THERMOCHROMIC PROPERTIES OF VANADIUM DIOXIDE FILMS OBTAINED BY MAGNETRON SPUTTERING

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The structural, electrophysical, and optical properties of thermochromic VO_2 films prepared by magnetron sputtering are investigated. It is shown that the thermochromic properties of VO_2 films can be improved in the case of their two-stage formation: sputtering at a substrate temperature of 200 °C followed by thermal annealing. The data of experimental studies confirm the formation of VO_2 crystallites with a mean size of 26 nm and a monoclinic crystal lattice in the investigated films. At the phase transition, the change of the film conductivity reaches 3 orders of magnitude, while the optical transmission (at the probing light wavelength $\lambda = 2$ μm) changes by a factor of 16. It is shown that the variation of annealing parameters of the synthesized films allows one to change their thermochromic properties. The obtained results are explained in the framework of the model of formation of VO_2 nanoinclusions.

1. Introduction

The synthesis of thermo- and electrochromic thin films, in which the optical transmission of a material can be significantly changed by varying the temperature or the electric field, represents an urgent problem due to the development of energy-saving technologies. Vanadium dioxide is considered to be one of the most promising materials for thermochromic coatings owing to the existence of the reverse transition from the semiconductor phase to the metal one at the temperature $T_t \approx 68$ °C [1, 2]. The phase transition is related to the transformation of the crystal lattice from the monoclinic structure (in this state, vanadium dioxide represents a narrow-band semiconductor with the energy gap width $E_g = 0.7$ eV) to the tetragonal one at temperatures exceeding T_t, at which the valence and conduction bands of VO_2 overlap and the material manifests metal properties [4–6]. Such a transformation of the crystal lattice lasts for $\sim$ 500 fs [6–7] due to the change of the sample temperature by less than 0.1 °C [8]. Such an abrupt transition causes the variation of the specific resistance of VO_2 by five orders of magnitude [3], whereas the light transmission in the infrared region (2–4.5 μm) changes by a factor of 1000 [4]. The possibility of a so fast transformation from the semiconductor state to the metal one is related to the very small variation of the volume of the VO_2 crystal under the phase transition ($\sim 0.044\%$) [6].

The problem that arises when synthesizing thermochromic films on the basis of vanadium is the possibility of the simultaneous formation of non-thermochromic vanadium oxides (VO, V_2O_3, and V_2O_5), which significantly complicates the optimization of the sputtering process [8].

The magnetron sputtering of stoichiometric thermochromic VO_2 films is usually carried out on a heated substrate ($\sim$400–500 °C) with a very accurate control of the oxygen concentration and other deposition parameters to minimize the content of non-thermochromic oxides in the film. For such films, the phase transition is observed without additional thermal treatments [1, 2, 5, 6, 9]. The sputtering of films on a substrate with a temperature < 400 °C does not allow one to obtain thermochromic films of vanadium dioxide. Only the subsequent thermal annealing performed in certain modes results in the appearance of thermochromic properties of the films [7, 11].

A remaining urgent problem is to decrease the phase transition temperature for VO_2 films, as well as the improvement of their optical parameters: the majority of the proposed techniques (introduction of W [12], Nb, Mo, and Li [10] impurities, oxygen implantation [4]) result not only in the decrease of the temperature T_t but also in a decrease of variations of the specific resistance and the optical transmission.

The aim of this work was to improve the thermochromic (electrical and optical) properties of synthesized VO_2 films at their two-stage formation: magnetron sputtering at the substrate temperature T_s=200 °C with the following thermal annealing in various modes.

2. Experimental Technique

Thermochromic VO_2 films were deposited using the magnetron sputtering technique in a VUP-5 set-up with a planar magnetron by means of magnetron sputtering of a vanadium target (with 99.7% purity). Before the deposition, the chamber was evacuated to vacuum $\sim 3\times10^{-4}$ Pa. The plasma was formed using a mixture of Ar with a precision-controlled portion of O_2 (from 2 to 10%). The pressure in the chamber was maintained constant (from 11 to 0.4 Pa) in the sputtering process. The films were deposited onto silicon plates and quartz glass at temperatures of 200 °C and 400 °C. After the sputtering, the samples were cooled to room temperature in the working chamber at a pressure of $\sim$ 0.2 Pa. A part of the obtained samples was thermally annealed in air or H_2 at temperatures T = 200–400 °C during 10–60 min.

The studied samples were used for measuring the specific resistance ρ and the optical transmission in the temperature interval 20–105 °C. The structural properties of samples were analyzed using the X-ray diffraction technique. The thickness of films was determined with the help of a profilometer.

3. Experimental Results

Figure 1 presents the specific resistances of the vanadium oxide films as functions of the deposition rate obtained for various oxygen concentrations in the mixture, a pressure of 0.53 Pa, and a substrate temperature of 400 °C. The specific resistance was measured at room temperature. At oxygen concentrations in the mixture equal to 2–3%, the vanadium dioxide films can be obtained only at low deposition rates. In these modes, an insignificant change of the deposition rate results in considerable variations of the film resistance. At oxygen concentrations in the mixture exceeding 8%, high-resistance films are obtained, whose resistance weakly decreases with varying the deposition rate. Such films are of light-yellow color, while their composition corresponds to that of V_2O_5.

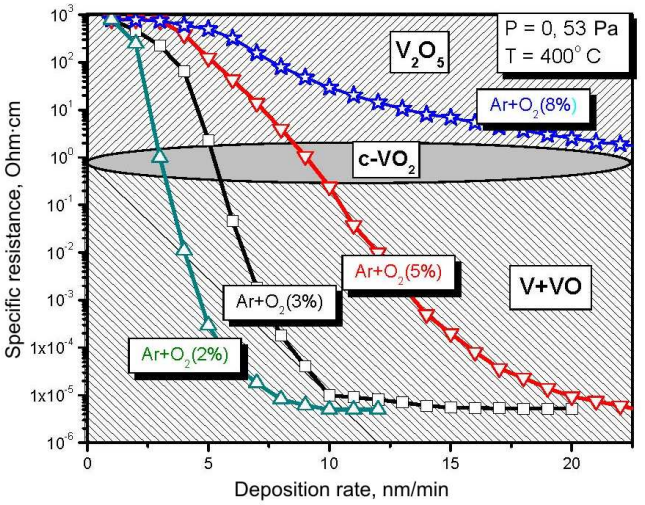

Fig. 1. Specific resistance of the obtained vanadium oxide films as a function of the deposition rate for various oxygen concentrations in the mixture

At deposition rates exceeding 15 nm/min and oxygen concentrations equal to 3–6%, conducting films with inclusions of pure vanadium are obtained.

Thus, on the one hand, the variation of technological parameters of the sputtering process (O_2 content in the mixture, pressure in the chamber, discharge power of a magnetron, and substrate temperature) resulted in a change of the rate of deposition of films and, on the other hand, in a change of their specific resistance allowing one to obtain films of various stoichiometric compositions: from pure vanadium to vanadium oxide V_2O_5.

So, in order to obtain films of polycrystalline vanadium dioxide with the phase transition using the heated substrate mode, it is necessary to very accurately choose the technological parameters of the sputtering process. On the one hand, they must provide the VO_2 stoichiometric composition and, on the other hand, to create conditions for the formation of the crystalline phase of vanadium dioxide (heating of the substrate to $T_s \geq 400$ °C during the sputtering). Based on the given data, we obtained VO_2 crystalline films using the sputtering in the mixture Ar + 5% O_2 at rates of 10–12 nm/min.

We also synthesized films at T_s = 200 °C that manifested thermochromic properties after the additional annealing at a temperature of 300 °C. The annealing of such films in air at temperatures lower than 300 °C (up to 60 min) had no effect on the thermochromic prop-

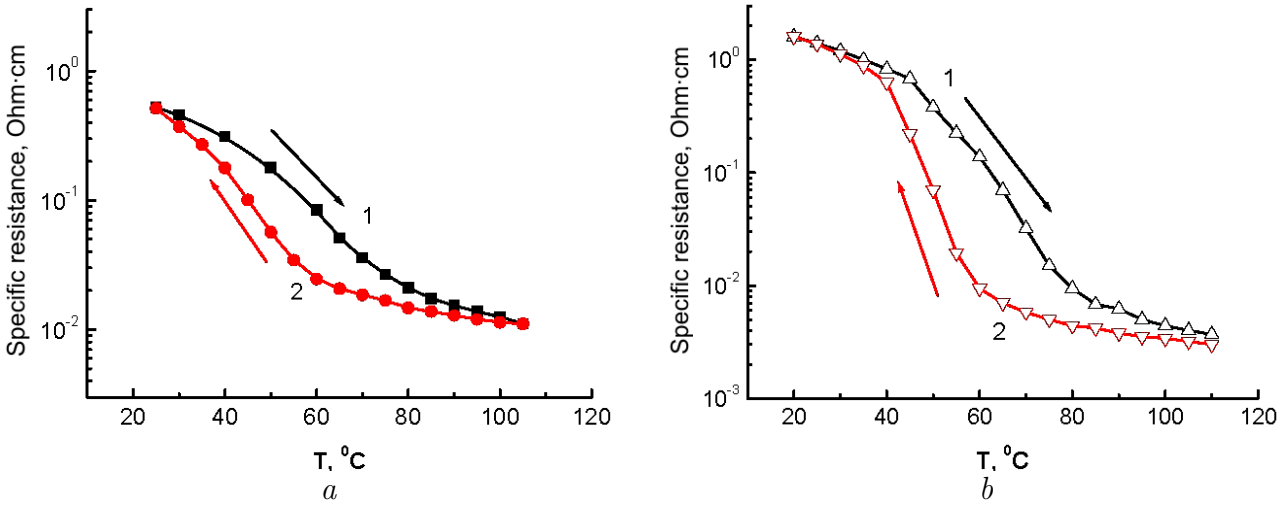

Fig. 2. Temperature dependence of the specific resistance of the obtained vanadium oxide films deposited at T_s = 400 °C (a) and deposited at T_s = 200 °C with the following 30-min annealing in air at 300 °C (b)

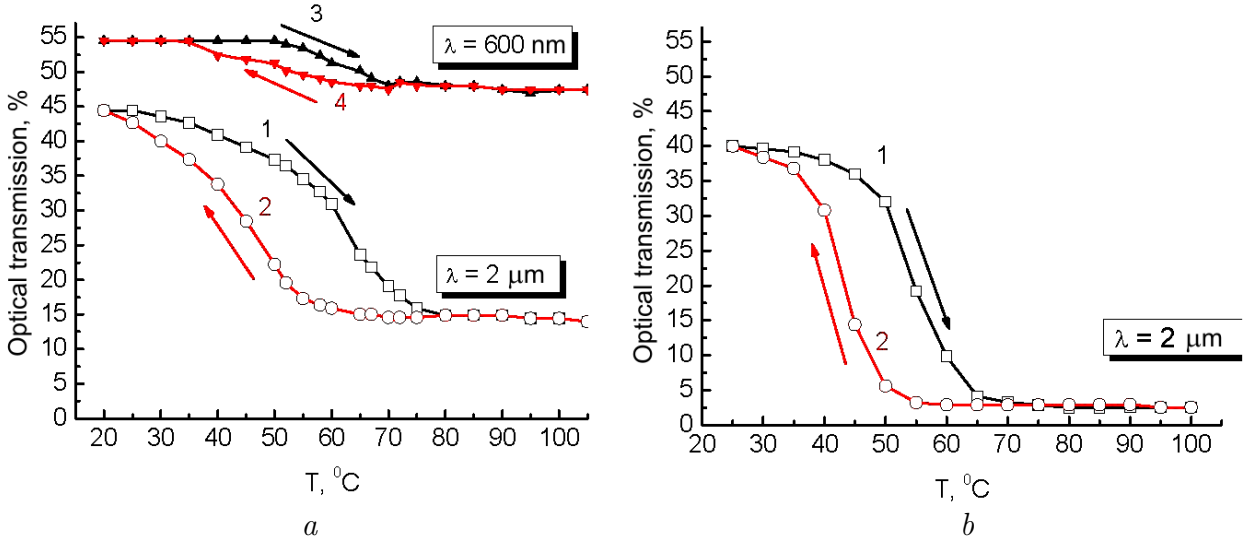

Fig. 3. Temperature dependence of the optical transmission of the vanadium oxide films deposited at T_s = 400 °C (a) and deposited at T_s = 200 °C with the following 30-min annealing in air at 300 °C (b)

erties of films, whereas the annealing at temperatures exceeding 350 °C resulted in their degradation.

Figure 2 presents the temperature dependences of the specific resistance of films in the case of heating (curve *1*) and cooling (curve *2*) of the sample. The heating of the films obtained by sputtering on a substrate at T_s = 400 °C resulted in the non-abrupt transition from the semiconductor state to the metal phase at a temperature of ∼62°C (Fig. 2,a). In this case, the specific resistance of the film decreases by almost two orders of magnitude. The reverse transition taking place at the cooling of the film is rather smeared and observed at a temperature of ∼47 °C. For the films obtained by sputtering on the substrate with T_s = 200 °C, the heating leads to a more abrupt transition at a temperature of ∼ 68 °C (Fig. 2,b). In this case, the specific resistance of the film decreases by more than two orders of magnitude. The reverse transition induced by the cooling of the film is observed at a temperature of ∼ 49 °C.

In Fig. 3, one can see the temperature dependences of the optical transmission of oxide vanadium films obtained at T_s =400 °C and T_s =200 °C with the following thermal treatment (curves *1, 3* – heating, curves *2, 4* – cooling). Heating the films with T_s = 400 °C, one reg-

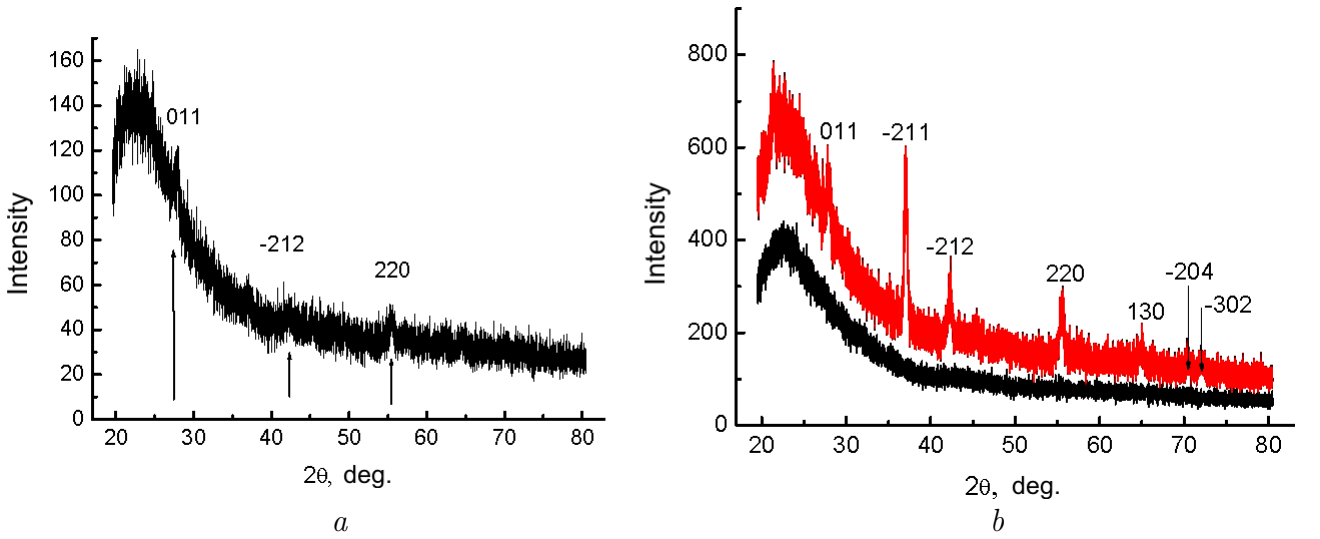

Fig. 4. X-ray diffraction by the vanadium oxide films deposited at $T_s = 400$ °C (a) and deposited at $T_s = 200$ °C (b, lower curve) with the following 30-min annealing in air at 300 °C (b, upper curve)

isters a non-abrupt transition at a temperature of ∼63 °C (Fig. 3,*a*, curve *1*), while the light transmission in the infrared region ($\lambda = 2$ μm) decreases from 45% to 15% (Fig. 3,*a*). The cooling of the samples resulted in the transition at a temperature of ∼49 °C (Fig. 3,*a*, curve *2*).

In the visible spectral region ($\lambda = 600$ nm), the optical transmission of these films also insignificantly decreased – from 55% (at room temperature) to 48% (at temperatures exceeding 80 °C).

The heating of the films with $T_s = 200$ °C annealed at $T = 300$ °C resulted in a more noticeable and abrupt decrease of the light transmission in the infrared region ($\lambda = 2$ μm): from 40% to 2.5% (Fig. 3,*b*). The transition temperature ∼55 °C appeared lower than that determined from the variation of the specific resistance by more than 10°C. The reverse transition (under cooling) was observed at a temperature of ∼ 43 °C. The optical transmission in the visible region ($\lambda = 600$ nm) remained practically constant at the heating of samples of the second group and amounted to ∼25%.

The discrepancy between the transition temperatures obtained from measurements of the specific resistance and the optical transmission was already observed earlier [13, 14] and was explained by the effect of additional optical excitation on measurements of the optical transmission.

The data on X-ray diffraction by the studied vanadium oxide films confirm the presence of VO_2 crystallites in them (Fig. 4). The films sputtered at $T_s = 400$ °C show weak peaks of X-ray diffraction by three crystallographic planes: (011), (212), and (220) of the VO_2 crystalline phase (Fig. 4,*a*). The Debye powder patterns of the films deposited at $T_s = 200$ °C do not contain peaks of X-ray diffraction by the crystallographic planes (Fig. 4,*b*, lower curve). The additional thermal treatment of such films results in the appearance of clear peaks at the X-ray diffraction by seven crystallographic planes: (011), (−211), (−212), (220), (130), (−204), and (−302) (Fig. 4,*b*, upper curve).

Figure 5 demonstrates the temperature dependence of the specific resistance of vanadium oxide films after the additional thermal annealing in various media. The annealing in air at a temperature of 300 °C (30 min) results in the increase of the specific resistance of the vanadium oxide films; moreover, the transition parameters do not change (see Table). The annealing in hydrogen at a temperature of 350 °C (30 min) leads to the decrease of the specific resistance of the films. In this case, the transition shifts toward lower temperatures (see Table).

In the inset of Fig. 5, one can see the result of analyzing the phase transition parameters with respect to the first derivative of the temperature dependence of the specific resistance performed for the sample deposited onto a substrate at $T_s = 400$ °C after the additional annealing in the H_2 atmosphere (350 °C, 30 min). According to the technique of this analysis described in [2], the maximum of the derivative corresponds to the transition temperature, the half-width of the curve $\frac{d(\log(\rho(T)))}{dT}$ characterizes the transition rate, whereas the area under

Parameters of the phase transition of synthesized VO_2 films

Film		Transition temperature, °C		Hysteresis, °C	Transition intensity
Sputtering temperature	Thermal treatments	heating	cooling		(orders of magnitude)
200 °C	–	–	–	–	–
	300 °C (air)	68.0	49.1	19.6	2.7
	350 °C (air)	77.3	41.6	35.7	2.2
400 °C	–	62.0	46.6	15.4	1.7
	300 °C (air)	62.4	47.1	15.3	1.4
	300 °C (H_2)	63.6	52.6	11.0	1.8
	350 °C (H_2)	54.5	37.3	14.2	1.7

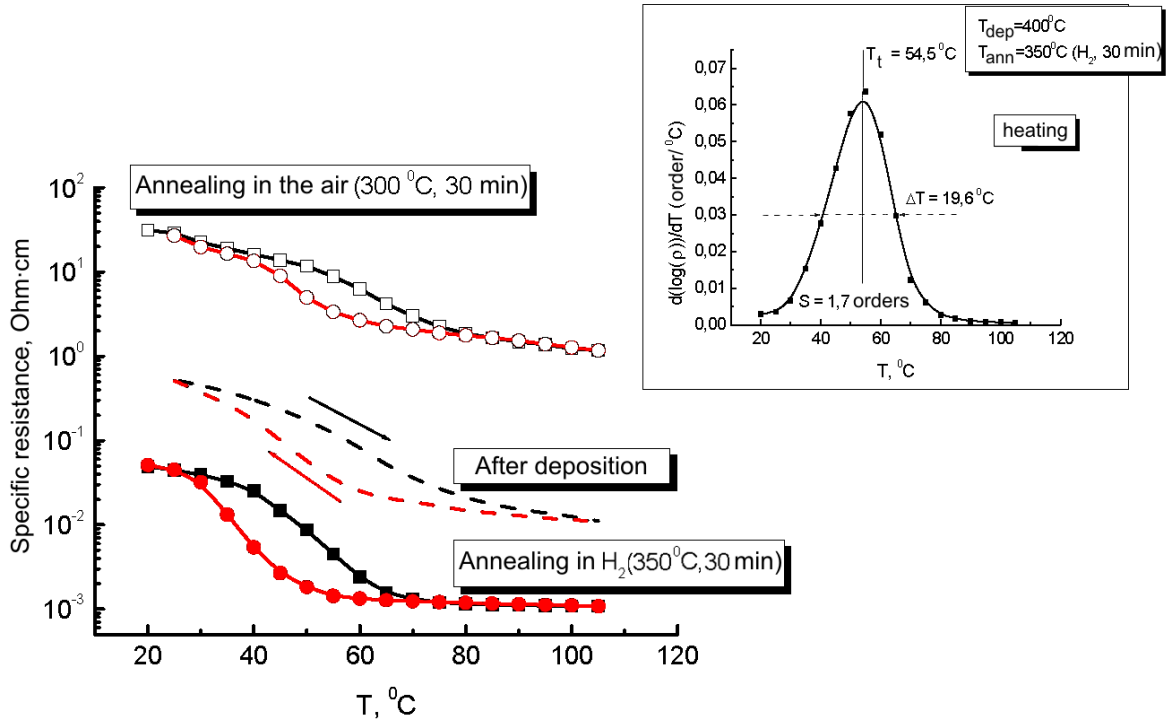

Fig. 5. Temperature dependence of the specific resistance of a vanadium oxide film under various annealing conditions. In the inset – an example of analyzing the transition parameters according to [2]

the curve shows the transition intensity, i.e. indicates the number of orders of magnitude, by which the specific resistance of the film decreases due to the transition.

We analyzed the obtained temperature dependences of the specific resistance for the samples after sputtering and thermal treatments. The results are shown in Table. For the films deposited at T_s = 400 °C, the transition temperature appears lower than that for films obtained at T_s = 200 °C. However, the transition intensity and the hysteresis for the films obtained at T_s = 200 °C were higher than those at T_s =400 °C. The transition rates for the films with T_s = 200 °C and T_s = 400 °C were practically equal and amounted to ≈ 20 °C.

4. Discussion of the Results

The obtained results (Fig. 1) demonstrate that the parameters of films deposited onto a heated substrate by magnetron sputtering significantly change due to insignificant variations of the technological modes (pressure in the working chamber, magnetron power, substrate temperature, or oxygen concentration in the mixture). This is related to the fact that a change of one parameter of the technological process induces a change of another one, so it is rather complicated to obtain a stoichiometric VO_2 film with thermochromic properties. In addition, the crystallization process runs simultaneously with the film growth, and the surface diffusion stimu-

lated by bombardment favors the origination of a phase with a smaller enthalpy variation ($\Delta H_{V_2O_5} = -1557$ cal/mole, $\Delta H_{VO_2} = -713$ cal/mole). From the spectra of X-ray diffraction by vanadium oxide films obtained at $T_s = 400$ °C, one can see that the fraction of the VO_2 phase is small (Fig. 4,*a*). The films grown under such conditions consist of the V_2O_5, VO, and unoxidized vanadium phases, as well as low-size VO_2 crystallites that provide insignificant reflections on the diffraction patterns. The weak intensity of the vanadium dioxide peaks at the Debye powder pattern of the samples synthesized at $T_s = 400$ °C does not allow one to estimate the average size of crystallites (Fig. 4,*a*). The shift of the transition temperature toward lower values and the large transition width are caused by the presence of V^{3+} cations related to a rise of the concentration of oxygen vacancies [15]. The low intensity of the transition in the films synthesized at $T_s = 400$ °C can be due to small dimensions of the crystallites [2, 7]. The thermal annealing of these samples in air leads to an enhancement of the specific resistance (Fig. 5), which is caused by the oxidation of vanadium inclusions and the formation of the V_2O_5 phase. The thermal annealing in the hydrogen atmosphere results in a decrease of the specific resistance of the film, which is due to the deoxidation of vanadium oxide. The transition parameters remain constant, which testifies to the invariance of the fraction of VO_2 inclusions.

At a substrate temperature of 200 °C, we observed the deposition of an amorphous VO_2 film that is crystallized during the following thermal treatments at temperatures of 300–350 °C (Fig. 4,*b*). The position of the diffraction peaks testifies to the formation of VO_2 crystallites exactly with a monoclinic crystal lattice. The pronounced peaks on the Debye powder patterns of these films allow one to estimate the sizes of vanadium dioxide crystallites by the Scherrer formula [2]. Such an estimate for the three peaks (−211), (212), and (220) yields the sizes of VO_2 nanocrystallites equal to 28, 26, and 25 nm, respectively. Thus, the average size of nanoclusters in the obtained vanadium dioxide films amounts to 26±2 nm. The determined values are in a rather good agreement with the literature data for vanadium dioxide films of the same thickness [2].

The difference between the transition temperatures (T_t) for the films obtained by sputtering on the substrate with $T_s = 400$ °C ($T_t = 62$ °C) and $T_s = 200$ °C with the additional annealing ($T_t = 68$ °C) can be explained by a higher imperfection of vanadium dioxide crystallites in the films obtained by the first technique. As was shown in [4], the formation of additional defects in VO_2 films results in a decrease of the transition temperature.

It is worth noting the difference between the values of transition temperature determined from changes of the specific resistance and the optical transmission for the films obtained at a substrate temperature of 200 °C after the additional annealing ($T_t = 68$ °C and $T_t = 55$ °C, respectively). The possible reason for such a difference lies in the presence of various size nanocrystallites in the film that undergo the phase transition at different temperatures. For conductivity, it is essential that the transition is realized in nanocrystallites of all sizes; while, for optical transmission, only in those that form the major part of the film. That is why the transition temperatures determined from the variations of the resistance and the optical transmission can be different, which still requires the further investigation.

5. Conclusions

We have studied structural, electrophysical, and optical properties of thermochromic VO_2 films obtained by magnetron sputtering. The effect of technological parameters of the synthesis of vanadium dioxide films on their properties is analyzed. The data on X-ray diffraction confirm the formation of VO_2 crystallites with a monoclinic crystal lattice and an average size of 26 nm in the synthesized films. It is shown that the thermochromic properties of VO_2 films can be improved in the case of their two-stage formation: sputtering at a substrate temperature of 200 °C followed by thermal annealing. At the phase transition in such films, the variation of the conductivity reaches 3 orders of magnitude, whereas the optical transmission changes by a factor of 16 (at the wavelength of probing light $\lambda = 2$ μm). The possibility of the controlled variation of the specific resistance of thermochromic films and the phase-transition temperature at the expense of a thermal treatment in the oxygen or hydrogen atmosphere is demonstrated. The physical mechanisms of the influence of a thermal treatment on the properties of thermochromic vanadium dioxide films are proposed. The obtained results are explained in the framework of the model of formation of nanoinclusions of the VO_2 crystal phase.

It is established that the phase transition temperature for the films sputtered on a hot substrate is lower than that for films obtained by sputtering on the "cold" substrate after an additional thermal treatment.

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ТЕРМОХРОМНІ ВЛАСТИВОСТІ ПЛІВОК ОКСИДУ ВАНАДІЮ, ОТРИМАНИХ МАГНЕТРОННИМ НАПИЛЕННЯМ

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Р е з ю м е

Досліджено структурні, електрофізичні та оптичні властивості термохромних плівок VO_2, отриманих магнетронним напиленням. Продемонстровано можливість поліпшення термохромних властивостей плівок VO_2 при їх двостадійному формуванні: напиленні при температурі підкладки 200 °C і подальшим термічними відпалом. Дані експериментальних досліджень підтверджують формування в досліджуваних плівках кристалітів діоксиду ванадію з середнім розміром 26 нм та моноклінною кристалічною ґраткою. При фазовому переході зміна провідності плівок досягає трьох порядків, а оптичне пропускання змінюється (при довжині хвилі зондуючого світла $\lambda = 2$ мкм) у 16 разів. Показано, що зміна параметрів відпалу синтезованих плівок дозволяє варіювати термохромні властивості плівок. Отримані результати пояснюються в межах моделі формування нановключень кристалічної фази VO_2.