Electrical and Optical Study of Transparent V-based Oxide Semiconductors Prepared by Magnetron Sputtering under Different Conditions

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Abstract. *This work is focused on structural, optical and electrical behaviors of vanadium-based oxide thin films prepared by magnetron sputtering under different conditions. Thin films have been deposited on glass substrates from metallic vanadium target at low sputtering pressure. Different working gases: argon/oxygen mixture, and especially pure oxygen gas, have been applied. Results of X-ray diffraction together with optical transmission and temperature-dependent electrical resistivity measurements have been presented. Transmission coefficient, cut-off wavelength and the width of the optical band gap have been calculated from optical measurements. The d.c. resistivity values at room temperature and thermal activation energy have been obtained from electrical investigations. The influence of sputtering process conditions on optical and electrical properties has been discussed.*

Keywords

Magnetron sputtering, vanadium oxide, optical properties, electrical properties.

1. Introduction

Nowadays, many new materials have been investigated for the purpose of their application in transparent electronics devices. Among them, oxides based on Ti, V and W turn out to be promising TOS (*Transparent Oxide Semiconductor*) candidates, along with other well known materials such as SnO_2, In_2O_3 or ZnO. Vanadium, as an element, creates many compounds with oxygen, resulting in materials with different structural, optical and chemical properties. Differences between various vanadium oxides depend on their structure which determines their specific properties [1-3].

In this paper, seven vanadium oxide thin films, manufactured by the magnetron sputtering process under different sputtering parameters, were researched with X-ray diffraction method, along with spectrophotometric and electrical investigations. The results were discussed according to the sputtering process parameters, under which each respective sample was created.

2. Fabrication of Thin Films

Physical vapor deposition and chemical vapor deposition methods are the most acknowledged optical coating fabrication methods. In the industry, pulsed laser deposition [4-6], ion plating [7] and magnetron sputtering [8-11] are among the most commonly used thin film deposition processes.

Special mechanical or optical properties of thin film coatings can be obtained in a variety of ways, depending on such factors as deposition parameters, the use of different material dopants and substrates. Moreover, in order to obtain the demanded ordered polycrystalline structure, additional post-process annealing can be applied [12].

Type of the structure obtained directly after the deposition is greatly affected by deposition parameters, such as: the type of deposited material, ion flux density and total energy of sputtered particles coming to the substrate, temperature at condensation site, density of impurity stream and, finally, the type of substrate along with its surface purity and structure.

Energy assigned to each particle of sputtered material plays a key role in the obtained material's structure. Low energy particles become immobilized directly after making contact with the surface of the substrate, resulting in porous structure, rarely usable from the point of view of electrical and optical properties of the coating.

The simplest way for raising particle energy in PVD methods is additional substrate heating, typically in 473 to773 K range. Additional thermal energy is enough for molecules to migrate on the substrate's surface, occupying lower potential energy sites. However, high temperature process may damage temperature-sensitive substrates. This problem can be overcome with an application of ion assisted deposition.

Another way is to perform sputtering process at low pressure. Therefore, the number of particle collisions in plasma can be reduced, increasing mean-free path; thus the energy of particles incoming to the substrate. Energy of the particles can be also changed by appropriate substrate polarization [13], influencing kinetic energy of ions coming from the target. Owing to different process modifications, structure of the deposited film receives extra energy, which results in high structure densification of the obtained thin film.

Sample	1	2	3	4	5	6	7
P (10^{-3} mbar)	1.8	3.5	2.9	3.1	2.4	3.4	3.0
W_g	O_2	Ar/O_2 (7/3)	Ar/O_2 (7/3)	O_2	O_2	O_2	O_2
S_p (kW)	1.3	0.40	1.14	1.16	1.14	1.17	0.23
S_t (K)	624	522	698	583	600	698	373
T_m	HT	CT	HT	HT	HT	HT	CT
S_b (V)	0	0	0	0	-27	-100	-100
Legend: P – pressure W_g – working gas S_p - sputtering power			S_t - substrate temperature T_m - Target mode S_b - Substrate biasing				

Tab. 1. Process conditions required the preparation of vanadium oxide thin films.

To allow the deposition process description by taking into account the different process parameters (temperature, pressure, flux density, substrate bias, etc.) mentioned above, a new parameter – total particle energy at the place of the thin film formation site – was introduced [14]. The total energy is a sum of particle kinetic and substrate thermal energy, as well as the energy coming from additional ions bombarding the substrate, what is required for chemical reactions, leading to the ordered structure growth of the thin film.

For the purpose of the investigations presented in this work, the influence of sputtering pressure, either Ar/O_2 mixture or pure O_2 as working gases, as well as sputtering power, substrate temperature and substrate bias on electrical and optical properties of vanadium pentoxide thin films have been studied. Additionally, hot target (HT) sputtering was introduced [15] and compared with standard cold target (CT) processes. Thin films were deposited on Corning 7059. The applied process parameters are listed in Tab. 1. All the thin films were prepared by sputtering of metallic vanadium target, 100 mm in diameter and the target to substrate distance was kept at 90 mm. The magnetron was powered with –1.5 kV in amplitude unipolar sinusoidal pulses. During the deposition processes of samples, the substrates were additionally heated.

3. Experimental Results

Structural investigation was performed with the aid of X-Ray Diffraction (XRD) method (Fig. 1). For measurements, Dron-2 powder diffractometer with CoKα filtration was used. After the deposition, samples 2–7 were well transparent and light yellow in color, what indicated their oxide nature. Sample 1 prepared at the lowest pressure (Tab. 1) of the pure oxygen was not transparent to visible light, what could be associated with its under-oxidation. This sample was then additionally annealed in air ambient at 873 K, what resulted in the thermal oxidation of the thin film.

XRD results of the prepared thin films are presented in Fig. 1. Sample 1 after the thermal oxidation displayed amorphous behavior and this result was not included in Fig. 1. XRD patterns recorded for samples 2-7 reveal the V_2O_5 microstructure. The details of structural parameters derived from presented XRD spectra are collected in Tab. 2. Application of pure oxygen (sample 4) resulted in 50 % decrease of the V_2O_5 crystallite sizes down to 9.4 nm as compared to the samples prepared with the use of Ar/O_2 mixture (samples 2 and 3), either with the application of CT or HT mode. Moreover, it also allowed the reduction of tension stress from +0.8 % down to +0.3 %. However, sputtering process in pure oxygen atmosphere with additional biasing (-27 V and -100 V) of the substrates resulted in the increase of crystallite size, again, up to about 17 nm. The same deposition conditions, but with the conventionally cooled target, resulted in the decreased crystallite size by 11 % down to 15.2 nm and the increased tension stress up to 0.8 %.

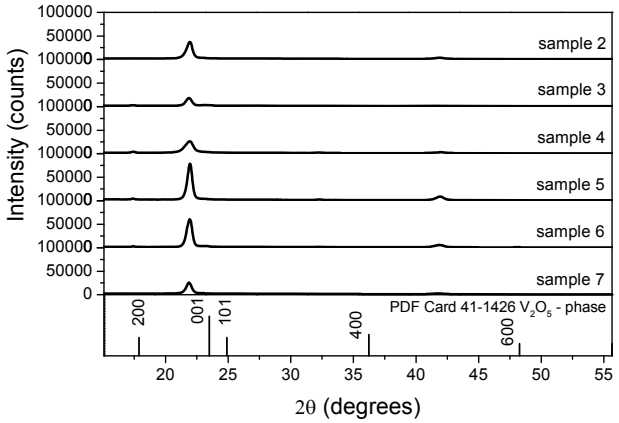

Fig. 1. XRD patterns of vanadium pentoxide thin films; at the bottom standard pattern for the V_2O_5 was included.

Sample	Phase	D (nm)	d_{PDF} (nm)	d (nm)	Δd (%)
1	amorphous	-	-	-	-
2	V_2O_5	14.8	0.4386	0.4403	+ 0.6
3		17.5		0.4420	+0.8
4		9.4		0.4400	+0.3
5		16.8		0.4400	+0.5
6		17.1		0.4403	+0.4
7		15.2		0.4420	+0.8
Legend: D – average crystallite size d – interplanar distance		d_{PDF} – standard interplanar distance $\Delta d = ((d-d_{PDF})/d_{PDF})\cdot 100$ %			

Tab. 2. XRD investigation results of vanadium oxides sputtered under different conditions.

For the purpose of optical properties investigation of the prepared vanadium pentoxide thin films transmission,

coefficient measurements were carried out over the 200 – 1000 nm optical range. Measurement apparatus consisted of Ocean Optics scientific grade QE65000 spectrophotometer and a coupled deuterium-halogen light source for UV-VIS illumination. Recording of transmission charts (Fig. 2) allowed the determination of the position of fundamental absorption edge (λ_{cutoff}) and the width of optical band-gap (E_g^{opt}) [8].

Sample 1 (Fig. 2a), since it was fabricated in near metallic-transition, directly after deposition was not transparent at all. After post-process additional oxidation, it became quite well transparent and yellowish in color. Fig. 2b presents transmission charts recorded for the remaining oxide samples. All of them were well transparent for the visible light with an average transmission at the level of 70 – 80 %. Visible minima and maxima are due to the interference effect occurring at the optical interfaces: thin film – air and thin film – substrate. Higher transmission observed in the samples 2 and 7 is due to lower light absorption in these thin films testified by their lower thickness; it should not be considered as a material property. For many oxide thin films the run of absorption characteristics near absorption edge obeys the well known Tauc relation. Most optical studies performed by others for V_2O_5 showed a good fit to experimental data with a direct forbidden or direct allowed in nature optically induced electronic transitions. The results calculated for the vanadium pentoxide thin films considered in this work have been collected in Tab. 3. All derived values are very close to each other for each sample, and they are similar to those reported in the literature, e.g. [16], [17].

Sample	Thickness (nm)	$T_{\lambda=550nm}$ (%)	λ_{cutoff} (nm)	E_g^{opt} (eV)
1	6500	38	440	2.45 (direct allowed) 1.99 (direct forbidden)
2	280	74	464	2.47 (direct allowed) 2.26 (direct forbidden)
3	700	64	485	2.43 (direct allowed) 2.21 (direct forbidden)
4	550	62	478	2.42 (direct allowed) 2.25 (direct forbidden)
5	600	60	489	2.45 (direct allowed) 2.24 (direct forbidden)
6	742	63	488	2.44 (direct allowed) 2.22 (direct forbidden)
7	160	80	454	2.43 (direct allowed) 2.24 (direct forbidden)

Tab. 3. Optical parameters obtained from transmission measurements for V_2O_5 thin films deposited on glass substrates under different conditions.

The study of electrical properties of V_2O_5 thin films was carried out through d.c. resistivity measurements performed at temperature range 300 – 420 K with the use of Keithley's semiconductor characterization system, type 4200-SCS. Based on the slope of $\log(\rho) = f(1000/T)$ chart, thermal activation energies E_ρ have been calculated using the exponential Arrhenius formula [18] (Fig. 3). All derived values were in 0.198-0.248 eV range. The detailed data has been shown in Tab. 4.

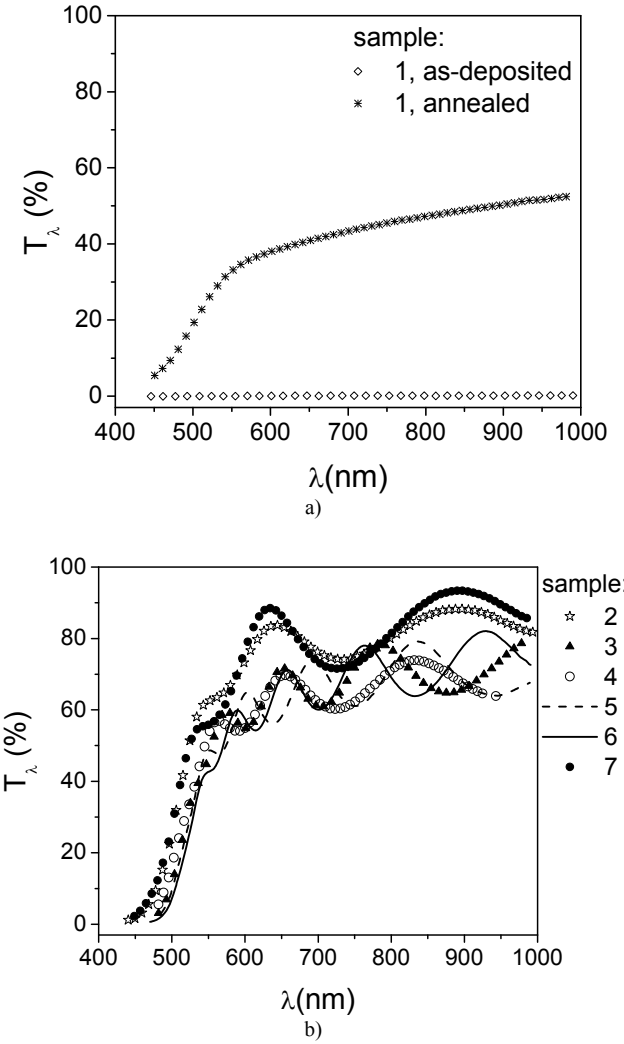

Fig. 2. Transmission of V_2O_5 thin films fabricated: a) by using the thermal oxidation and b) in Ar/O_2 mixture and pure O_2 working gases under different process conditions.

Sample	ρ_{300K} (Ωcm)	E_ρ (eV)
1	$1 \cdot 10^8$	0.215
2	$4.8 \cdot 10^3$	0.227
3	$2 \cdot 10^2$	0.237
4	$5.3 \cdot 10^1$	0.204
5	$1.3 \cdot 10^2$	0.248
6	$4{,}5 \cdot 10^2$	0,198
7	$1.5 \cdot 10^1$	0.204

Tab. 4. Electrical parameters determined from thermoelectrical measurements for V_2O_5 thin films deposited on glass substrates under different conditions.

The comparison of electrical resistivity derived for each sample we now follow with the preparation process conditions (Tab. 1). The highest resistivity (nearly of an insulating materials) at the level of 10^8 Ωcm was recorded for the sample 1 prepared by thermal oxidation (Fig. 3a). The sample 2, prepared by using typical CT sputtering process, displayed semiconducting properties and its resistivity at room temperature was at the order of 10^3 Ωcm. Application of the HT mode (sample 3) resulted in about

one order lower resistivity of the prepared V_2O_5 thin film. Further, almost one order lower resistivity was recorded for the sample 4 prepared with the application of both the HT and oxygen only as a reactive and working gas. However, the application of substrate polarization with the negative substrate biasing (samples 5 and 6) resulted, in turn, in the increased thin films resistivity. In Fig. 3b temperature dependent resistivity plots recorded for the sample 6 (HT, U_{bias}= -100 V) and for the sample 7 (CT, U_{bias}= -100 V) have been compared. What is more, during the deposition process of sample 7, the substrate was heated to lower (373 K) temperature than it was in case of all other samples. As it could be observed, that sample had the lowest resistivity of all of the prepared thin films (Tab. 4).

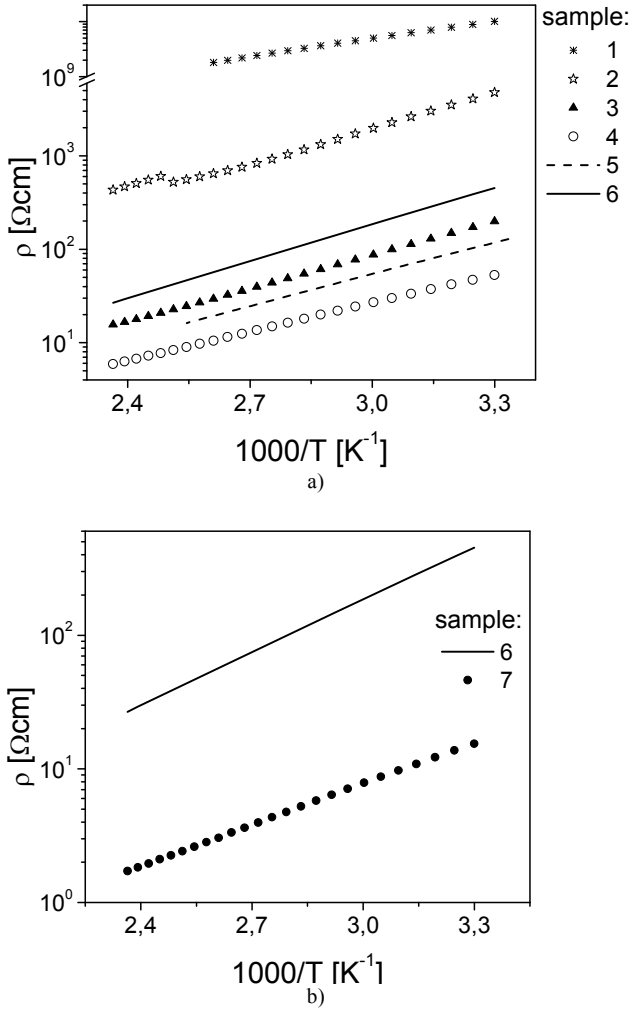

Fig. 3. The d.c. resistivity vs. temperature dependence for V_2O_5 thin films sputtered under different conditions.

4. Conclusions

In this work, selected sputtering process conditions affecting total energy of the particles condensing at the place of the thin film creation such as HT or CT sputtering, low pressure sputtering, Ar/O_2 or O_2 working gas, substrate heating and/or polarization, have been employed for studying structural, optical and electrical properties of vanadium oxide thin films. The results have shown that all the films (besides the sample 1 prepared by thermal oxidation) display V_2O_5 structure with crystallite size in the range of about 9 to about 17 nanometers. Meaningful reduction in the crystallite size was observed for the sample 4 prepared in HT mode with O_2 as working gas and without additional substrate polarization (sample 4). However, the lowest resistivity was recorded for the sample 7 prepared in CT mode, with O_2 and with reduced substrate temperature. From optical transmission results, and taking into account different thickness of the prepared thin films, one can conclude that the applied different process parameters slightly influence optical properties of the prepared samples.

Acknowledgements

This work was financed from the sources granted by the Polish Ministry of Science and Higher Education in the years 2009-2011 as a research project number N N 508 1329 37.

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