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Doped vanadium oxides phase transitions vapors influence

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Abstract

The methods of vanadium dioxide synthesis were developed. The first one is based on the decomposition of vanadyl oxalate VOC_2O_4 obtained by the dissolution of vanadium oxide (V) in ethanedioic acid solution with consequent heating. The second one uses the magnetron sputtering of metallic vanadium with its consequent soft oxidation. Investigations of the transition temperature in vanadium dioxide influence by the material doping and adding MoO_3 , Bi_2O_3 , SnO_2 , NiO , CuO , Co_3O_4 as well as by the presence of various gases and vapors in the atmosphere were made.

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1. Introduction

The main purpose of the present work is to demonstrate that vanadium dioxide and its compounds are suitable candidates to contribute to an improvement of chemical sensors concerning their sensitivity, selectivity and stability. In order to realize this, it is proposed to use the effect of a giant change of the electrical conductivity within the temperature region of phase transition metal–semiconductor. It is well known that gas adsorption can modify the concentration of charge carriers. Hence, gas adsorption at temperatures, close to the metal–semiconductor (dielectric) transition temperature, can vary the energy gap width of VO_2 and, consequently, remarkably influence its electrical conductivity. A possibility to obtain a metal–insulator transition by means of chemisorption of hydrogen on the surface of VO_2 film was reported already [1].

The mechanism of environmental action on electric parameters of the matter in the region of phase transition does not differ from that for any other region. Essential for these

interactions is the effect of amplifying caused by a liability of crystalline and electronic structures in the transition range.

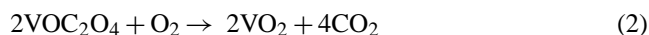
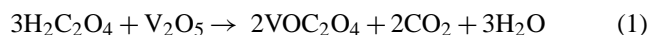
Vanadium compounds have catalytic activity in oxidation reactions. For example, such phases as $\text{Li}_x\text{V}_2\text{O}_5$ and $\text{Fe}_x\text{Li}_2\text{O}_5$ have very high selectivity and catalytic activity to oxidizing reactions of organic compounds. In particular, such activity is observed in oxidizing reactions of aromatic compounds: *p*-heptane, butane, benzene, toluene, aromatic alcohols and aldehydes, of heterogeneous ring compounds, sulphonations of benzenes, etc. [2–4]. Application of vanadium oxides for oxydation of CO and SO_2 seems promising. The interaction connected with electrons transfer on the surface of the oxide (catalytic agent) should result in modification of charge carriers concentration in the bulk too. Therefore, one can expect, that VO_2 and its compounds with other oxides might be successfully applied to detect reducing gases, and, in particular, vapors of organic compounds, in particular of alcohol, ketones, aldehydes, benzene in air.

2. Experimental

There are different methods to form film coatings on the basis of vanadium oxides. Usually the layers are prepared by

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the pyrolysis of vanadium-organic compounds (pyrolysis of the acetylacetonate of vanadyl), sol-gel methods, and also methods of thermal and cathode evaporation [5–7]. In order to obtain vanadium dioxide we used the method of decomposition of vanadyl oxalate (VOC_2O_4) which in its turn had been obtained by the dissolution of vanadium oxide (V) in ethanedioic acid solution with heating:



The initial films were obtained by dip coating and jet plating of the solution of vanadyl oxalate on polished substrates of polycrystalline glass. It is worth mentioning that different plastifiers were added in the vanadyl solutions in order to improve the adhesion to the substrate, rheological properties of the solutions as well as the homogeneity of the substrate coverage. A vast series of matters were studied for the use in this role. A composition on the basis of ethanol and polyvinyl alcohol has shown the best properties from the point of view of homogeneity of the film plating, its density and the adhesion to the substrate. The plated solutions were dried in the UHF furnace. The obtained films were annealed in a nitrogen atmosphere at different temperatures. The study of the optimal layer annealing temperature was carried out. The annealing of the films was performed within the temperature interval of 650–1100 K. The optimal range was established as 820–850 K. This is the range of the best concise of the cell parameters and best quality of the phase transition conductance curve shape.

X-ray phase analysis (XPA) of the matter obtained after decomposition of oxalate of vanadyl was performed: Cu K(-radiation, voltage 30 kV, current 10 mA; the range of angles $2\theta = 15\text{--}85^\circ$, speed of $20^\circ \text{ min}^{-1}$).

We also used the method of thin films preparation of vanadium dioxide by the magnetron sputtering of metallic vanadium (99.9% purity) with its consequent soft oxidation. The sputtering was carried out in an argon atmosphere (10^{-2} Pa) with a potential of 500 V. The etching current was about 15–20 mA. The sputtering of the films lasted 300 s. It was observed, that in the case of longer sputtering a partial oxidation of both the film and the target takes place. The last effect leads to a decrease in the sputtering rate and to a degradation of the film performance.

The influence of substrate properties on the properties of the films was studied. In this case thin films of vanadium dioxide are favorable objects of study in the view of a presence of semiconductor to metal phase transition (SMPT). Its presence and the magnitude are the testimonies of a thin film perfection. For samples preparation we used the substrates of polycrystalline glass, single-crystalline silicon (1 0 0), oxidized single-crystalline silicon (Si/SiO_2), glasses, titanate-zirconate of lanthanum-calcium. The substrates were treated in the peroxide-ammonia mixture, washed out in distilled water and then desiccated.

The soft oxidation technique in an inert atmosphere with water vapour was designed for making of the oxide layers based on VO_2 . Nitrogen bubbled through the bi-distilled water with expenditure of 1 l/min and moved in a furnace. The heating of the substrates with metallic films was carried out in this furnace. The temperature of annealing was varied from 500 up to 850 K. The temperature range 670–720 K was optimal as at lower temperatures oxidation did not take place, higher temperatures led to destruction of the layer.

Resistance-temperature dependences of the layers by the two-probe method on air were obtained. A cell with a possibility to control the atmosphere in it was constructed to perform these measurements. Ohmic In-Ga electrodes were formed on the film surface. The pinch platinum electrodes were delivered to them. The electrical resistance was measured by a voltmeter with an error not higher than 0.1%. The measuring temperature interval was 300–520 K. Temperature in the cell was monitored with calibrated chromel-alumel thermoelectric couple located closely to the sample.

To study the sensor properties of the obtained layers we analyzed a temperature dependence of the films resistance in the presence and in the absence of the following gases and organic vapors in the atmosphere: CO (200–1000 ppm), NH_3 (50–400 ppm), NO_x (10–1000 ppm), ethanol (10–50 ppm), *p*-xylem (10–50 ppm), acetylacetone (10–50 ppm), benzyl (10–50 ppm), toluene (10–50 ppm), deacon (10–50 ppm), dimethyl formamide (10–50 ppm), 1,4-dioxane (10–50 ppm)). The study of the gas sensitivity of VO_2 was carried out on thick-film samples. The paste prepared from an oxide powder and alcohol was plated on the polycrystalline glass substrates by the method of printing. The obtained films were tempered in a nitrogen atmosphere.

3. Results and discussion

XPA of the matter obtained after decomposition of oxalate of vanadyl was carried out by confrontation of values of angles of the characteristic peaks and the intensities of investigated matter with the values taken from the catalog (International Centre for Diffraction Data joint Committee on Powder Diffraction Standards, ICDD JCPDS). The obtained data clearly shows a presence of vanadium dioxide (see Fig. 1). Other phases of vanadium oxides are not revealed.

For a part of the samples tested in the air atmosphere the decrease of resistance with its consequent increase at some temperature is observed that indicates a presence of the semiconductor to metal phase transition (SMPT). In the range of transition temperatures the resistance of layers varies within two orders of magnitude that is in agreement with the data on vanadium dioxide films available in the literature [1]. The SMPT occurs in a temperature range of 300–340 K with a temperature hysteresis about 10–25°. Vanadium dioxide is known as a material with a first-order phase transition, and such a hysteresis is a characteristic one for the material.

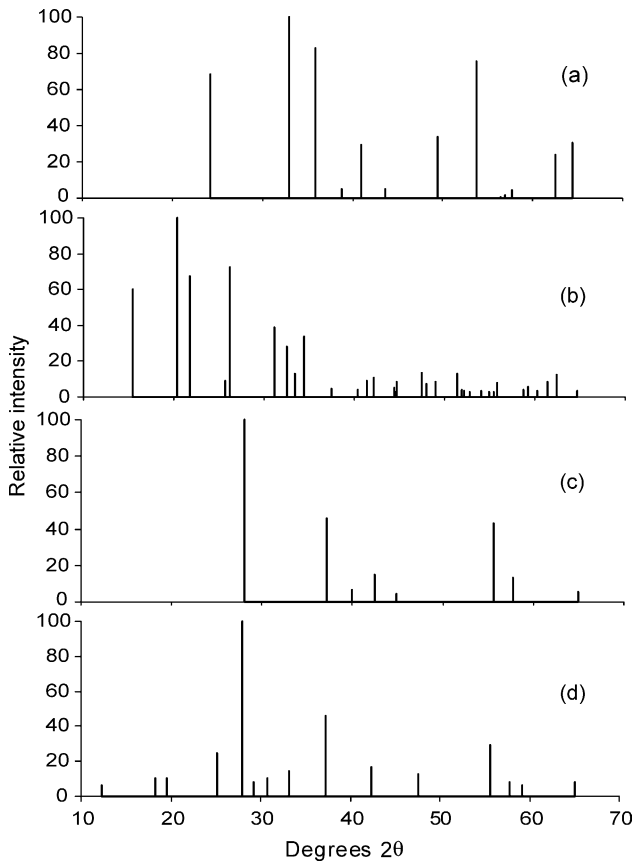


Fig. 1. X-ray diffraction patterns for V_2O_3 JCPDS 71-0347 (a), V_2O_5 JCPDS 75-0457 (b), VO_2 JCPDS 73-2362 (c), obtained VO_2 (d).

The temperature dependences of resistance for two heating–cooling cycles are given in Figs. 2–4.

The transition temperatures for all samples were lower, than for single-crystal samples (~ 340 K) [1]. The transition for the films obtained by magnetron sputtering was more abrupt than this for the films obtained by the decomposition of vanadyl oxalate. Temperature dependence of resistance demonstrate, that the substrate used remarkably influences the

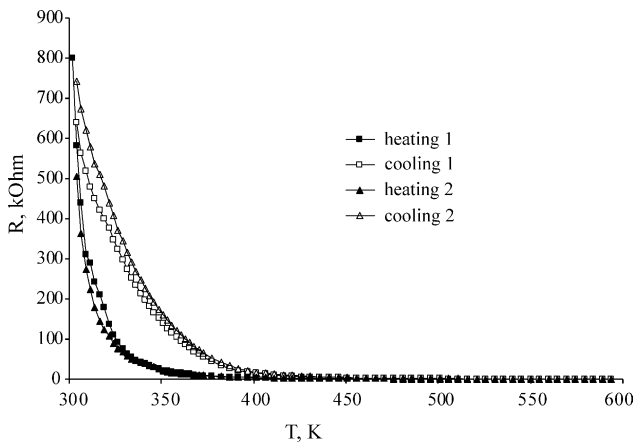


Fig. 2. Temperature dependence of the film resistance of vanadium dioxide obtained by decomposition of vanadyl oxalate.

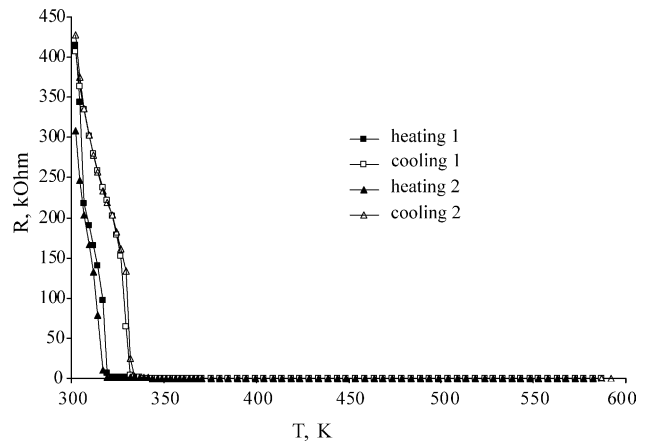


Fig. 3. Temperature dependence of the resistance film of vanadium dioxide obtained by magnetron sputtering with soft oxidation (the substrate is oxidized monocrystalline silicon).

electrical properties of the films. The best results were obtained when the smooth substrates (a silicon oxide, polished polycrystalline glass) were used. For such samples the transition temperature is higher, electrical physical properties are more stable in time.

It is also necessary to study the film behavior after phase transition. In our experiments the metallic nature of conductivity after transition was not observed. The conductivity continued to increase (Fig. 5). Such a behavior may be due to the presence of vanadium oxide (V) trace amounts in vanadium dioxide samples (or its appearance over a partial oxidation on air of vanadium dioxide during measurements). Then the co-existence of competitive mechanisms of conductivity is possible. Thus, exponential increase of the carriers density with temperature for semiconducting V_2O_5 overlaps decrease of conductivity (the power law from temperature) of the metallic phase of vanadium dioxide.

Other approach in definition of this effect, connected with disordering of VO_2 lattice is also possible. For VO_x the Schot-

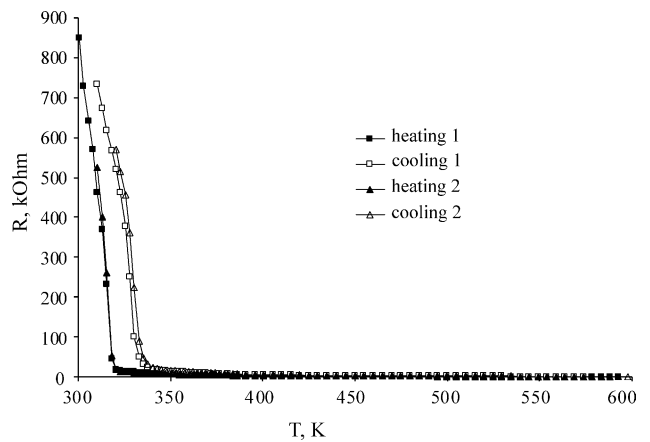


Fig. 4. Temperature dependence of the film resistance of vanadium dioxide obtained by magnetron sputtering with soft oxidation (the substrate is polycrystalline glass polished).

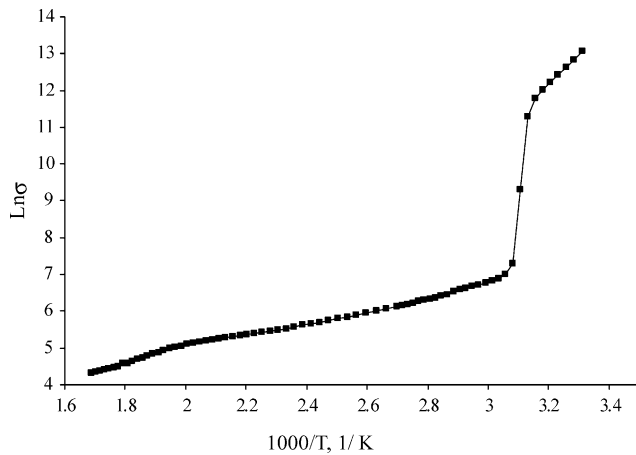
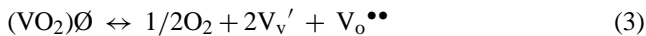


Fig. 5. Temperature dependence of the conductivity of vanadium dioxide thin film samples obtained by magnetron sputtering with soft oxidation (the substrate is oxidized single-crystalline silicon).

ky imperfections are characteristic. Thus, the disordering in vanadium dioxide lattice may be described as



or



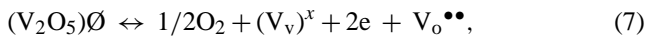
further ionization



or



Thus, with the temperature increase the processes of disordering in the lattice of vanadium dioxide may lead to the appearance of the carriers, and, consequently, to the increase of conductivity. Then, the presence of impurities of vanadium oxide (V) may result in a disordering of its lattice by the following equation:



This also contributes to the increase in conductivity.

We also studied an influence of doping on transition temperature in vanadium dioxide. The samples were manufactured by a ceramic process. We prepared the compositions on the basis of VO_2 with a different content (0.1–50 mol%) of MoO_3 , Bi_2O_3 , SnO_2 , NiO , CuO , Co_3O_4 . This dopants and additives were selected using a supposition, that the intercalation of these elements in the lattice of vanadium dioxide will provoke a magnification of the transition temperature because of a possible chemical contraction, breaking vanadium pairs in dioxide [1]. It is known, that increase of phase transition temperature, indispensable for the majority of gases registration, is provided by an introduction of elements with lower valence (less than 4). Besides, the Fermi level is decreased. It is known from the catalysis electronic theory, that this causes processes of donor adsorption. On the other hand, adding

components with higher valence decreases of the phase transition temperature (though often only slightly). But in this way the Fermi level is increased, that initiates acceptor adsorptive processes. At the same time, these components can be catalysts of preferential directions of reactions. Tungsten and molybdenum oxides were used as such additives. From the obtained mixture of oxides we prepared 0.8 ± 0.1 mm thick tablets with diameter of 9 mm. The optimal conditions of the thermal processing were found; particularly, the best results were obtained for the temperature of 925 K. After the first processing the samples were chafed, and the firing cycle was repeated.

To study an influence of the admixtures on the transition temperature, the temperature dependencies of electric conductivity (ac and dc current modes) and Zeebeck voltage were measured. The measurements were carried out in the temperature range of 290–450 K. The upper limit was set in order to prevent a possible oxidation of vanadium dioxide. The analysis of the obtained data showed, that no one of the admixtures mentioned above influences the transition temperature remarkably. Thus, the admixtures of cobalt, tungsten and molybdenum decrease the temperature of the SMPT (several K). The temperature range of the transition reaches 20–25°. The samples with a small amount of Bi (0.5–5%) and Sn (0.1–0.5%) have transition temperatures that are slightly higher than those of the undoped samples. The temperature range of the SMPT for these concentrations appears to be narrow. For the samples doped with tin a weak temperature dependence of electric conductivity within a temperature range of 350–370 K was observed. This can be attributed to the following competitive processes: first, the conductivity turns to be of a metallic type; second, the admixture is activated. The doping level being increased, both the magnitude of SMPT and the transition temperature become smaller. We shall also mention the positive influence of trace amounts of the admixtures on sintering ability of VO_2 ceramics. The results of the electrical measurements are presented in Fig. 6. When the doping level increases the SMPT magnitude increases too.

An interesting behavior of the samples doped with bismuth is found: the introduction of small amounts of the

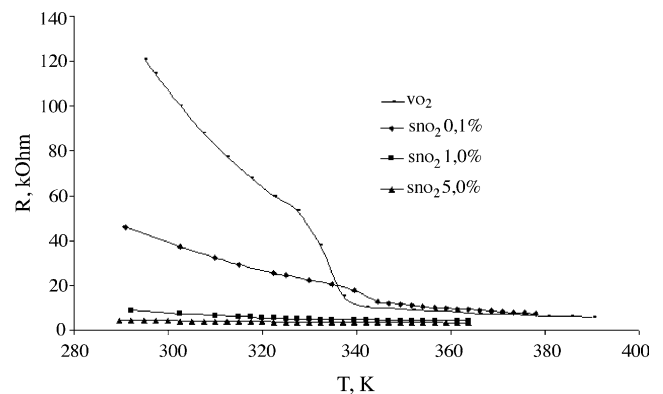


Fig. 6. Temperature dependence of resistance of the bulk samples of VO_2 doped with SnO_2 .

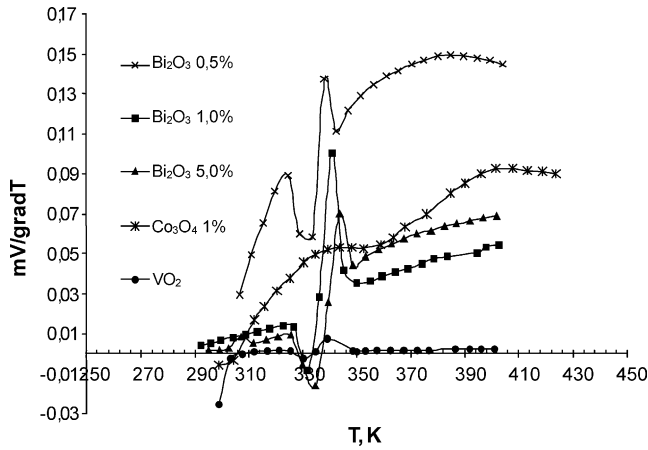


Fig. 7. Temperature dependence of Zeebeck coefficient for the samples of vanadium dioxide doped with Bi_2O_3 , Co_3O_4 .

dopant results in a strong increase of the Zeebeck coefficient; however, the effect becomes less remarkable for higher concentration levels (Fig. 7). The similar behavior is observed in classic doped semiconductors (Ge, Si). The conductance type changes within the range of the phase transition.

Measurements of the response were performed in a hermetic unit. The maximum change of the sample resistance was registered when introducing of the vapor-and-gas mixture with a constant rate of the airflow. The gas sensitivity was calculated from the obtained data according to the following expression:

$$S = \frac{R - R_0}{R_0} \times 100\%, \quad (8)$$

$$S' = \frac{R_0 - R}{R} \times 100\%, \quad (9)$$

where R_0 is the sample resistance in the air, R the resistance of the sample if the corresponding substance is present (both quantities are functions of temperature). Eqs. (8) and (9) were used for the calculations of the film's response to the gases increasing or decreasing its resistance, respectively.

The gas sensitivity was investigated in the temperature range of 298–520 K. The VO_2 samples added or doped with WO_3 (1, 3, and 5 mol%), Bi_2O_3 (0.5 and 1%) MoO_3 (5, 10, and 20%), SnO_2 (1, 5, and 10%), NiO (5, 10, 20, and 50%), CuO (0.5, 3, and 10%) were studied. The best sensitivity to NO_x was found for the samples with Mo. Fig. 8 demonstrates the dynamic response of the VO_2 with 10 mol% Mo for three cycles gas inlet—pumping-out of 100 ppm NO_x . The film shows a good reproducibility of the response; the film resistance returns to the initial (reference) value within 5% of accuracy after the atmosphere regeneration.

No response to CO , NH_3 , *p*-xylene, benzene, decane, dimethylformamide, 1,4-dioxane was registered. The best results were obtained for acethylacetone (50 ppm) and ethanol

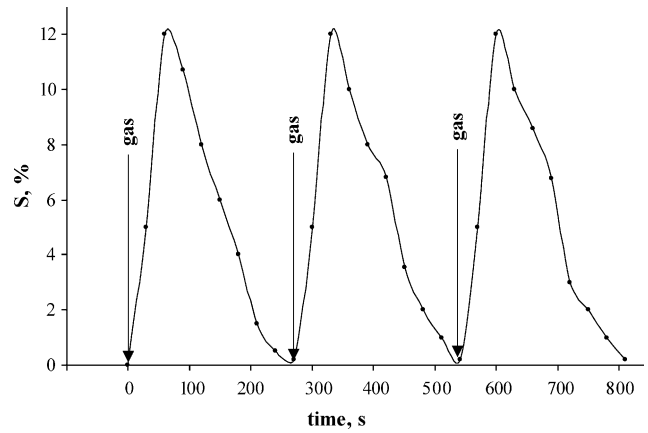


Fig. 8. Time dependence of sensitivity at 100 ppm NO_x of the samples VO_2 with 10 mol% MoO_3 ($T = 480$ K).

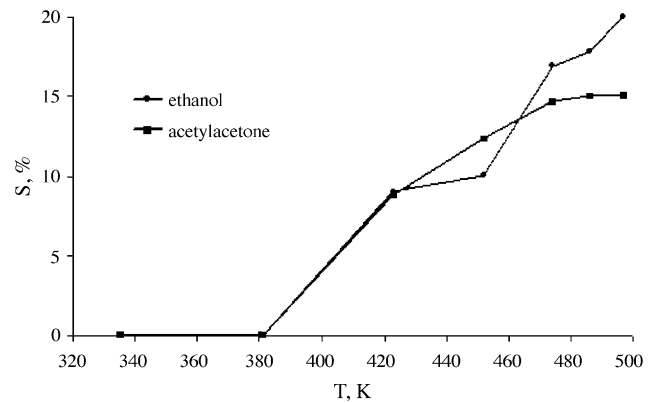


Fig. 9. The sensitivity of the samples VO_2 with 50 mol% NiO vs. temperature at 50 ppm acethylacetone and ethanol. Reduction time 5–10 s.

for VO_2 with a high concentration of NiO (50 mol%) and CuO (10 mol%) (see Figs. 9 and 10). But no significant influence of gases and vapors on the phase transition parameters was registered. Generally, the sensitivity increases with temperature.

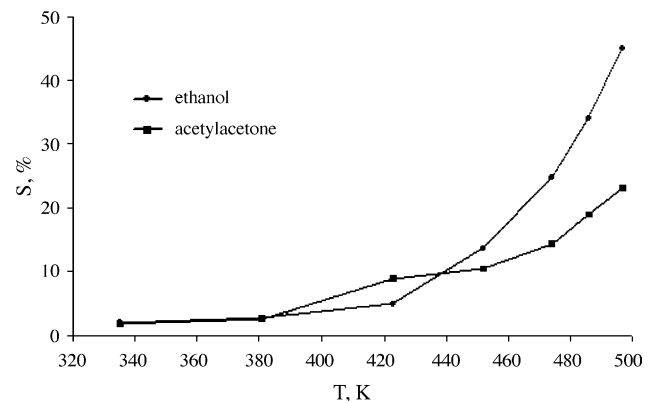


Fig. 10. The sensitivity of the samples VO_2 with 10 mol% CuO vs. temperature at 50 ppm acethylacetone and ethanol. Reduction time 5–10 s.

4. Conclusion

The task to utilize phase transition giant conductance change for gas sensor device was unsuccessful. The reason is vanadium dioxide structure: in the semiconductor temperature region it has almost molecular crystalline structure with localized V–V bonds, insensitive to external impacts. From the other temperature side the metal conductance does not favor substantial charge carriers change when chemisorption occurs. Besides, we could not increase SMPT temperature substantially by doping vanadium dioxide up to favorable to gas–solid interaction one. This is also the reason of low sensitivity. But the composite samples with NiO, CuO, were found to be sensitive to oxygen-containing VOC vapors (acetylacetone and ethanol) and with MoO₃—to NO_x. The probable reason for this is metal (VO₂)–semiconductor (other metal oxide) junctions between the grains. This problems are the matter of further investigations.

References

- [1] A.A. Bugaev, B.P. Zaharchenia, F.A. Chudnovsky, Semiconductor–metall phase transition and it applications, Nauka, Leningrad, 1979, p. 183.
- [2] J. Norris, The role of precious metal catalysts, in: P.T. Mosely, B.C. Tofield (Eds.), Solid State Gas Sensors, Alam Higer, Bristol/Philadelphia, 1987, pp. 124–138.
- [3] Catalytic properties of substances. Reference Book, Kiiiv, Nauk, Dumka, 1975, p. 1464.
- [4] Y.I. Ermakov, V.A. Zaharov, B.N. Kuznetsov, Complexes fixed on oxide medium in catalysis, Novosibirsk, Nauka, 1980, p. 74.
- [5] G.A. Rozgonyi, J. Pilitow, Preparation of thin films of vanadium (Di-, Sequi-, Pent-) oxide, J. Electrochem. Soc. 115 (1) (1968) 56–57.
- [6] L. Ryabova, et al., Preparation and properties of pyrolysis of vanadium oxide films, J. Electrochem. Soc. 119 (1972) 427–429.
- [7] D.H. Hensber, Transport properties of sputtered vanadium dioxide thin films, J. Appl. Phys. 39 (1968) 2354–2360.

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