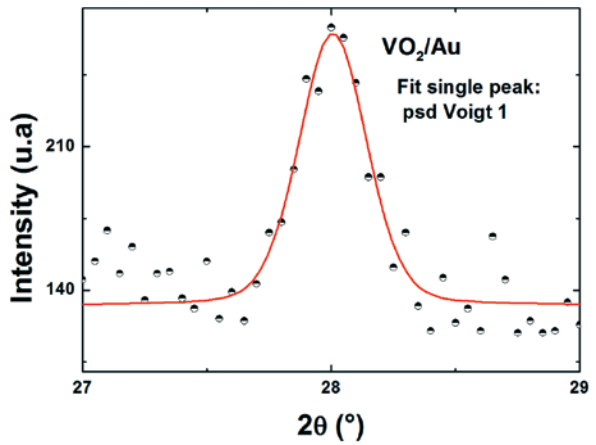

Fig. 6 : Example of an interpolation around 2θ = 28,007° by pseudo-Voigt1 function sample (VO_2/Au).

The value of D is about 25 nm for the (VO2/Au) sample and about (26-25) nm for the (VO_2/SiO_2/Si) sample. The difference between the grain size measured by XRD and SEM is due to the fact that DRX gives the elementary grain size while de SEM gives a coalescence of several grains.

2. Microanalysis

An elementary chemical microanalysis by the EDX (Energy Dispersive X-ray) method was carried out in order to perform a quantitative elemental analysis of samples surface. This allow to investigate thin films composition and thus deduce the approximate concentration of each element. Energy Dispersive Spectroscopy (EDS) allows to identify what those particular elements are and their relative proportions (Atomic % for example). Initial EDS analysis usually involves the generation of an X-ray spectrum from the entire scan area of the SEM. Below is a secondary electron image of specimens and the corresponding X-ray spectra that was generated from the entire scan area. The Y-axis shows the counts (number of X-rays received and processed by the detector) and the X-axis shows the energy level of those counts. The EDS software associates the energy level of the X-rays with the elements and shell levels that generated them. In the EDS spectra of Fig. 7 and Fig. 8, we can notice the presence of atoms of the deposited element, vanadium as well as oxygen.

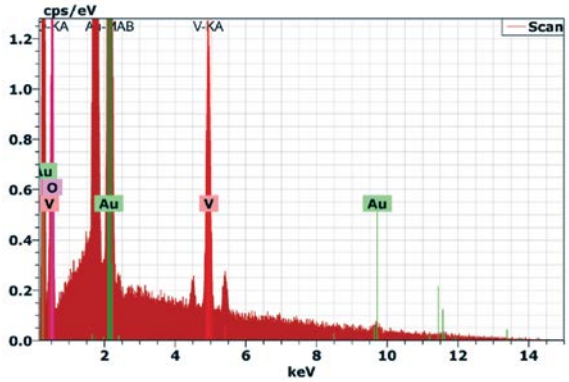

Fig. 7 : EDS Spectrum of (VO2/Au) Sample.

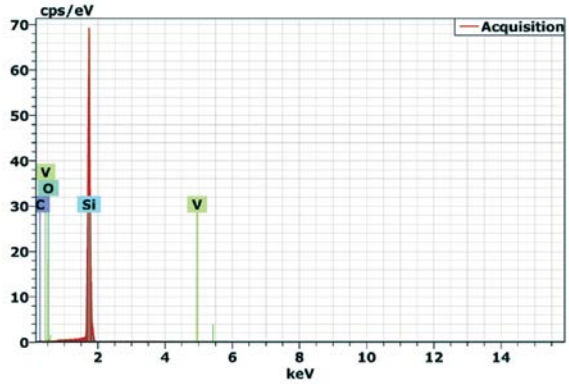

Fig. 8 : EDS Spectrum of (VO_2/SiO_2/Si) Sample.

3. Thickness measurement

SEM observations were made on cross sections. These cuts are easy to make on deposits having as base silicon substrate. These observations make it possible to measure the thickness of deposited layers as well as to observe the morphology of their growths.

Fig. 9 shows a cross-section of (VO_2/Au) sample. We can observe four parts of different contrasts, starting from the right. The first is identified as the silicon substrate, a second layer of SiO_2 with a dark contrast whose thickness is estimated about 450 nm, followed by a third layer with a brighter contrast which corresponds to the gold (Au) electrode with a thickness of about 200 nm and finally a fourth layer of VO_2 with a thickness of about 500 nm.

To confirm the thickness measurement, we plotted the EDS analysis profile of the elements along the thickness for (VO_2/Au) sample (we are interested in vanadium). We note that the thickness of the VO_2 in this case is estimated to be around 500nm (see Fig. 10) which coincides with the measurements made by the SEM.

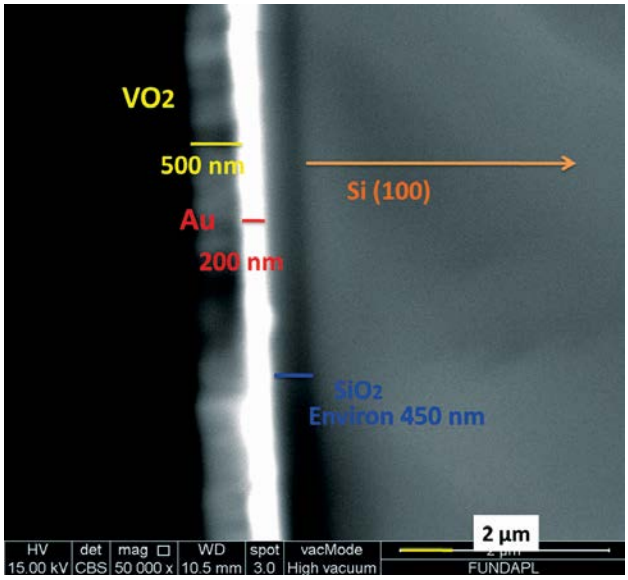

Fig. 9 : SEM image of (VO_2/Au) cross-sections.

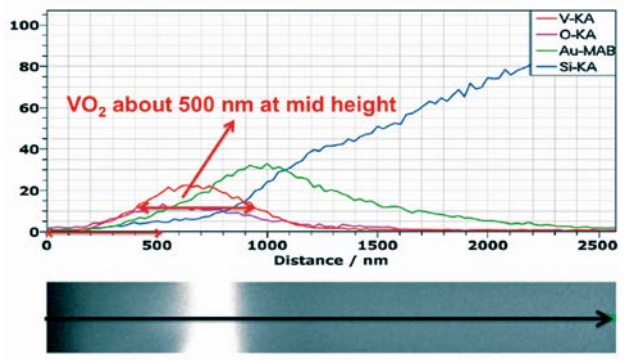

Fig. 10 : EDS analysis profile of the elements along the thickness of the deposited layers, (VO_2/Au).

Fig. 11 shows a SEM image of a (VO_2/SiO_2/Si) sample cross-section. We can clearly see that the thickness of the VO_2 layer is estimated to be about 750 nm, followed by a 2 µm thick of thermal silicon dioxide and the bulk silicon substrate Si (100).

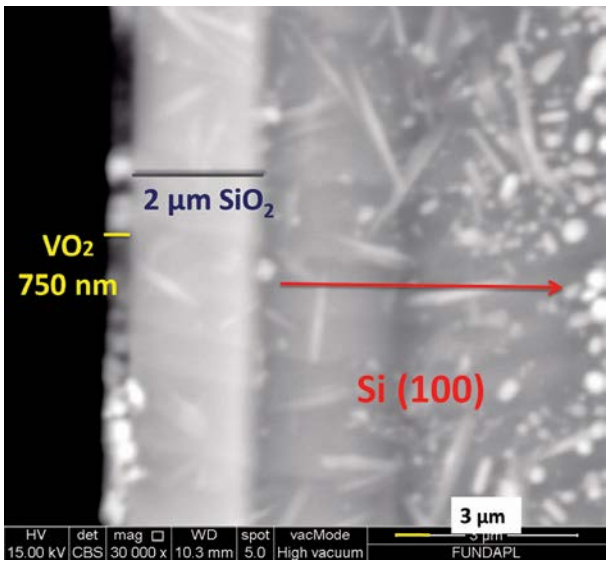

Fig. 11 : SEM images of VO_2/SiO_2/Si (100) cross-sections.

IV. CONCLUSION

A VO_2 thin film has been elaborated using PLD technique. We have used two different buffer layers SiO_2 and Au to study the effect of substrate on structural and microstructural properties. This study was investigated using scanning electron microscopy and related energy dispersive X-ray analyses (SEM-EDX). In conclusion, we have noticed that VO_2 grains change shapes depending on the substrate type. For vanadium dioxide grains grown on gold Au (111) thin layer, a trapezoid-like shape with size about 70-90 nm were obtained. VO_2 grains shape grown on silicon oxide (SiO_2) are more elongated. They are nanoplatelets-like in shape due to a preferential 2D growth in the case of silicon substrate with a grain size approximately around 70-90 nm for the width and around 500 nm for the length. In addition, structural characterizations show that our VO_2 deposits promote a preferential direction which is (011). Finally, we can conclude that substrate type strongly affects the VO_2 growth rate ; hence the obtained vanadium dioxide thickness value. Indeed, the better crystal quality of the film is, the better transition's properties are.

V. ACKNOWLEDGMENT

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