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Structural and optical properties of vanadium oxides prepared by microwave-assisted reactive magnetron sputtering

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In this work, structural and optical properties of vanadium oxides have been presented. Thin films were manufactured by microwave-assisted magnetron sputtering process. Particles were sputtered from a vanadium target in Ar/O_2 atmosphere. Oxygen partial pressure was changing from 3×10^{-4} to 7×10^{-4} Torr. After the deposition, the thin films were additionally annealed at 400 °C in ambient air in order to oxidize the films.

Structural investigation was performed with the aid of X-ray diffraction measurements and Raman spectroscopy. The results obtained from both methods have revealed that as-deposited films were amorphous, while annealed films had V_2O_5 crystal form. Optical properties were determined by transmission measurements in the spectral range from 250 to 2500 nm. As-deposited films had low transmission (below 10%), but oxidization by additional annealing of the structure resulted in the increase of the transmission level up to about 20 and 43% at 650 nm wavelength for samples prepared under 3×10^{-4} and 7×10^{-4} Torr oxygen partial pressure, respectively. The analysis of the structure and optical properties of the thin films has revealed the influence of deposition parameters on the properties of vanadium oxides.

Keywords: vanadium oxide, sputtering, structural properties, optical properties, annealing.

1. Introduction

Transition metal oxides have been a subject of research in recent years in view of their fundamental and technological aspects. Among these, vanadium creates many compounds with oxygen; these have different structural, optical and chemical properties.

Meaningful differences between the properties of different phases of vanadium oxides like VO, VO_2, V_2O_3 and V_2O_5 depend on their structure, which determines other properties. Different forms of vanadium oxides can be obtained by changing the deposition process parameters, or by post-process treatment, *e.g.*, additional annealing. From the application point of view, the most interesting vanadium oxides are VO_2 and V_2O_5. Vanadium dioxide is a very good candidate for thermochromic coatings due to the change of properties from semiconducting to semimetal at 68 °C. Vanadium pentoxide (V_2O_5) is a thermodynamically stable form which exhibits electrochromic properties. V_2O_5 thin films can also be used in optical filters, reflectance mirrors, smart windows and surfaces with tunable emittance for temperature control of space vehicles [1]. It can be received by selecting deposition parameters or by the annealing of VO_2 above 350 °C.

Thin films of vanadium pentoxide can be prepared by various methods, such as sputtering [2], thermal evaporation [3], pulse laser deposition [4], sol–gel [5], e-beam deposition [6], *etc*. Properties of the V_2O_5 films are strongly dependent on the method of their synthesis, due to the fact that V_2O_5 loses oxygen when is heated in vacuum or in reductive atmosphere. This causes partial dislocation and oxygen removal from the V_2O_5 lattice, which results in the formation of defects or in a reduced phase in the resulting layers.

In this work we have studied the structural and optical properties of V_2O_5 thin films deposited onto glass substrates by d.c. reactive magnetron sputtering. The results obtained from X-ray diffraction (XRD), Raman spectroscopy and transmission measurements are presented and connected with different O_2 partial pressure controlled during sputtering deposition.

2. Experimental details

Vanadium oxide films with the thickness of 200 nm were deposited from a vanadium target on chemically – and ultrasonically – cleaned fused silica substrates by magnetron sputtering with a microwave source to improve the plasma ionization. The pre-cleaning in reactive microwave oxygen plasma was performed for 15 minutes. In this project, a MicroDyn® 4000 apparatus equipped with Advanced Energy MDX 10 power supply with Sparkle V arc controller and with plasma source was used [7, 8]. The target was a high purity (above 99.99%) vanadium plate (127×380 mm). The target-to-substrate distance was approximately 122 mm. The substrate holder was rotated with the speed of 1 cycle per second. The cathode was water-cooled.

Sputtering was done in plasma containing mixture of Ar–O_2 gases, at two different partial pressure of oxygen: 3×10^{-4} (S1 – sample 1) and 7×10^{-4} Torr (S2 – sample 2). The total gas pressure was kept at about 4.2×10^{-3} Torr. Pressures of argon (working gas) and oxygen (reactive gas) were controlled by flow mass controllers. The d.c. power during the film deposition was about 4 kW. The deposition time was 40 min. After the deposition process, the manufactured films were oxidized at 400 °C for 2 hours in ambient air to form V_2O_5 phase. The thickness of the prepared thin films

T a b l e 1. Details of sputtering process during vanadium oxide films fabrication.

Deposition parameters	
Voltage [V]	450
Current [A]	8.5
Microwave power [kW]	4
Oxygen partial pressure [mTorr]	0.3
Deposition rate [Å/s]	0.8

was measured during the deposition process with Coat Monitor software, which was based on optical monitoring of samples. This system allows to precisely control the film thickness during the deposition process. The deposition conditions are listed in Tab. 1.

The film structure was determined by X-ray diffraction (XRD) analysis using a Rigaku diffractometer with a Cu-filtered Kα source. The phase identification based on XRD diffraction data was made with the help of Joint Commission on Powder Diffraction Standards (JCPDS) database (no. 77-2418 for V_2O_5). Raman spectroscopy was recorded by a Nicolet Almega XR dispersive raman spectrometer equipped with an optical microscope at room temperature with an excitation of the argon ion laser (476.5 nm). Optical transmissions of the films were measured in the spectral range from 250 to 2500 nm by a PerkinElmer Lambda 900 spectrophotometer system with tungsten and deuterium lamps as light sources.

3. Results and discussion

Directly after the deposition, the vanadium oxide films were amorphous. After the deposition, the additional annealing at 400 °C in ambient air was applied in order to oxidize and form crystalline structure. Structural analysis of the annealed films

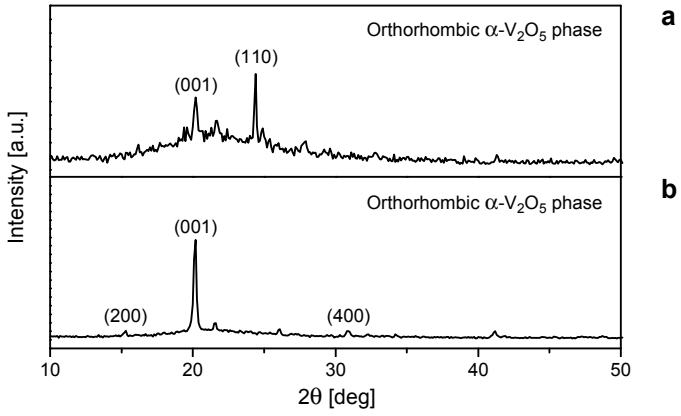

Fig. 1. XRD patterns of annealed (400 °C) vanadium oxides deposited at: 3×10^{-4} Torr (**a**) and 7×10^{-4} Torr (**b**) of oxygen partial pressure.

based on XRD measurements (Fig. 1) reveals V_2O_5 phase. Signed peaks for S1 and S2 films were located at $2\theta = 20.2°$, 24.4°, 15.4° and 30.9° and corresponded to the (001), (110), (200) and (400) reflections, respectively, of the orthorhombic α-V_2O_5 phase according to the JCPDS file (no. 77-2418). Thermal oxidation of vanadium oxides causes an increase in atoms energy, which results in higher mobility. Finally, it induces recrystallization and an increasing order of the structure.

The crystallite size, *D*, determined from the XRD measurements by Scherrer's formula, takes the value of about 52 and 33 nm for S1 and S2 samples, respectively. As it can be seen in Tab. 2, the crystallite size decreases (of about 40%) when oxygen partial pressure during the deposition process increases from 3×10^{-4} to 7×10^{-4} Torr. The interplanar spacing, *i.e.*, the *d* value of the films, was calculated from the position of the most intense peak using Bragg's law. The obtained films revealed a larger *d* value in comparison to standard data in the Powder Diffraction File (PDF), which was due to the tension stress developed in the films.

The Raman spectra of S1 and S2 samples after the heat treatment process at 400 °C (Fig. 2) also reveal V_2O_5 phase and confirm the XRD results. The change in the molecular polarizability associated with the vibrational mode of the molecule causes the Raman shift and gives useful information about the structure in the form of

T a b l e 2. Structural properties of vanadium oxide thin films annealed at 400 °C.

Sample	*D* [nm]	*d* [nm]	Type of stress
S1, annealed at 400 °C	51.9	0.36455 $d_{PDF} = 0.34045$	Tension
S2, annealed at 400 °C	33.0	0.43942 $d_{PDF} = 0.4368$	Tension

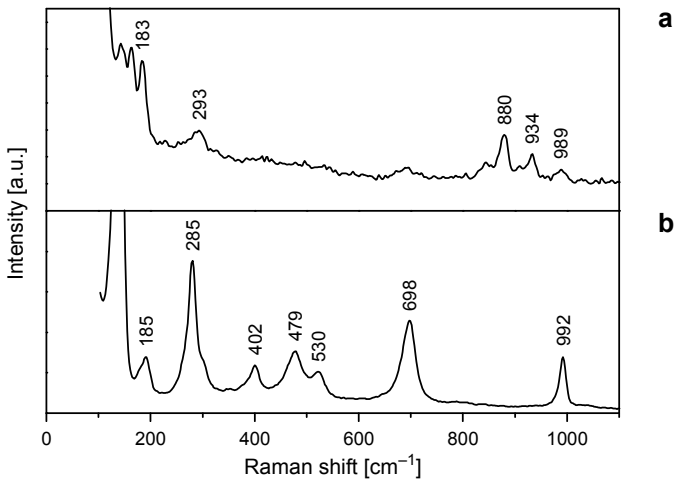

Fig. 2. Raman spectra of annealed (400 °C) vanadium oxide thin films prepared with different partial pressure of O_2: 3×10^{-4} Torr (**a**), and 7×10^{-4} Torr (**b**). Used laser excitation was 476.5 nm.

different type of vibrations. The layered-like structure of crystalline α-V_2O_5 is built up from VO_5 square pyramids shearing edges and corners [9]. The peaks located at 183 and at 185 cm^{-1} can correspond to lattice vibration. The two peaks located at 285 and 402 cm^{-1} are assigned to the bending vibration of the V=O bonds [10]. The peak located at 479 cm^{-1} is assigned to the bending vibrations of the bridging V–O–V (doubly coordinated oxygen). The peak at 530 cm^{-1} is assigned to the triply coordinated oxygen (V_3–O) stretching mode which results from edged-shared oxygens in common to three pyramids. The other peak at 698 cm^{-1} is assigned to the doubly coordinated oxygen (V_2–O) stretching mode which results from corner-shared oxygens common to two pyramids [10]. The presence of these vibrations indicates the layer--like structure of V_2O_5 films. The peak located at 938 cm^{-1} might be attributed to the Raman active mode of VO_2 [11]. The V^{4+}=O bonds are due to a direct conversion from V^{5+}=O bonds and/or breaking of the single oxygen bonds involving V^{4+} ions. The peaks located at 989 and 992 cm^{-1} correspond to the terminal oxygen stretching mode which results from the unshared oxygen [12].

Raman peaks located at 293 and 880 cm^{-1} do not correspond to any Raman peak published in the literature [13]. MANNING and PARKIN [13] have suggested that those peaks do not correspond to V_2O_5 or V_6O_{13} and may be due to a phase of vanadium oxide not yet detected by X-ray diffraction measurements.

Transmission spectra of the annealed samples have been presented in Fig. 3. The results have shown that as-deposited films have low transmission (in VIS range: 5% and 13% for S1 and S2 films, respectively; in NIR range the average value was 42% and 62% for S1 and for S2 sample, respectively). Additional annealing at 400 °C results in an increase of transmission level for both samples in the whole spectral range. The transmission level rises up to: 20% and 43% in VIS range and 58% and 72% in NIR range, for S1 and for S2 thin films, respectively. The increase of transmission of

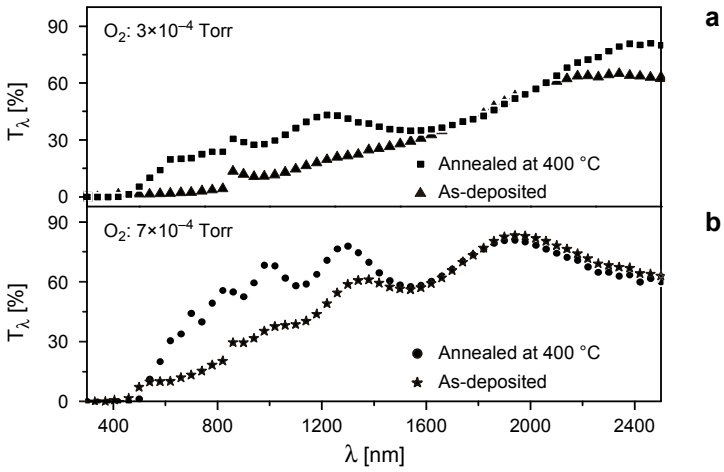

Fig. 3. Optical transmission spectra of as-deposited and annealed (400 °C) vanadium oxide thin films prepared in different partial pressure of O_2: 3×10^{-4} Torr (**a**), and 7×10^{-4} Torr (**b**).

vanadium thin film is caused by the oxidation and recrystalization of the film during the annealing in high temperature.

Additionally, for the annealed films, the optical band gap and refractive index have been calculated. The extrapolating of the absorption data gives the best linearization for the direct forbidden transition. The evaluated optical band gaps for the S1 and S2 films are very similar and equal 2.37 and 2.35 eV. Obtained results are comparable with the values reported by several authors [14, 15]. The refractive index (determined at 650 nm) for the films prepared at different oxygen partial pressure has a value between 2.62 and 2.45 for S1 and S2 samples, respectively. These values are a bit higher than the values reported by other authors [16, 17]. It could be observed that the packing density is related to the refractive index. The refractive index shows a considerable decrease. The packing density decreases when the sputtering pressure is increased from 3×10^{-4} to 7×10^{-4} Torr.

4. Conclusions

In this work, optical and structural investigations of vanadium oxide thin films have been presented. Thin films were manufactured by plasma enhanced reactive magnetron sputtering process under different oxygen partial pressure, 3×10^{-4} and 7×10^{-4} Torr. The XRD measurements and Raman spectroscopy revealed amorphous nature of as-deposited thin films. Additional post-process annealing in ambient air, at 400 °C for 2 hours, results in the recrystallization of the film. It has been found that well--crystallized V_2O_5 can be obtained by controlling the sputtering pressure. As-deposited films were slightly transparent in visible light range and the transmission T_λ was increasing in near infrared light range up to about 40% and 60% for S1 and S2 films, respectively. The annealing of the films and oxidation effect result in the increase of transmission level.

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