The effect of thermal cycling on the properties of VO_{2±}Y materials

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Abstract. The article presents the research results of the thermal cycling influence on the ratio of the ultimate composition, chemical state and electrical resistance of VO_{2±}Y system materials. It is established that for all VO_{2±}Y system materials a phase transition semiconductor-metal (PTSM) is observed at temperature of ~ 340 K, accompanied by a sharp change in electrical resistance both before and after thermal cycling. Despite the fact that PTMD retained after thermal cycling, the resistivity jump Δln(R/R₀) at PTMD for all test materials decreases, the transition temperature becomes more diffused. It is shown that after a series of 30 thermal cycles, the ratio of the surface ultimate composition of all the materials under study changes to a decrease in the oxygen content. Minimal changes in properties as a result of thermal cycling are observed in vanadium dioxide of stoichiometric composition. According to the results of XPS spectra, it was determined that V^{4+} oxide predominates in the surface layer of VO₂ samples, both before and after thermal cycling, and there are also small inclusions of V^{5+} oxide.

1. Introduction
Vanadium dioxide under heating undergoes a phase transition semiconductor-metal (PTSM) at transition temperature T₁ ~340K. PTSM is accompanied with a sharp change in thermal, electrical, magnetic and optical properties of materials, and it is widely used in practice [1-5]. During the operation of materials based on vanadium dioxide, a change in their properties is noted. The study of the molar heat capacity at constant pressure (at temperatures less than 20 K), as well as X-ray analysis combined with the pycnometric density measurement showed that polycrystalline vanadium dioxide has a significant amount of point crystal lattice defects [6, 7]. It was determined [5] that during thermal cycling of vanadium dioxide VO₂, a change in the ratio of the ultimate composition tends to decrease in the oxygen content. It is noted in a number of articles that vanadium dioxide is metastable under natural conditions and it is subject to spontaneous oxidation under the influence of atmospheric oxygen to V₂O₅ (V) oxide leading to a change in its properties. Deviation from stoichiometry, both with an excess of anion vacancies and with an excess of anions in interstitial spaces, also leads to a change in the properties of the material [8, 9]. The effect of thermal cycling on the electrical properties of VO_{2±}Y, on the change in the ratio of the ultimate and chemical composition of the dioxide remains poorly studied.

2. Problem statement
The main objective of this work is to study the effect of thermal cycling on the electrical properties of VO_{2±}Y system materials at PTSM, on the ratio of the ultimate composition of these materials, and also to study the chemical composition of VO₂.
3. Theory

The original vanadium dioxide of the stoichiometric composition VO$_2$ was prepared by dissociating vanadium oxide V$_2$O$_5$ (V$_2$O$_5$) at temperature 1300 K in vacuum (at pressure $5 \times 10^{-2}$ Torr) within 7 hours. Compounds VO$_{2+Y}$ (VO$_{1.990}$, VO$_{1.995}$) were obtained by subsequent dissociation of the initial sample in deeper vacuum at different temperatures, and VO$_{2+Y}$ (VO$_{2.010}$, VO$_{2.030}$) were obtained by oxidation of vanadium dioxide of stoichiometric composition in air at 600 K, varying the time of oxidation.

The obtained materials were subjected to x-ray phase analysis on an x-ray diffractometer Shimadzu Maxima_X XRD-7000, which showed that the materials obtained for the research are single-phase, fine black powders.

Each of the materials obtained was subjected to successively 30 thermo cycles. At each thermal cycle, the material was initially heated to ~360 K and cooled to ~310 K, the partial pressure of oxygen was maintained equal to the atmospheric pressure. Thermal cycling (TC) of the material was carried out in a hermetically sealed capsule in a muffle furnace WiseTherm FHP-05.

For the analysis of the ultimate and chemical composition of vanadium dioxide of stoichiometric composition before and after thermal cycling a surface-sensitive X-ray photoelectron spectroscopy (XPS) method was used. When measuring XPS spectra, the pressure in the analytical chamber was ~$10^{-9}$ Torr. The estimated depth of samples analysis with the XPS method is ~ 1 – 3 nm.

To clarify the ultimate composition of materials before and after thermal cycling, the method of X-ray spectral analysis was used on JEOL JCM – 5700 scanning electron microscope, accelerating voltage was 15 kV, and the beam current was 1.0 nA.

Measurements of the electrical resistance in the heating and cooling modes were carried out using the standard two-contact method with the bridge MO-61 in the temperature range from 300 K up to 400 K with a relative error less than 6%, the temperature was recorded with a graduated copper-constantan thermocouple.

4. Experimental results

The dependences of the relative electrical resistance on temperature for vanadium dioxide VO$_2$, both in the heating mode (solid line) and in the cooling mode (dashed line) of the sample are shown in Fig. 1. $R_0$ is the electrical resistance of the material at 400 K. At PTMD there is an abrupt change in the electrical resistance from the semiconductor state to the metallic one, as well as the hysteresis, as for the starting material, Fig. 1 (a) ($\Delta \ln(R/R_0)$ is about 6, the hysteresis width is $\Delta T_1$, ~4 K), as for the material after 30 thermal cycles, Fig. 1 (b) ($\Delta \ln(R/R_0)$ is about 3.5, the hysteresis width is $\Delta T_1$, ~7 K).

Similar results were obtained for other samples; the results are presented in Table 1.
Table 1. Comparative table of the parameters of vanadium dioxide before and after thermal cycling

| Compound | Starting material | Material after 30 thermal cycles |
|----------|-------------------|----------------------------------|
|          | $\Delta \ln (R/R_0)$ | $\Delta T_1$, K | V/O | $\Delta \ln (R/R_0)$ | $\Delta T_1$, K | V/O |
| VO$_{1.990}$ | 2.3 | 4 | 1.60 | 1.5 | 8 | 3.17 |
| VO$_{1.995}$ | 1.5 | 6 | 1.60 | 1.0 | 10 | 3.18 |
| VO$_{1.997}$ | 2.4 | 5 | 1.59 | 1.2 | 9 | 3.18 |
| VO$_2$ | 6.0 | 4 | 1.59 | 3.5 | 7 | 3.19 |
| VO$_{2.010}$ | 5.0 | 5 | 1.58 | 3.2 | 10 | 3.19 |
| VO$_{2.030}$ | 1.6 | 5 | 1.57 | 1.0 | 10 | 3.20 |

$\Delta \ln (R/R_0)$ is the change in electrical resistance at PTSM; $\Delta T_1$ is PTSM temperature range; V/O is the ratio of the content of vanadium to oxygen in the sample (according to the results of the EMS).

XPS spectra of VO$_2$ powders before and after thermal cycling are presented in Fig.2. Vanadium lines are observed in the XPS spectra of both samples: V 2s (binding energy is ~ 630 eV), V 2p (binding energy is ~ 515 eV), V 3s (binding energy is ~ 70 eV) and V 3p (binding energy is ~ 40 eV); oxygen: O KLL auger-transition line (binding energy is ~ 70 eV), O 1s (binding energy is ~ 970 eV) and O 2s (binding energy is ~ 25 eV); carbon: C 1s (binding energy is ~ 284 eV); nitrogen: N 1s (binding energy is ~ 400 eV).

The presence of a carbon line is associated with the presence of contaminants in the samples and on their surface; apparently, their presence is due to the peculiarities of the samples receiving and storing. The presence of nitrogen is apparently due to its adsorption from the atmosphere. The high surface area of vanadium oxide powder does not allow removal of the entire layer adsorbed on the surface during the ion cleaning process. For a quantitative analysis of the samples composition, oxygen lines O 1s were selected. The results of the quantitative analysis are presented in Table 2.

![Figure 2](image_url)  
**Figure 2.** Review XPS spectra of vanadium oxide samples: (1) is starting VO$_2$, (2) is VO$_2$ after thermal cycling (30 cycles). $I_r$ is intensity in relative units.
Table 2. The results of the quantitative analysis of VO$_2$ powders before and after thermo cycling according to XPS data

| Sample        | Concentration, at. % |
|---------------|----------------------|
|               | [V] | [O] | [C] | [N] |
| VO$_2$        | 21.9 | 53.2 | 23.7 | 1.2 |
| VO$_2$ + TC   | 25.3 | 51.6 | 21.4 | 1.7 |

It is shown that the spectra of VO$_2$ samples both before and after thermal cycling have the same shape (Fig. 3), and the positions of the main maxima O 1s and V 2p$_{3/2}$ coincide and they are 530 and 516.5 eV, respectively. The energy gap $\Delta$ between the maxima is 13.5 eV.

According to [10] the position of the maximum V 2p$_{3/2}$ for V$^{4+}$ oxide is 516.1 eV, and the value of the parameter $\Delta$ is 13.9 eV. For V$^{5+}$ oxide characteristic position of the maximum V 2p$_{3/2}$ is 517.1 eV, and the value of the parameter $\Delta$ is 12.9 eV.

Figure 3. XPS spectra of VO$_2$: (1) is starting, (2) is after thermo cycling, $I_n$ is normalized intensity
The main characteristics of the spectra shown in Fig.3 and 4 are given in Table 3. Data from Table 3 proves that the oxygen and vanadium lines in the XPS spectra of the starting and thermally cycled powders have similar values of the FWHM parameter. This also testifies the fact that the chemical environment of vanadium is identical in these samples.

Table 3. Characteristics of XPS spectra of samples V 2p$_{3/2}$ and O 1s vanadium dioxide before and after thermo cycling

| Sample   | V 2p$_{3/2}$ | O 1s | Δ, eV |
|----------|--------------|------|-------|
|          | Position of maximum, eV | FWHM, eV | Position of maximum, eV | FWHM, eV |       |
| VO$_2$   | 516.5        | 2.65 | 530.0 | 2.03 | 13.5   |
| VO$_2$+TC| 516.5        | 2.73 | 530.0 | 1.93 | 13.5   |

5. Discussion

For all the materials studied, there is a sharp change in the electrical resistance at temperature $\sim$ 340 K. Vanadium dioxide of stoichiometric composition VO$_2$ has the largest jump in electrical resistance $\Delta \ln (R/R_0) =$ 6. With deviation from stoichiometry, both decreasing and increasing the oxygen content, the electrical resistance jump at PTSM is unsystematically reduced. An increase in the oxygen content in the sample leads to an increase in the hysteresis width by 25%. With a decrease in the oxygen content for VO$_{1.995}$ the hysteresis width increases by 2 times.

As a result of thermal cycling, all materials have a decrease in the electrical resistivity at PTSM up to $\sim$ 50% and an increase in the hysteresis width is observed; for most materials $\Delta T$, increases by 2 times. At temperatures above the phase transition temperature, the electrical resistivity does not depend on temperature; in the temperature range from 300K up to $\sim$ 340 K temperature dependence of the resistivity is characteristic of semiconductors.

According to the results of the X-ray analysis, it was determined that the oxygen concentration as a result of thermal cycling is significantly reduced for all materials up to $\sim$50%.
It can be concluded from the results of the XPS analysis of the analyzed samples spectra, that $V^{4+}$ oxide predominates in the surface layer of VO$_2$ samples both before and after thermal cycling and there are also small inclusions of $V^{5+}$ oxide.

According to the results of the content of oxygen and vanadium atomic concentrations in the studied samples in the composition of VO$_2$ samples before thermal cycling, it can be concluded that there is some excess of oxygen. This excess may be due to the oxidized state of carbon, which is part of the samples in large quantities. In addition, it is also possible to form V$_2$O$_5$ oxide on the surface of the powder granules as a result of natural oxidation. After thermal cycling, as in the case of X-ray analysis, a decrease in the oxygen content on VO$_2$ surface is observed.

6. Conclusion

It was proved that for all materials of VO$_{2+y}$ system a phase transition semiconductor-metal is observed, and it is accompanied by a sharp change in electrical resistance both before and after thermal cycling. Despite the fact that PTMD retained after thermal cycling, the resistivity jump $\Delta \ln(R/R_0)$ at PTMD significantly reduced to 50%, the transition temperature becomes more diffused. The ratio of the surface ultimate composition of all the materials studied tends to decrease the oxygen content. Vanadium dioxide of stoichiometric composition has the maximum jump in electrical resistance at PTSM before and after thermal cycling.

7. References

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