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

Yu. Goltvyanskyi, I. Khatsevych, A. Kuchuk⁎, V. Kladko, V. Melnik, P. Lytvyn, V. Nikirin, B. Romanyuk

V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41 Prospect Nauki, Kyiv 03028, Ukraine

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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.

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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 VO2 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 VO2 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 VO2 phase formation in the film. At the first stage of this method, the amorphous film with a composition close to VO2 was deposited (at 200 °C) on the substrate. Regimes of deposition provide nucleation of VO2-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 VO2 phase and suppresses growth of the other vanadium oxides (V2O3, V2O5, V2O5).

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

⁎ Corresponding author. Tel./fax.: +380 44 525 5724.
E-mail address: an.kuchuk@gmail.com (A. Kuchuk).

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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

VO₂ thin films were deposited on glass and silicon substrates by reactive DC magnetron sputtering of the metallic vanadium target (99.96%) in O₂/Ar gas mixture. Operation parameters of film deposition varied in the following ranges: content O₂ in prepared O₂/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 VOₓ films (1.4 ≤ x ≤ 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 (H₂, N₂, O₂) or in N₂ + O₂ 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 Kr radiation, λ = 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 JEOI JAMP 9500 F) and X-ray diffraction (XRD, PANalytical X’Pert Pro MRD XL) methods. The optical transmittance and specific characteristics 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 VOₓ 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 ≈ 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 LH, and deposited at middle temperatures with a low oxygen content is referred to as ML.

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 HM, ML and LM (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 HM, left). The crystallites sizes lie within the range 50 to 300 nm, and these do not change after annealing. According to XRD data, samples HL contain a mixture of vanadium oxides, so for the samples HM (Fig. 1, sample HM, right) the monoclinic phase of VO₂ dominates, and in the HM samples the dominating phase is VO₂. After deposition, the HM and HL films do not have thermochromic properties, while the HM samples demonstrate good thermochromic properties. When heating the sample HM 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 (O₂ and H₂) the significant changes of the film content were observed. For HH and HL films (see Table 1) after annealing, thermochromic properties arise. Annealing of HM 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 HM) 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.
3.2. Middle temperature deposition (M-series)

Deposition of the films with a low oxygen concentration (samples ML) within the temperature range 250–300 °C allows to create mainly the amorphous structure (Fig. 1, sample ML, right, lower curve) with crystalline rhombohedral V2O3 inclusions. During annealing, these inclusions grow, and the amorphous film structure is transformed into the polycrystalline one (Fig. 1, sample ML, right, upper curve). Except this, the main number of V2O3 inclusions were transformed into VO2 crystallites, although there remains a significant part of the amorphous phase in the film (Fig. 1, sample ML, right, upper curve).

Thermochromic effect is very small in this film, the IR-transmission changes only two times (Fig. 2). Nevertheless, the film resistivity decreases by almost three orders of magnitude after heating from 0 to 45 °C (Fig. 3) and TCR value is 7%/K. An important point is that the thermal hysteresis of resistance is absent. According to AFM data (Fig. 4), the ML film, as in the case of sample HM, is structurally rather inhomogeneous, although it has the considerably lower roughness of about 1 nm. Amorphous films MM and MH after deposition contain V2O5 and VO2 nano-inclusions, but VO and V2O3 crystalline phases are absent in the films. Therefore, after annealing in oxygen or in the mixture of oxygen and nitrogen, films have a high resistivity due to the high content of V2O3 phase. Only annealing in hydrogen atmosphere can reduce the
The resistivity of these films, but the functional properties of these films are not well pronounced.

### 3.3. Low temperature deposition (L-series)

The principle of thermochromic film creation by using low-temperature deposition was described in detail in our previous papers [24]. With proposed conditions of deposition and subsequent annealing (sample LM), we can synthesize the polycrystalline film where monoclinic phase of vanadium dioxide dominates (Fig. 1, sample LM, right, upper curve). When the temperature rises above the critical temperature, the monoclinic structure of the film is transformed into the tetragonal one [24]. This phase transition leads to 40-fold reduction of film transmittance in the infrared region (Fig. 2), and the resistance decreases by four orders of magnitude (Fig. 3). Since the AFM images in regimes of relief determination and of registration of visco-elastic properties are almost identical (Fig. 4), it indicates high structural homogeneity of the film.

The slightest deviation from this deposition mode (LM) can produce a completely amorphous film (LH) or film containing a mixture of nanocrystals of various vanadium oxides (LL) (close to the M series). In both cases, subsequent thermal annealing does not lead to the appearance of good thermochromic properties of the films, although they (like LL, LH) can be suitable for using in the microbiomaterial systems.

The optical absorption coefficient (α) can be calculated from the following relation [27]:

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}}$$

Where $R$ and $T$ are the spectral reflectance and transmittance and $d$ is the film thickness.

For greater optical density ($\alpha d > 1$), the interference effects due to internal reflections as well as reflectance at normal incidence are negligible ($R \approx 0$) and optical absorption coefficient (α) is given by an approximate formula: $\alpha = \frac{1}{d} \ln \left(\frac{1}{R}\right)$.

The absorption coefficient, $\alpha$, due to interband transition near the band-gap can be described as $\alpha \propto \frac{1}{\lambda^2}$ versus photon energy $\alpha \propto \frac{1}{\lambda^2}$ where $\nu$ is the frequency of the incident radiation, $h$ is the Plank’s constant, $C$ is a constant, $E_{g}^{\text{mon}}$ is the optical energy gap of the material and exponent $n$ determines the type of electronic transition causing the absorption and can take values of (1/2) for direct allowed, (3/2) for direct forbidden, 2 for indirect allowed and 3 for indirect forbidden transitions.

The spectral dependence of the film absorption coefficient in the plot of $(\alpha \nu)^{1/n}$ versus photon energy $\alpha \propto \frac{1}{\lambda^2}$ allows to determine the value of the optical energy gap $(E_{g}^{\text{mon}})$ [5,29,30]. Fig. 5 shows the plot of $(\alpha \nu)^{1/n}$ versus photon energy for samples LM, ML, HM in the assumption that in our films the direct allowed transitions are realized ($n = 1/2$). The phase with the band gap 2.3–2.7 eV in all the films is present. This band gap value is typical for phase VO$_2$ [5,6,30,31], and it is almost independent of the film temperature. Also, in the plot one can distinguish a linear part that corresponds to the band gap of 0.7 eV, 0.4 eV and 0.45 eV for LM, ML and HM samples, respectively. The band gap value of 0.7 eV is typical for the monoclinic phase VO$_2$ [29,32]. When heating the films above 68°C, there arise changes in the spectrum ($E_{g} = 0$), which indicates transformation of the VO$_2$ band structure from the semiconductor to the metallic state.

### 4. Discussion

As can be seen from the presented results (see Table 1), the best thermochromic characteristics (LM, HM) and/or higher TCR values (LM, ML, MM, HM) are obtained for the films with the stoichiometry index $X_{\text{stoich}}$ close to 2. In general, it should be emphasized that the deposition and annealing regimes, under which the film was formed with the index X below 1.85 or above 2.15, are not discussed in this paper, because they have failed to form functional films suitable for practical use.

Samples LM, ML, HM have similar values of average elemental composition ($X_{\text{stoich}}$), but their crystalline structure is quite different (Fig. 1). If the series of samples H and M contain crystals with sizes ranging from ten to several hundred nanometers and are randomly oriented, in the sample LM the size of crystals becomes significantly large (up to a few micrometers). After the deposition process, the concentration and sizes of VO$_2$ nanocrystallites in the LM film are so small that we do not fix their presence by SEM and XRD methods. The annealing process drastically changes the structure of the LM film (Fig. 1, sample LM, right). The LM film thickness is 100 nm, therefore we can say that in this case the regime for formation of flat (plate type) crystals was realized, the lateral dimensions of which were more than one order of magnitude greater than the thickness. This is because the conditions of low-temperature annealing and low-oxygen content in gas mixture ensured growth only for those few nuclei of VO$_2$ crystalline phases that were formed during deposition. VO$_2$ crystal growth occurs under favorable conditions, because the nuclei concentration is low, and competition between adjacent growing crystals is absent. These films demonstrate a powerful thermochromic effect (Fig. 2) due to a high specific content of monoclinic phase of vanadium dioxide. This thermochromic effect and a significant change in resistivity (Fig. 3) are related with changes of crystalline VO$_2$ band gap (Fig. 5) from the value of $E_{g} = 0.7$ eV in the monoclinic modification to the value of $E_{g} = 0$ in the tetragonal.
Deposition at the temperature above 250 °C (M-series) allows to form a set of different vanadium oxide nanocrystallites in the amorphous film. The crystallites formed in the film during deposition are the centers for further film crystallization. After annealing, the ML film has stoichiometry close to VO₂ and consists of crystallites with different phases of vanadium oxide (VO₂, V₂O₃), which is evident from the diffraction of X-rays (Fig. 1, sample ML, right, upper curve). Although annealing allows to stimulate or suppress (it depends on conditions) the growth of certain crystalline phases, nevertheless all the nuclei simultaneously grow in a limited space, and the crystals do not swell to a large size, as in the case of LM. As a result, the films have a small amount of VO₂ crystals, and the thermochromic effect is very weak, but the presence of VO₂ and V₂O₃ provides high TCR and presence of V₂O₃ provides a high conductivity of the film.

It is important for practical use to minimize hysteresis of electrical resistance when heating and cooling the film. The hysteresis absence in ML and MM samples can be explained by small VO₂ nanocrystal sizes and their defectiveness. The transition temperature in these samples decreases to 40 °C, and TCR increases up to 7.0% in this region. Also, it must be taken into account that the film contains other vanadium oxides, and this temperature dependence of the film resistance is the sum of dependences of all the structural film components.

In the series H, a high temperature of the substrate provides formation of the film crystal structure directly during deposition process, in
dependencies of the absorption coefficient (Fig. 5) indicate the presence of $V_2O_5$ phase in all the films. We think that $V_2O_5$ in all the films is mainly amorphous, because the XRD data do not confirm the presence of crystalline phase of $V_2O_5$, and the band gap value for amorphous $V_2O_5$ lies in the same range as for crystalline $V_2O_5$ [27,30].

Since the films deposited on the glass substrate are polycrystalline, with different grain sizes, they show inheritency to their fractal properties [35]. Properties of fractal systems are determined by fractal dimension that, in its turn, depends on the procedure of film deposition. A dimension of the given fractal defines the possibility to create the conductivity percolation cluster [26] between the objects (crystallites VO$_2$), and it determines the abruptness and temperature of the phase transition.

Creation of different structures (depending on temperature and other technological factors) is controlled by the presence of crystalline phase nuclei and growth kinetics (limited by neighboring nuclei, or unlimited, when nuclei are far apart). Depending on the growth conditions, a fractal structure of a different dimension is generated, which affects the degree of conductivity of percolation cluster disorder. In its turn, it affects the kinetics of the phase transition (mainly temperature dependence of conductivity). To explain mechanisms of this phase transition, it is important to discover infinite hierarchy of critical factors influencing the stress distribution in the percolation cluster skeleton.

Summing up the results, we can say that the two-step method for the synthesis of vanadium oxide films allows to efficiently influence on the structure of the films and make it possible to create materials with different functional properties. For high quality thermochromic coatings, the most promising are those deposited at low temperatures (L series). In the process of low-temperature annealing, high-ordered polycrystalline film of monoclinic vanadium dioxide is formed.

To synthesize materials with a high TCR value, deposition within the temperature range of 250–300 °C (M series) is suitable. This regime allows creation of the set of vanadium oxide nanocrystals. After low-temperature annealing, this set is transformed into polycrystalline film with high value of TCR –7% and low resistivity.

5. Conclusion

Low-temperature annealing procedures for the VO$_x$ films (1.8 < x <2.2) can significantly change their component composition and crystalline structure. By creating the conditions for the preferential growth of certain structural and phase components of vanadium oxides, one can achieve: formation of the single-phase-ordered VO$_2$ phase in the film, which is characterized by a high thermochromic effect; formation of a film sensitive to infrared radiation and consisting of a mixture of crystallites containing various vanadium oxides with a high TCR value, low hysteresis parameters and resistivity at temperatures close to room temperature. The important point for formation of functional properties is the state of the film after deposition. Only amorphous films with rare nanocrystalline inclusions are the most suitable object for controlled crystallization and modification of crystals under the subsequent low-temperature annealing. In this relation, it is necessary to carry out a detailed analysis of the fractal properties of vanadium oxide films and determination of the shape of the crystallites and their ability to fill the space, which will enable to determine the fractal dimension.

The use of the multi-step technology makes it possible to control the structure of the films and thus obtain the objects with different fractal dimensions and functional properties.

Certainly, the two-step method for creation of films can have numerous variants for optimization of the offered synthesis conditions (parameters of deposition and annealing) and for creation of new ones. Technological conditions listed in Table 1 should be considered as indicative recommendations to obtain specific functional properties of the films. For effective practical application of this method, the suggested technological regimes unconditionally need clarification and

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**Figure 5.** Plot of $(a(hv))^2$ versus photon energy $(hv)$ for films LM, ML, HM at temperatures below (open symbols) and above (filled symbols) the temperature of SMT. The dashed lines are extrapolation to the $(a(hv))^2 = 0$ value – indicate the optical energy gap $E_g$. The inset is the enlarged image in the long-wave range of the spectra.

optimization based on more detailed investigations using modern methods of experiment planning and optimization technology [36,37].

References