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Structural transformation and functional properties of vanadium oxide films after low-temperature annealing

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ABSTRACT

A two-step method is offered for the synthesis of vanadium oxide films to purposely change their functional properties. Vanadium oxide films were deposited on glass and silicon substrates by using magnetron sputtering of the vanadium target at various substrate temperatures (180–500 °C). During deposition, the substrate temperature predetermines structural and functional properties of the films after their following low-temperature (250–350 °C) annealing. In the films deposited at low substrate temperatures (200–220 °C), after low-temperature annealing there formed are flat crystallites of vanadium dioxide with lateral sizes 1 to 2 μm, which provides a high thermochromic effect. In the films deposited at temperatures of 250–300 °C, during the following low-temperature annealing the microcrystalline mixture of different vanadium oxides (50–150 nm) is formed, which provides a high value of the thermal coefficient of resistance for these films (7%/K). The low temperature annealing practically does not change the properties of films deposited at temperatures of 450–500 °C.

1. Introduction

Vanadium oxide films attracted much attention from researchers because of their unique properties and prospective applications in various devices such as sensors, micromechanical and microelectronic systems, and others [1–4]. The operation principle of these devices is based on the effect of structural change of crystalline vanadium dioxide from monoclinic modification to the tetragonal one at temperatures above the critical temperature (T = 68 °C). This structural transformation is accompanied by a change of the band structure resulting in the change of film properties from semiconductor to metallic ones (SMT — semiconductor-to-metal transition). For practical application, the most widely used films are those which demonstrate the significant changes in the resistance (for microbolometers) or in the transmission spectrum (for thermochromic coatings) with changing temperature.

Vanadium oxide films with high-temperature coefficient of resistance (TCR ~2–4%/K) were used for production of uncooled microbolometers [1,5–7]. Thermochromic coatings are the important elements for creating systems of heat and light flow regulation, and they can significantly save energy consumption [2,3,8–11]. Therefore, creating both types of these materials, methods of formation and investigation of their properties are topical, as it is proven by numerous publications in this field [1,2,5,6,9–20]. Operation characteristics of devices that use SMT effect depend primarily on the specific composition of the VO_2 phase in the film, structure parameters, and presence of impurities, so that regimes of deposition and annealing are crucial for creating some fixed functional properties of the film. The film deposition process is usually realized at sufficiently high temperature close to ~500 °C, which provides crystallization of VO_2 phase [8,10,17,19–22]. It was shown in our previous papers [23,24] that the two-step method to form vanadium dioxide films allows manufacturing of the material with excellent thermochromic characteristics due to predominantly high-ordered VO_2 phase formation in the film. At the first stage of this method, the amorphous film with a composition close to VO_2 was deposited (at 200 °C) on the substrate. Regimes of deposition provide nucleation of VO_2-nanocrystallites in the film, and they grow intensively at the second stage during a low-temperature (300–350 °C) annealing. As a result, the synthesis process becomes more adjustable and allows to produce a nanocrystalline film containing mainly the VO_2 phase and suppresses growth of the other vanadium oxides (VO, V_2O_3, V_2O_5).

To describe transport properties of disordered structures, where the phase transition "metal–insulator" exists, the model of percolation cluster near the percolation threshold is used [25]. In particular, random walks on percolation fractals and related to fractal dimension were studied using the methods of computation [26].

To clarify the mechanism of conductivity near the phase transition in the structures consisting of different vanadium oxides in polycrystalline and amorphous phase mixture, it seems promising to use the models of fractal percolation network in fractal systems of the corresponding dimension.

This work is an extension of our previous studies aimed at ascertaining the structural features of synthesized films and demonstrates possibility to control modification of phase composition of the films during low-temperature annealing to obtain certain functional properties. Our studies have shown that using the two-step principle of film

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formation and changing the synthesis conditions it is possible to create both vanadium oxide films with high TCR (~7%/K) or the effective thermochromic films (40-fold changes in IR transmittance).

2. Experiment

VO_x thin films were deposited on glass and silicon substrates by reactive DC magnetron sputtering of the metallic vanadium target (99.96%) in O_2/Ar gas mixture. Operation parameters of film deposition varied in the following ranges: content O_2 in prepared O_2/Ag mixture (4–15%); pressure (0.13–1.33 Pa); discharge power (50–90 W) and substrate temperature (180–500 °C). This made it possible to obtain VO_x films ($1.4 \leq x \leq 2.4$) of different structural (amorphous, nanocrystallized and mixed) and composition phases. The thickness of the films was controlled by profilometer (Alpha-step 100) and typical value was about 100–150 nm, and deposition rate was in the range of 0.13–0.22 nm/s. After deposition, the films were annealed within the temperature range of 250–350 °C for 10 up to 300 min. Annealing was carried out in atmosphere of various gases (H_2, N_2, O_2) or in $N_2 + O_2$ mixture. The AFM tapping mode was applied and high resolution silicon tips with nominal upper radius of 10 nm were used. The SEM operating voltage was 5 kV.

X-ray diffraction (XRD) study was carried out using X'Pert-MRD diffractometer with Cu K_α-radiation, $\lambda = 0.15418$ nm, in Bragg–Brentano geometry.

The structure and phase changes in films on each stages of the synthesis process were examined with Scanning Electron Microscopy (SEM, TSCAN MIRA 3), Atomic-Force Microscopy (AFM, NanoScope IIIa Dimension 3000TM), Auger Electron Spectroscopy (AES, Auger Microprobe JEOL JAMP 9500 F) and X-ray diffraction (XRD, PANalytical X'Pert Pro MRD XL) methods. The optical transmittance and specific resistivity of the films were measured within the temperature range of 0 to 90 °C after formation of the film.

3. Results

Table 1 shows the basic technological regimes for VO_x film synthesis and main physical characteristics of the films. In the table there are the modes of synthesis of films that provide the highest value of the functional properties of each series sample.

All the films can be separated into three series with different temperatures of deposition: series L corresponds to low temperatures (200–220 °C), series M — middle temperatures (250–300 °C), and H — high temperatures (450–500 °C). For convenience in interpretation of the results and discussion, we separated samples of each series as three types with a low ($x < 2$), medium ($x \cong 2$) and high ($x > 2$) oxygen concentration: *L*, *M* and *H*, respectively. Thus, all the samples have the labels (two letters) where the first letter indicates the temperature range of the film deposition and the second one — oxygen content in the film. For example, the sample deposited at low temperatures and having a high oxygen content is referred to as L*H*, and deposited at middle temperatures with a low oxygen content is referred to as M*L*.

After deposition in each series of the samples, there are films with a different composition of components, because film composition is strongly dependent on the discharge power, oxygen content in a gas mixture and pressure in the vacuum chamber. Therefore, to obtain films with the specified functional properties in each case, it is necessary to make their own low-temperature annealing (atmosphere, temperature and time). The best functional properties (highest TCR or availability of the thermochromic effect) were obtained for the samples of H*M*, M*L* and L*M* (in Table 1 marked by bold type). So it is just for these samples that the detailed results are presented in this paper.

3.1. High temperature deposition (H-series)

Due to the high temperature of substrate for H-series samples, all the films have a polycrystalline structure just after deposition (Fig. 1, sample H*M*, left). The crystallite sizes lie within the range 50 to 300 nm, and these do not change after annealing. According to XRD data, samples H*L* contain a mixture of vanadium oxides, so for the samples H*M* (Fig. 1, sample H*M*, right) the monoclinic phase of VO_2 dominates, and in the H*H* samples the dominating phase is V_2O_5. After deposition, the H*H* and H*L* films do not have thermochromic properties, while the H*M* samples demonstrate good thermochromic properties. When heating the sample H*M* from 0 up to 100 °C, the transmission in the infrared region decreases by 3 to 4 times (Fig. 2), and the resistivity – by 80 to 100 times (Fig. 3).

Low-temperature annealing had no influence on surface morphology, but due to reactions with active gases (O_2 and H_2) the significant changes of the film content were observed. For H*H* and H*L* films (see Table 1) after annealing, thermochromic properties arise. Annealing of H*M* samples leads to stabilization of thermochromic characteristics (without annealing of the samples, drift of parameters was observed in a few weeks) and reducing the hysteresis parameters of the films when heating and cooling.

Fig. 4 (sample H*M*) shows AFM images of the film surface (left) and image with registration of visco-elastic properties (right). The surface roughness is 5 nm. Since the image obtained after registration of visco-elastic properties is quite different from results of surface topography, it may indicate structural inhomogeneity of the film.

Table 1
Regimes of VO_x film synthesis and their physical characteristics.

VO_X deposition			Annealing			Properties				
Series (T°_{dep},C)	Type	$X_{dep.}$	Gas	$T_{ann.}$ (°C)	t (min)	$X_{ann.}$	℧ (Ohm × cm)	TCR (%/K)	$A_{t.chr}$	ΔT (°C)
L (200–220)	*L*	1.4–1.9	O_2	350	200	1.8–1.9	1.35	2.8	1.9	32.3
	M	**1.9–2.0**	**$N_2 + O_2$**	**300**	**30**	**1.9–2.0**	**6.2**	**4.7**	**40.0**	**9.0**
	H	2.0–2.2	H_2	250	100	2.0–2.1	3.35	2.1	2.4	14.2
M (250–300)	*L*	**1.4–1.8**	**O_2**	**300**	**300**	**2.0–2.15**	**1.06**	**7.0**	**1.8**	**1–2**
	M	1.8–2.0	$N_2 + O_2$	300	60	1.9–2.0	7.33	3.9	2.2	8.1
	H	2.1–2.3	H_2	270	90	2.1–2.2	2.03	1.8	1.4	12.3
H (450–500)	*L*	1.6–1.8	O_2	300	60	2.0–2.1	3.25	1.2	1.5	27.2
	M	**1.8–2.0**	**$N_2 + O_2$**	**300**	**30**	**1.85–2.0**	**0.7**	**2.9**	**3.2**	**15.3**
	H	2.0–2.3	H_2	270	40	1.9–2.1	2.32	1.7	3.1	11.0
	M	1.9–2.1	Without annealing			1.9–2.1	0.61	4.3	3.0	15.4

T_{dep} – temperature of substrate at film deposition.
$X_{dep.}$ and $X_{ann.}$ – ratio between oxygen and vanadium concentration (measured by AES) for deposited and annealed films, respectively.
T_{ann} – temperature of annealing.
t – time of thermal annealing.
℧ – specific resistance of the film at room temperature.
TCR – temperature coefficient of resistance of the film at room temperature.
$A_{t.chr}$ – ratio between transmittance of light with $\lambda = 2.5$ μm through the film at the temperatures of 20 °C and 90 °C.
ΔT – difference between temperature of SMT of the film at heating and cooling.

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