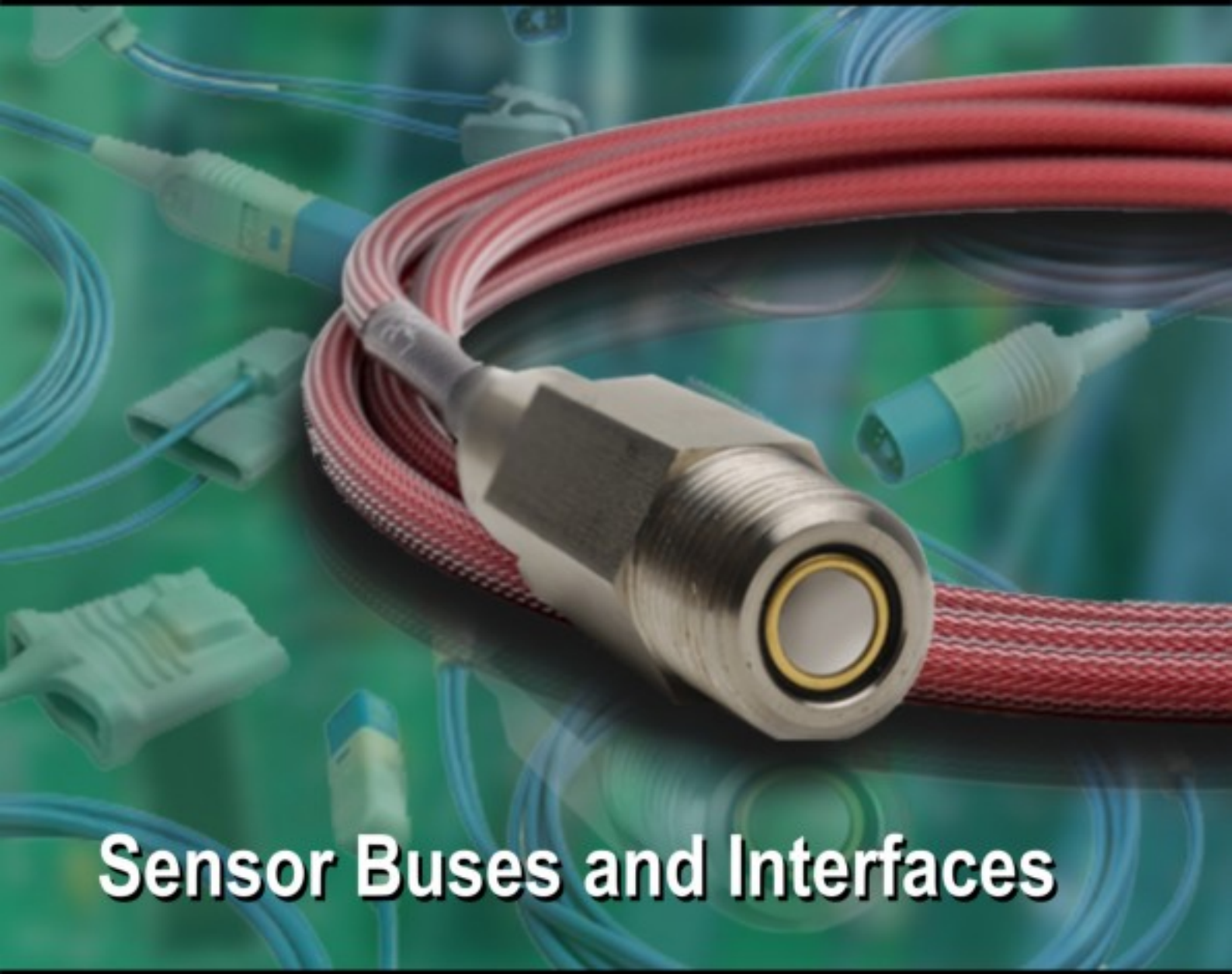
ISSN 1726-5749

SENSORS & TRANSDUCERS

vol. 92
5/08



Sensor Buses and Interfaces

International Frequency Sensor Association Publishing

IFSA

Sensors & Transducers

Volume 92
Issue 5
May 2008

www.sensorsportal.com

ISSN 1726-5479

Sensors & Transducers Journal (ISSN 1726-5479) is a peer review international journal published monthly online by International Frequency Sensor Association (IFSA).

Sensors & Transducers Journal

Contents

Volume 92
Issue 5
May 2008

www.sensorsportal.com

ISSN 1726-5479

Research Articles

Authors are encouraged to submit article in MS Word (doc) and Acrobat (pdf) formats by e-mail: editor@sensorsportal.com
Please visit journal's webpage with preparation instructions: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm

Sensors & Transducers Journal, Vol. 92, Issue 5, May 2008, pp. 69-86

www.sensorsportal.com

Sensors & Transducers

ISSN 1726-5479

http://www.sensorsportal.com

Vanadium Doped Tungsten Oxide Material - Electrical Physical and Sensing Properties

[1] SHISHKIN N. Y., [1] CHERKASOV V. A., [1] KOMAROV A. A., [1] BASHKIROV L. A., [2] BARDI U., [3] GUNKO Y. K., [4] TARATYN Y. A.

[1] Belarus State University of Technology, Sverdlov st. 13-A, Minsk 220050, Belarus
E-mail: nickoshi@yahoo.com

[2] Dipartimento di Chimica, Università diFirenze, Polo Scientifico di Sesto Fiorentino, 50019 Firenze, Italy

[3] Department of Chemistry, Trinity College, Dublin 2, Ireland

[4] Minsk Research Institute of Radiomaterials 86, Kizhevatova str., 220024, Minsk, Belarus

Received: 14 April 2008 /Accepted: 20 May 2008 /Published: 26 May 2008

Abstract: The electrical physical and sensing (to VOCs and inorganic gases) properties of vanadium doped tungsten oxide in the regions of phase transition temperature were investigated. Vanadium oxide (II) dimerization was observed in the doped material, corresponding to new phase transition. The extreme sensitivity and selectivity to chemically active gases and vapors in small concentrations: CO, NOx, NH_3 acetone, ethanol near phase transitions temperature was found. Sensor elements were manufactured for the quantitative detection (close to 1 ppm) of alcohol and ammonia.

Keywords: NO_x, Alcohol, Ammonia, Gas sensor, WO_3 and V_2O_5 films, Phase transition, Ceramic compositions

1. Introduction

VOCs are important pollutants in many technological processes. Nitrogen oxides (NO and NO_2, NO_x) are very poisonous causing air pollution, ethanol and ammonia are the gases to be detected in small amounts in technology and food industry [1]. Different oxide semiconductors are used for NO_x detection [2-4]. WO_3 is considered as one of the candidates for NO_x-sensing materials [5]. The investigations of tungsten trioxide - metal oxide (MO_x) systems have indicated the improvement of

sensor properties over the basic electrochromic tungsten oxide [6-16]. Composite WO_3 - MO_X films have been prepared by vacuum evaporation [6, 7], electrodeposition [8, 9], sputtering [10], electron-beam deposition [11] and sol-gel deposition [12-16] techniques.

WO_3 can exist in various crystalline modifications: tetragonal (> 740°C), orthorombic (~330-740°C), and also in the monoclinic (17-330°C), triclinic (-40 - +17°C). The region of oxide homogeneity is narrow. Non-stoichiometry of WO_{3-x} can reach stoichiometries such as $WO_{2,96}$. Tungsten oxide WO_3 alongside with vanadium oxides (with oxidation states lower than 5), exhibit a metal - semiconductor phase transition. The temperature of this phase transition depends on the stoichiometry. Considerable changes of the WO_3 electrical conductance is observed for phase transitions at lower than ambient temperatures. The electroresistance decreases with diminution of the oxygen content (the electron concentration increases). However the consequences of this phase transition on the manufacturing of sensors was neglected up to now. Nevertheless, the phenomena of sharp change of resistance in proper temperature region may be promising for utilization as gas-sensitive state.

The mobility of carriers, calculated from Hall and conductance measurements, decreases with diminution of the oxygen content. The best interpretation of electrical properties is possible assuming that the WO_{3-x} non-stoichiometrical phases are constructed from blocks of stoichiometrical WO_3 and sites containing defects. It is quite probable that in tungsten oxide (6) there is a potential hill between WO_3 and WO_{3-x} (WO_3 with defects) phases showing a p-n junction.

It is possible to decrease the temperature of the phase transition by increasing the degree of non-stoichiometry of the oxide. It is possible to change the oxygen concentration and, as a consequence the degree of non - stoichiometry of WO_3 by high temperature treatments in a gas flow with various partial pressure of oxygen. Also, the replacement of W^{6+} ions with ions of different transition elements may result in temperature decrease and increase. Being a non-equilibrium process, doping is more stable that the furnace treatment process.

The temperature interval suitable for gas sensor operating covers the interval of 120-250°C. One of the phase transition temperatures of tungsten oxide with considerable change of electrical conductance is lower (17°C), another is higher (330°C). So the task is to shift it to adjust phase-transition temperatures of the material to the interval 120-250°C. The doping of WO_3 with vanadium oxides may help to solve the problem. First, if we dope WO_3 with oxide of vanadium - the metal with lower valence,- vanadium may substitute not the phases of non-defect blocks WO_3 (see above), but the WO_{3-x} region. This may take place for better structural correspondence of VO_y to WO_{3-x} ($y < 2.5$) (comparative to WO_3 lack of oxygen in VO_y). This way VO_y may stabilize the non-stoichiometry of tungsten oxide. Another possibility is vanadium-doped blocks formation with p-type semiconductance.

2. Experimental

We prepared WO_3 based materials using conventional ceramic technology. The starting material was commercial analytical grade WO_3. Also V_2O_5 of analytical grade was utilized as a dopant and additive.

The initial materials were mixed, wet-milled, formatted with binding agent into pellets of 10 mm diameter and 1 mm thickness at forming pressure of 120 MPa. Then they were dried and calcined. The specimens were sintered at the temperatures from 823 °C to 923 °C in air with soaking time of 12-15 h.

The measured porosity of the sintered samples was about 12 %. The compositions of the ceramic samples were as follows $(1-x)WO_3+xV_2O_5$, where x = 0.05; 0.04; 0.035; 0.02; 0.015; 0.01; 0. Measurements of electrical properties were conducted on the pellets with Ag electrodes and In-Ga

alloy Ohmic contact electrode coated on both surfaces. Pressing electrodes were made of platinum. Direct current conductance, Zeebeck voltage, capacitance and conductance at the frequency about 1 MHz AC measurements were performed in the temperature region of 290 – 550 K.

For possible improvement of sensor properties some of the 2 % at. V ($0{,}99WO_3$+ $0{,}01V_2O_5$) layers we activated the films by palladium, considered to be a good catalytic agent in different reactions. The activation of the surface was carried out by printing on the surface and impregnating the volume with small amounts of palladium. The methods used are summarized in Table 1.

Table 1. Methods of palladium catalyst additions to the $0{,}99WO_3$+$0{,}01V_2O_5$ material.

Method	Burning out conditions	N of the film
1.Palladium chloride solution (1 at.%) was added to the mixture of $0{,}99WO_3$+$0{,}01V_2O_5$ (1:20 vol.) with further careful milling, film printing with a consequent calcination	1h – 80 °C 1h – 230 °C 4h – 600 °C	1
2.Well mixed of the powders of $PdCl_2$ and $0{,}99WO_3$+$0{,}01V_2O_5$ (1:50 at. parts) with ethanol was printed on the substrate	1h – 80 °C 1h – 230 °C 4h – 600 °C	2-4
3.Film surface of $0{,}99WO_3$+$0{,}01V_2O_5$ was impregnated with palladium chloride solution (1 at.%) by a drop wise method with consequent heat treatment	1h – 80 °C 1h – 230 °C 4h – 400 °C	5-7

The initial measurements of the electrical properties were made on thick films produced by screen printing using crystalline glass, mica coated with silicium dioxide and alumina as substrates. Most experiments were conducted on crystalline glass as a more stable substrate. Ag electrodes were preprinted or In-Ga electrodes pasted over. The thickness of the layers was about 10^{-5} m. The samples, which had demonstrated best characteristics as sensing material, were utilized for production of the sensor elements, based on microelectronic technology. Measurements were made in a gas flow principal chamber and with constant gas content mode. Gas concentration varied with gas blender. The volatile organic compounds concentration was controlled by calculating partial vapour pressure temperature dependence over the liquid. The chamber was placed into the oven.

X-ray diffraction analysis was carried out on samples containing 0.05; 0.04; 0.035; 0.02 (0.02 - at ambient temperature and 515K); 0.015; 0.01 (0.01 - at ambient temperature and 515 K) at. parts of V and pure WO_3 using Cu K_a radiation. Cell parameters – a,b,c, beta were calculated and compared to the monoclinic (I) modification (a=72.97 nm, b=75.39 nm, c=76.88 nm, β=90°88", PDF# 43-1035).

3. Results and Discussion

3.1. Tungsten Oxide (6) Based Samples

The electroconductance of non-doped WO_3 (as well as doped) has the peak at the phase transition temperature (17°C), clearly observed by DC, AC and dielectric measurements (Fig. 1-4) was studied up to 600 K. In the investigated region the conductance has n-type character (after 17°C) with predictable behavior (Fig. 10).

For the samples containing vanadium oxide, the temperature of the phase transition (at 17°C) slightly shifts to higher temperatures (by 1-5K) by the composition with 8 % at. V and then drops again (Fig. 2, 3). At temperatures over the monoclinic - triclinic phase transition, the conductance of the doped samples changes in an irregular way.

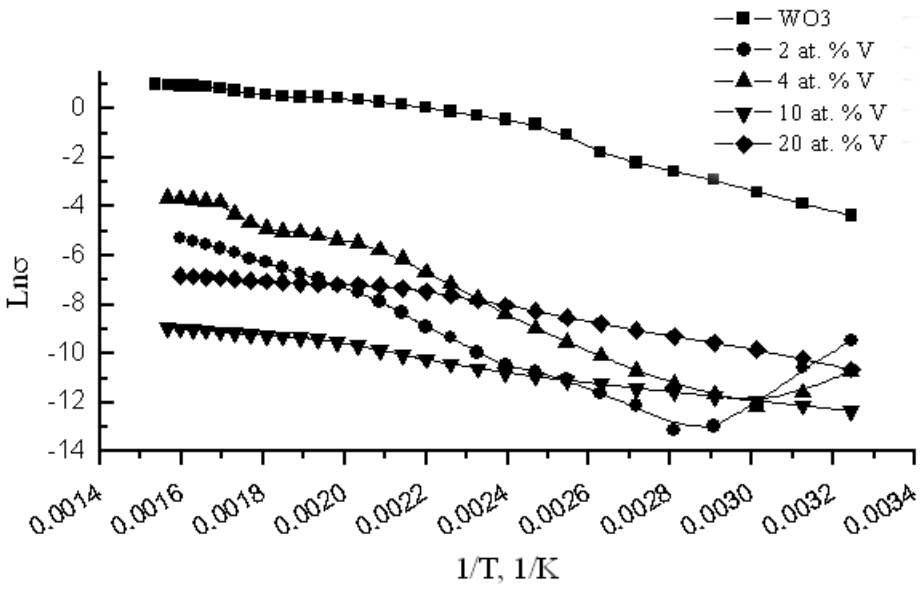


Fig. 1. Temperature dependence of conductance ($Ohm^{-1}m$) WO_3 and $WO_3+V_2O_5$ ceramic samples (DC).

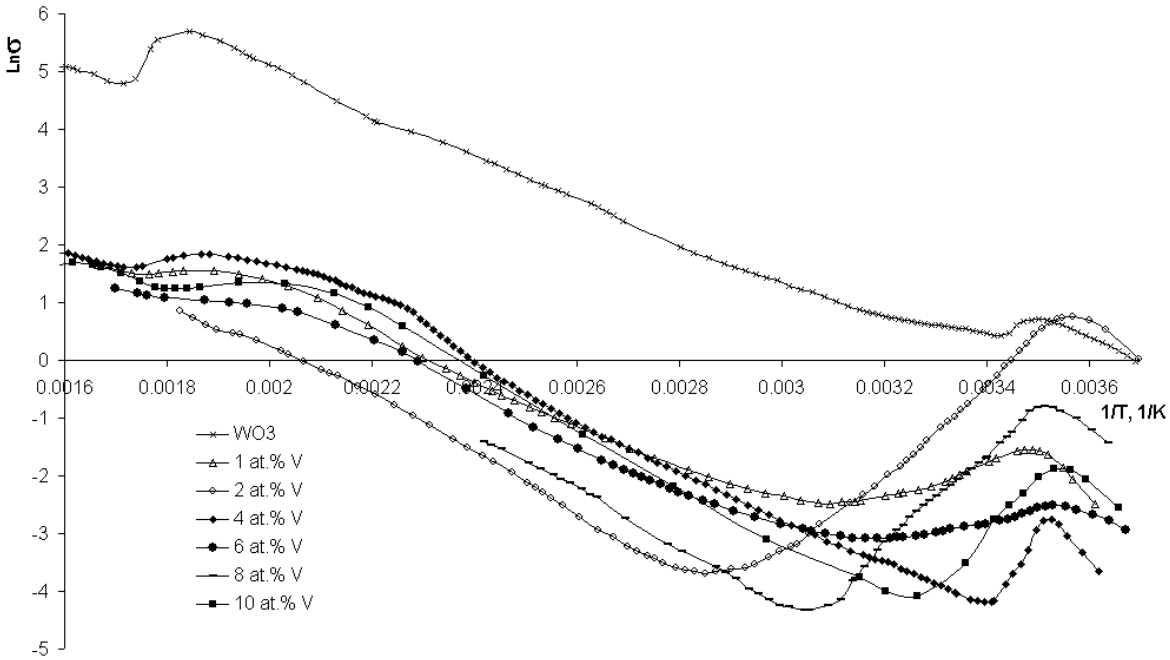


Fig. 2. Temperature dependence of conductance ($Ohm^{-1}m$) WO_3 and $WO_3+V_2O_5$ ceramic samples (AC 1 MHz).

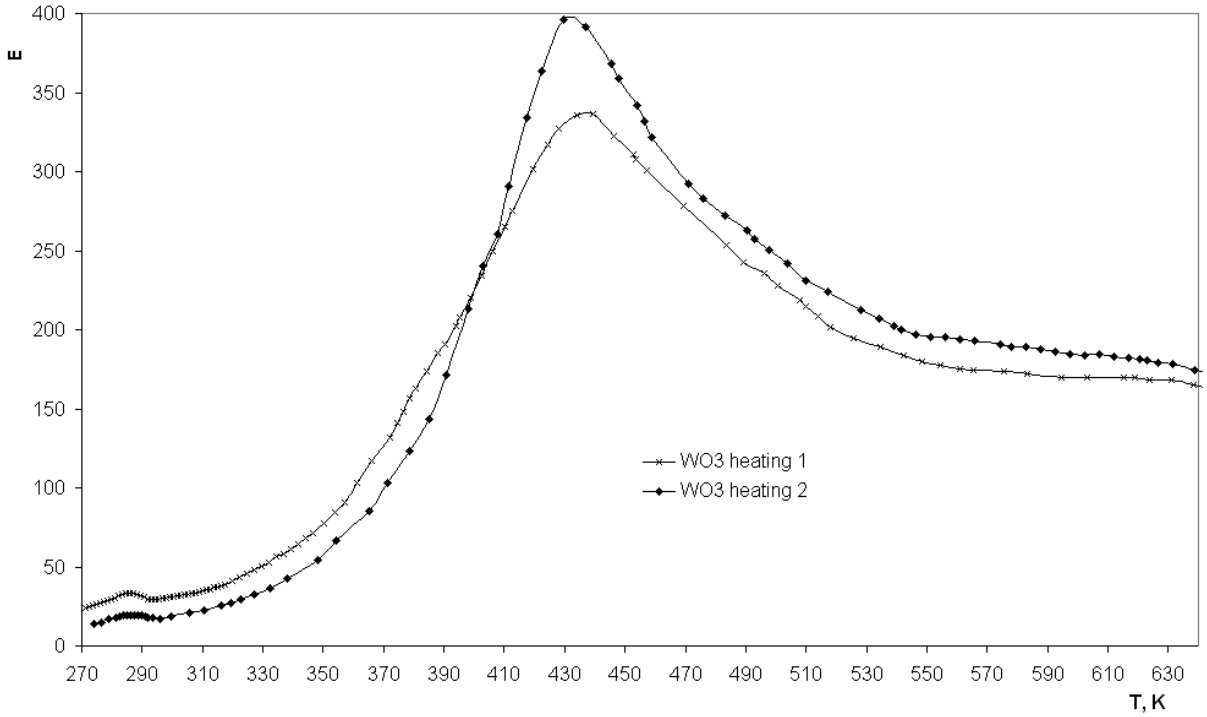


Fig. 3. Dielectric permeability (1 MHz) of WO_3 ceramic samples vs. temperature.

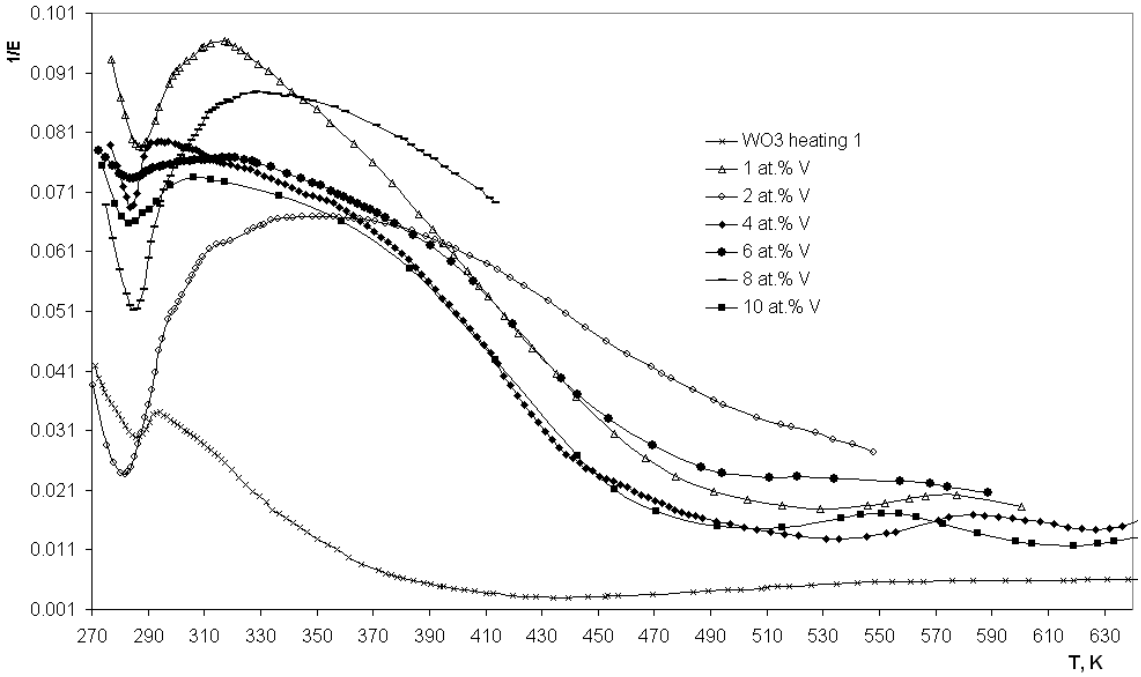


Fig. 4. Reverse dielectric permeability (1 MHz) of WO_3+V_2O_5 ceramic samples vs. temperature.

The compositions with 2-4 at.% of vanadium show peculiarities in the 40-100°C region when measuring in direct current, (DC) but no such phenomena for measurements in AC (1 MHz) currents of conductance and permeability (Fig. 1-4). The existence of these phenomena is supported by the measurements of the cell parameters (Fig. 7). Peculiarities are observed for the samples with 3-4 at.% V. A minimum of the b, c, beta values corresponds to these compositions. Moreover, the cell parameters dependence may explain the conductance behavior. Initial adding of V_2O_5 to WO_3 results in tungsten ions substitution by vanadium ions. This doping results in b, c parameters decreasing. The reason is that vanadium ion (5) size – 0.04 nm - is lower, than that of tungsten (6) – 0.065 nm. This

phenomena is being observed for the samples by the concentration value of vanadium of about 6-8 at.%. Further adding of vanadium could result in either new vanadium oxide phase formation or interstitial defects formation. The two processes are likely to take place. Higher concentration of vanadium oxide (over 20% at.) may produce double-phase material (V_2O_3 phase found by X-ray, (Table 2). At the same time, the cell parameters increase in the range over 8 at. % V. This supports the idea of interstitial defects formation. In this way, the system of W-V oxides at lower vanadium content (up to 20 at.%) may be divided into three fields (at least). First, pure WO_3, second a region containing up by 6 at.% of vanadium, characterized by the substitution of regular tungsten ions by vanadium ones, the third characterized by interstitial defects of vanadium and (or) new phase of vanadium oxide (3) formation.

The conductance peculiarities in the mentioned cases may be explained as related to the formation of defects in the initial material WO_3. This phenomenon may be represented by the equilibrium.

$$2WO_3 \Leftrightarrow O_2 + 2W_w^{\prime} + \mathbf{V}_o \tag{1a}$$

or

$$0 \Leftrightarrow O_2 + \mathbf{V}_o^{\cdot\cdot} + 2e'. \tag{1b}$$

As well known, bulk WO_3 is an n-type semiconductor and its conductance increases with temperature. Considering the conductance temperature dependence we take into account (1a) equilibrium constant (K) under constant oxygen partial pressure:

$$K= \sigma^3 = \exp(-\Delta G_{1a}/kT);$$

$$\ln\sigma = A - (\Delta H_{1a}/3k)(1/T).$$

The charge carriers increase also results in the growth of the dielectric permeability. The activation enthalpy of conductance was found to be about 1 eV. Such value is much lower than the band gap of tungsten oxide (2.5 eV). This supports the impurity character of conductance.

The initial (up to 6-8 at.%) vanadium oxides dissolution in tungsten oxide lattice can occur according the schemes:

$$V_2O_5 = 2V_W' + \mathbf{V}_o \tag{2a}$$

and

$$1/2\ \mathbf{V}_o^{\cdot\cdot} + 1/4O_2 = h^{\cdot} \tag{2b}$$

or

$$1/2\ \mathbf{V}_o^{\cdot\cdot} + 1/4O_2 + e' = 0 \tag{2c}$$

and

$$V_2O_5 + 2e' = 2V_W' + \mathbf{V}_o^{x} \tag{2d}$$

These relations demonstrate that at low temperatures the doped material may be a compensated n-type semiconductor. When temperature increases, the equilibrium (1) may prevail. The combination of the (1) and (2) equations results in the dependence of the charge carriers concentration as follows:

$$\ln(B\sigma^3 + C\sigma^2) = A - (\Delta H_{1a}/k)(1/T).$$

So the dependence of lnσ - 1/T has two slopes - $\Delta H_{1a}/2k$ (low temperatures) and $\Delta H_{1a}/3k$ (high temperatures). The experimental data support this assumption (Fig. 1-4). But the conductance behavior in the temperature region 60-80°C requires more attention. Zeebeck voltage measurements prove that the samples are n-type semiconductors. As it becomes clear, while preparing the samples, only the reaction (2a) may take place at cooling the sample, at least for the temperatures lower of about 20°C. And the quantity of vanadium built into the tungsten lattice does not exceed 8 at.% V. Only when increasing temperature, the reactions (2b, c) "begin". Reaction (1b) also takes place, but in substantial degree at higher temperatures.

We studied the time-dependent behavior of the 2 % at. V sample (Fig. 5). Oxygen dissolution in the lattice takes place for a long period of time (in the region 20-80°C).

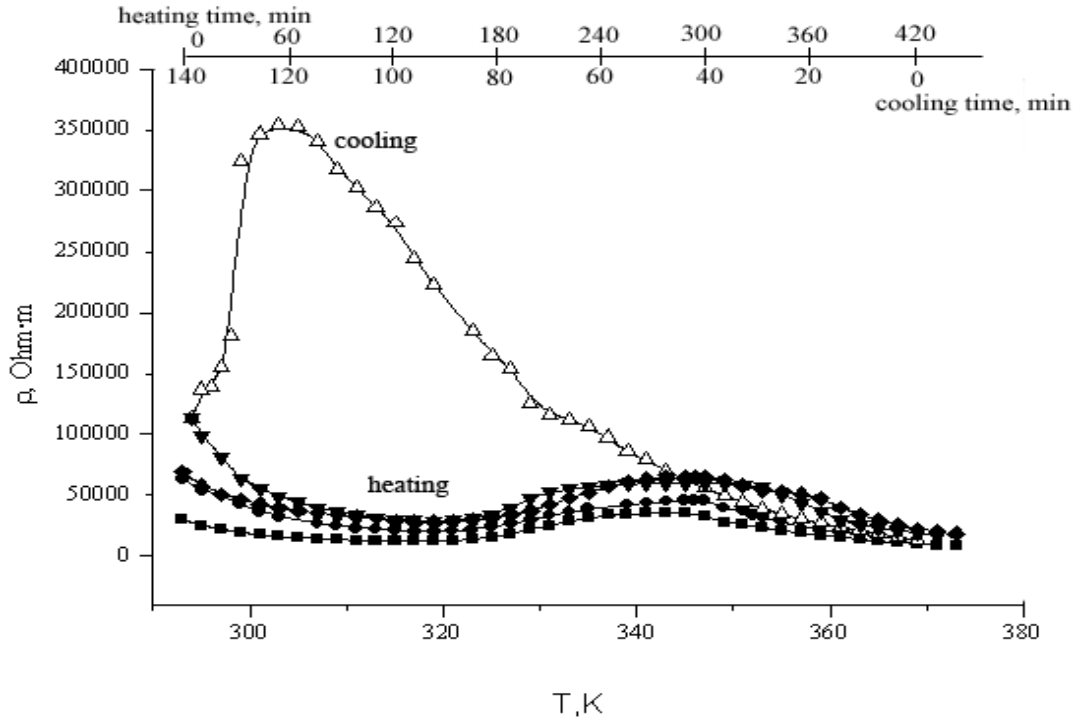


Fig. 5. Temperature dependence of resistance when heating and cooling WO_3 ceramic samples (DC): demonstration of oxygen invasion time dependence.

According to X-ray data on cell parameters (Fig. 6, 7), a complete substitution of the W units by V appears to occur at 8 at.% V. After this concentration is achieved, the doping occurs by interstitial invasion of V as follows:

$$V_2O_5 = 2V_i^{\cdots} + 5/2O_2 + 6e' \quad (3a)$$

or

$$V_2O_5 = 2V_i^{\cdot} + 5/2O_2 + 2e' \quad (3b)$$

and without ionization

$$V_2O_5 = 2V_i + 5/2O_2. \quad (3c)$$

In this way the material behavior returns to that of initial (WO_3), but with alter absolute values of conductance. The cell parameters increase because for the dilating action of interstitial vanadium atoms.

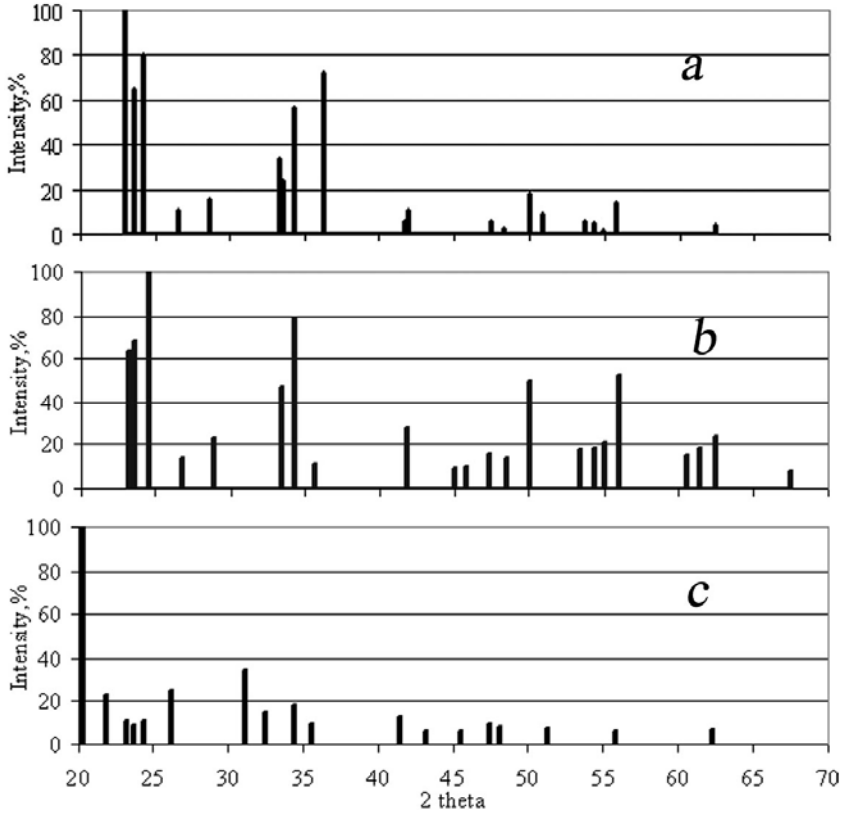


Fig. 6. X-ray diffraction patterns of WO_3 (a); $0.99WO_3+0.01V_2O_5$ (b); V_2O_5 (c).

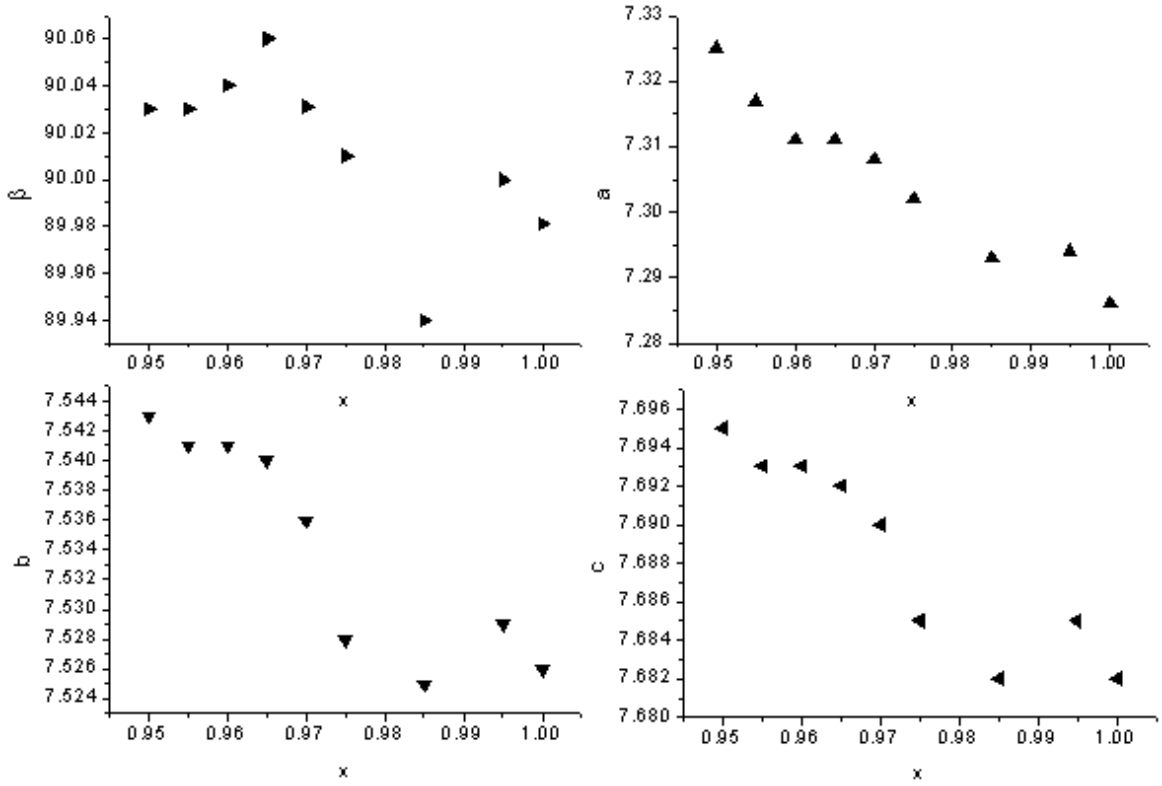


Fig. 7. X-ray diffraction obtained cell parameters (a, b, c, beta) of $(1-x)WO_3 + xV_2O_5$ compositions.

Another interpretation of the phenomena taking place with the 2-4 at.% doped samples is as follows. Instead of (2a) mechanism of doping another one may take place on heating (electrons were obtained by the reaction (1)):

$$2V_W' + 2e' = 2V_W'' [(VO_2)_2]. \quad (4a)$$

And if electron concentration (1) is low:

$$2V_W' = 2V_W'' [(VO_2)_2] + 2h. \quad (4b)$$

In this case, dimeric vanadium dioxide formation may be observed. The reasons for this are sterical factors too. Moreover, at low temperatures, vanadium dioxide exists in the form of molecules and electrons are localized. Further heating leads to dissociation of dimeric molecules and higher conductance of metallic type. Phase transition occurs at about 340 K. At this point, the behavior of conductance corresponds to the observed one (Fig. 1-4). The idea is supported by heating-cooling cycles (Fig. 5): when cooling, lack of oxygen (according to (1)) results in high electron concentration and stabilization of dimeric vanadium dioxide. The slow oxygen diffusion converts dioxide to pentoxide, it is the reverse reaction (4a) at lower temperatures than that of phase transition. The phenomenon disappears for higher concentration of vanadium for steric factor: cell parameters increase and do not allow close contact for vanadium ions. The V-V bond breaks.

On the basis of the X-ray data (Table 2, Fig. 6, 8, 9), it would be also possible to propose the formation of a V_2O_3 at high vanadium concentrations (over 20 % at.). However, the X-ray results may be also the effect of vanadium presentation (3b) in interstitial position. The replacement with vanadium oxide (3) may not occur, as charge difference (with tungsten) is too great. Therefore such oxide may exist as a separate phase. Probably disordering of vanadium oxide in a separate phase occurs:

$$V_2O_3 + 1/2O_2 + 2e' \Leftrightarrow 2/3\mathbf{V}_V''', \quad (5a)$$

$$V_2O_3 + 1/2O_2 \Leftrightarrow 2/3\mathbf{V}_V''' + 2h^{\cdot}. \quad (5b)$$

The content ratio of separate phase of vanadium and vanadium in the WO_3 lattice is a matter of discussion.

Table 2. X-ray diffraction data of the $0.9WO_3+0.1V_2O_5$ sample.

Sample $0.9WO_3 0.1V_2O_5$		**Standard**				**Sample $0.9WO_3 0.1V_2O_5$**		**Standard**			
		WO_3		**V_2O_3**				**WO_3**		**V_2O_3**	
dA	**Int**	**dA**	**Int**	**dA**	**Int**	**dA**	**Int**	**dA**	**Int**	**dA**	**Int**
7.087	8.9					1.9838	6.8				
3.8455	99.9	3.8500	100			1.9242	22.0	1.9230	20		
3.7966	69.3	3.7500	65			1.8836	10.7	1.8780	10		
3.6463	80.0			3.6500	60	1.8277	28.0			1.8300	25
3.3523	13.3	3.3500	10			1.8081	17.0	1.8060	16		
3.1036	29.3	3.1000	25			1.7119	11.3	1.7160	10		
2.6928	51.8	2.6860	35	2.7000	80	1.6903	35.0	1.6880	16	1.6900	100
2.6534	41.1	2.6620	35			1.6739	11.0	1.6740	10		
2.6216	51.0	2.6330	50			1.6446	6.0	1.6450	6		
2.5276	7.0	2.5250	6			1.5347	10.7	1.5350	10		
2.1673	16.6	2.1730	16			1.4906	8.0	1.4930	6		
2.0223	7.1	2.0180	10								

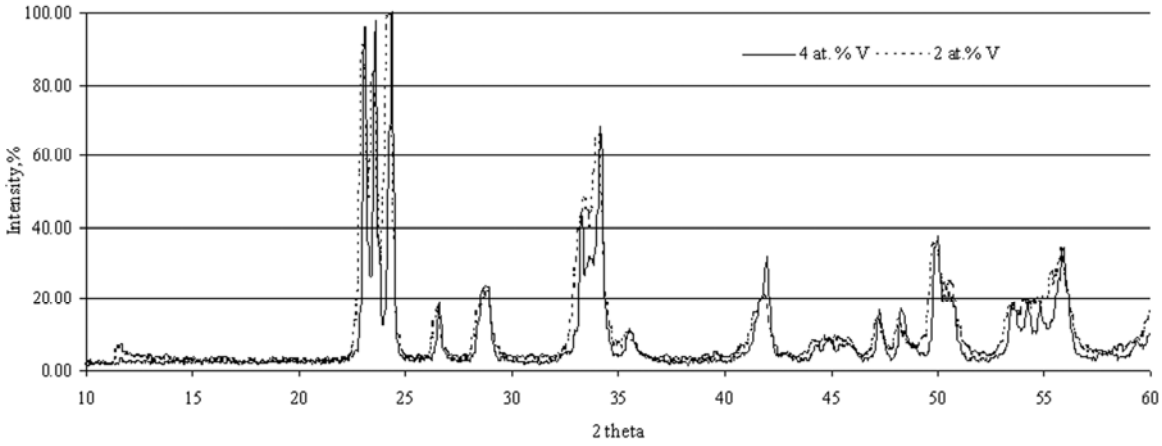


Fig. 8. Initial X-ray diffraction patterns of $0.99WO_3+0.01V_2O_5$ and $0.98WO_3+0.02V_2O_5$ samples.

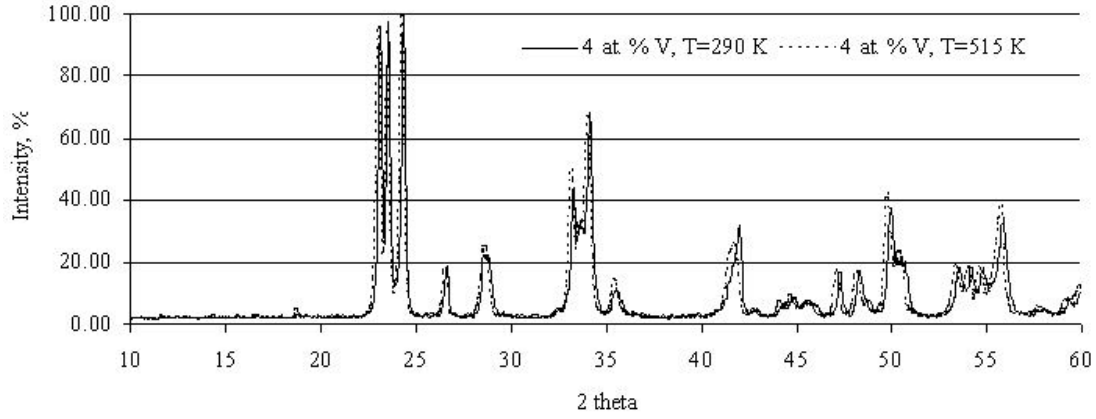


Fig. 9. Initial X-ray diffraction patterns of $0.98WO_3+0.02V_2O_5$ sample at different temperatures.

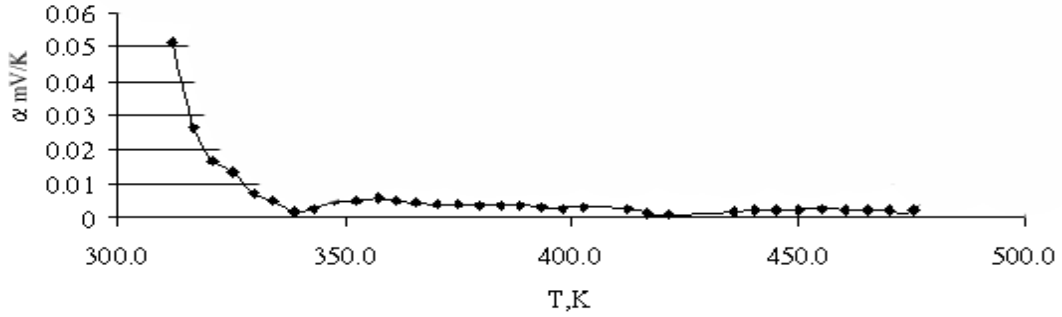


Fig. 10. Zeebeck voltage of WO_3 sample.

3.2. Sensing properties measurements

WO_3 films obtained by screen printing have shown high sensitivity to nitrogen oxide (5 ppm) and sulfur oxide (4) (10 ppm) at the temperatures close to those of phase transition. With alcohol vapor (100 ppm) the electroresistance did not significantly vary. The presence of benzaldehide (100 ppm) did not change the resistance (Table 3, Fig. 12). This behavior is explained by n-type semiconductance of WO_3 samples and the oxidizing character of NOx, amphoteric of SO_2 and reduction of benzaldehide and alcohol.

The values of the response and optimum or maximum operating temperatures at impulse inlet of the mixture are shown in Table 3.

Table 3. The best responsivity of the WO_3 based samples to some gases and vapors.

Sample	**Gas**	**Response, %**	**Temperature, K**
1. WO_3	Ethanol	40	450
	NO_x	8000	450
	SO_2	4000	460
	Benzaldehide	1	420
2. $0.99WO_3 + 0.01V_2O_5$	CO (impulse)	608	620
	CO (const)	244	600
	NH_3	300	570
	benzene	155	560
	toluene	350	560
	dimethyl formamide	40	298
	1,4 - dioxane	95	298
	p-xylene	310	536
	decane	5	440
	Ethanol	900	490
3. $0.9WO_3 + 0.1V_2O_5$	Ethanol	170	430
	NO_x	70	490
4. $0.98WO_3 + 0.02V_2O_5$	NH_3	300	300
	dimethyl formamide	150	540
	acethylacetone	115	495
	p-xylene	70	512
	ethanol	300	512

The films with 2 - 20 % at. vanadium content had lower responses to the presence of NO_2 in comparison with "pure" WO_3 films. It is clear from above discussion that the samples have compensated n-type conductivity, lower than for the case of WO_3. But these samples have higher sensitivity to alcohol vapors. This fact is in agreement with the expected behavior of n-type conductance of the material and red-ox character of the gases.

The most promising results in terms of sensitivity were obtained for 2-4 % at. vanadium content. The response of the 2 and 4 at. % V compositions to different gases and vapors of organic matters (NH_3, CO, dimethyl formamide, benzen, toluene, 1,4 - dioxane, p-xylene, decane) was examined and the main interest was focused on reduction gases. Gases with the following concentrations were obtained and utilized: CO - 20-10000 ppm, ammonia - 5-160 ppm, benzen - 1-40 ppm, toluene 1-12 ppm, 1,4-dioxane - 1-26 ppm, decane and ethanol -5 - 20 ppm (Table 3).

The response signal of the materials with conductivity of n-type to reduction gases was evaluated as:

$$(Rair - Rgas) / Rgas\ 100\ \%.$$

It is known, that CO is a strong reducing gas, but usually it requires a catalyst to react. Nevertheless, substantial response to CO is evident for the 2 at.% V composition (Fig. 11, Table 3, 100 ppm). CO was obtained by formic acid decomposition with concentrated sulphuric acid.

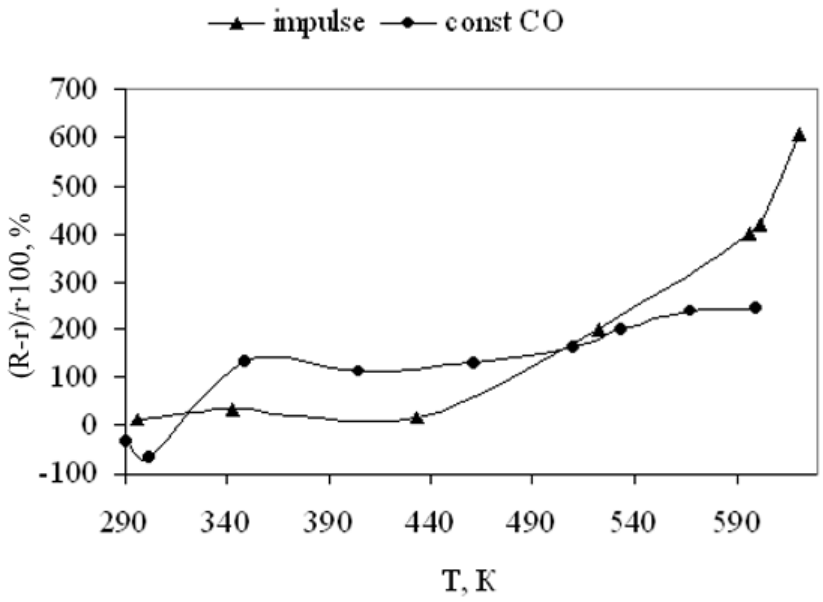


Fig. 11. Temperature dependence responsivity of the film $0.99WO_3 + 0.01V_2O_5$ to CO depending on the mode of the mixture inlet.

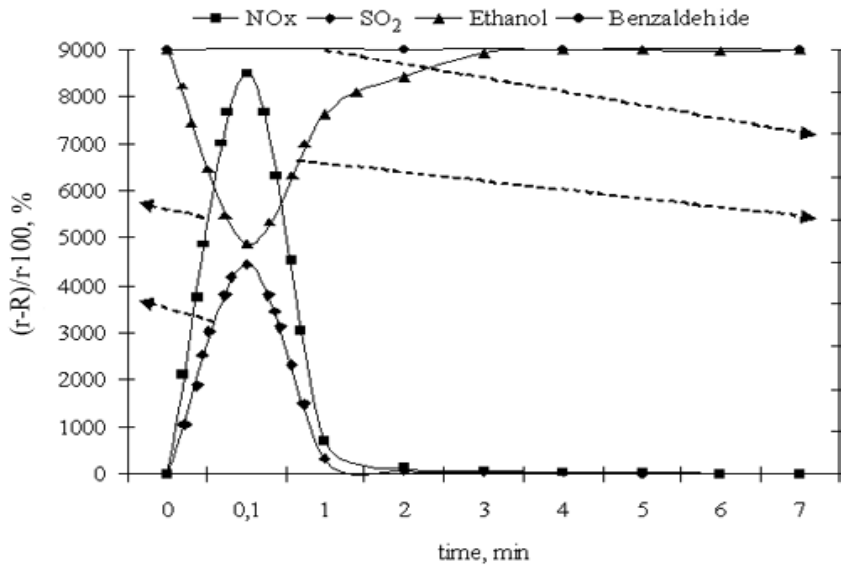


Fig. 12. Sensor properties of WO_3 ceramic layers.

Impulse inlet and flow stream methods were utilized to introduce CO mixture into the chamber. Interaction of the semiconducting oxide surface with CO may be described as:

$$CO_{gas} \leftrightarrow CO_{ads}$$

or

$$CO + O^-_{ads} \rightarrow COO^-_{ads}$$

$$COO^-_{ads} \rightarrow CO_{2\,ads} + e$$

or with lattice oxygen (less probable)

$$CO_{ads} + O^{2-} \leftrightarrow CO_{2\ ads} + 2e$$

$$CO_{2ads} \leftrightarrow CO_{2gas}$$

The density of oxygen ions adsorbed on the surface decreases and electrons are donated to the material again. The result is an increase in the samples conductance at high-temperatures, where the carriers of n-type predominate. Large response times (20-30 s) and reduction periods (10-30 min) were observed. This is the expected behavior for the samples without catalyst.

The best results were observed for the flow method. The first maximum of sensitivity was found at 340 K – that is at the temperature of minimal conductance and electron concentration. This result provides good support to the idea of abnormal sensitivity of the material at the temperature of phase transition. Of course, higher sensitivity is found at higher temperatures, mainly because of higher reactions speed rate. Moreover, the impulse inlet method demonstrates higher responses. But these results can be explained by kinetic factors.

Films on the base of $0{,}98WO_3+0{,}02V_2O_5$ were obtained by two method:

1) Screen printing of the sensing composition with consequent heat treatment, then silver electrodes burnt in;
2) Shaped silver contacts were deposited with subsequent printing of the material. The responsivity was evaluated in a stream with stationary values of gas concentration and with impulse input of gas in an airflow.

Responsivity to ethanol, ammonia, p-xylene, acethylacetone was explored. High responsivity to ethanol was found. To some gases high responsivity was found at room temperatures. However, as tungsten oxide is very sensitive to moisture at room temperatures, the response may be the result of the presence of water vapor as the vapor-gaseous mixtures were obtained by barbotage through solutions (for example, ethanol, ammonia). Our detailed study did not support this assumption: moisture did not effect the conductance in substantial degree. The responses to most organic matters for thick films of $0{,}98WO_3+0{,}02V_2O_5$ composition in all temperature interval were inappreciable (Fig. 13) except for ethanol. Regarding ethanol, we observed that the resistance on the low-temperature site increased, whereas it decreased at higher temperatures. To all gases small responses strictly at phase transition temperature region are observed. Very strong, but irreversible sensitivity before phase transition, connected with VO_2, was observed for ammonia. This irreversible adsorption takes place due to ammonia donating free electron pair to oxygen vacancies near vanadium (strong complex-formating ion). It liberates electrons captured by the vacancy:

$$\mathbf{V}_o^{x} + NH_3 = NH_3{:}\mathbf{V}o^{\cdot\cdot} + 2e'.$$

Considering that these semiconductor samples are materials with mixed conductivity, it is more probable that the density of charge carriers is low at these temperatures. For the films with interdigitated contacts, a drop of resistance and the response magnitude is observed, as contrasted for the films with side contacts. But an essential drop of resistance the response reduces not proportionally to resistance decrease. So at 534 K the resistance of the film with side contacts is lower than that of the film with interdigitated contacts of a factor of 30. The response magnitude has decreased only 2.4 times (from 1100 to 456 %), as the square for chemosorption between the electrodes is reduced. Fig. 14 demonstrates the influence of the sensing element production method and method of mixture inlet on responsivity to ethanol of the $0{,}98WO_3+0{,}02V_2O_5$ composition. From the data set it is possible to conclude, that by selection a combination of analyzable gas - operating temperature, it is possible to distinguish selectively many gases.

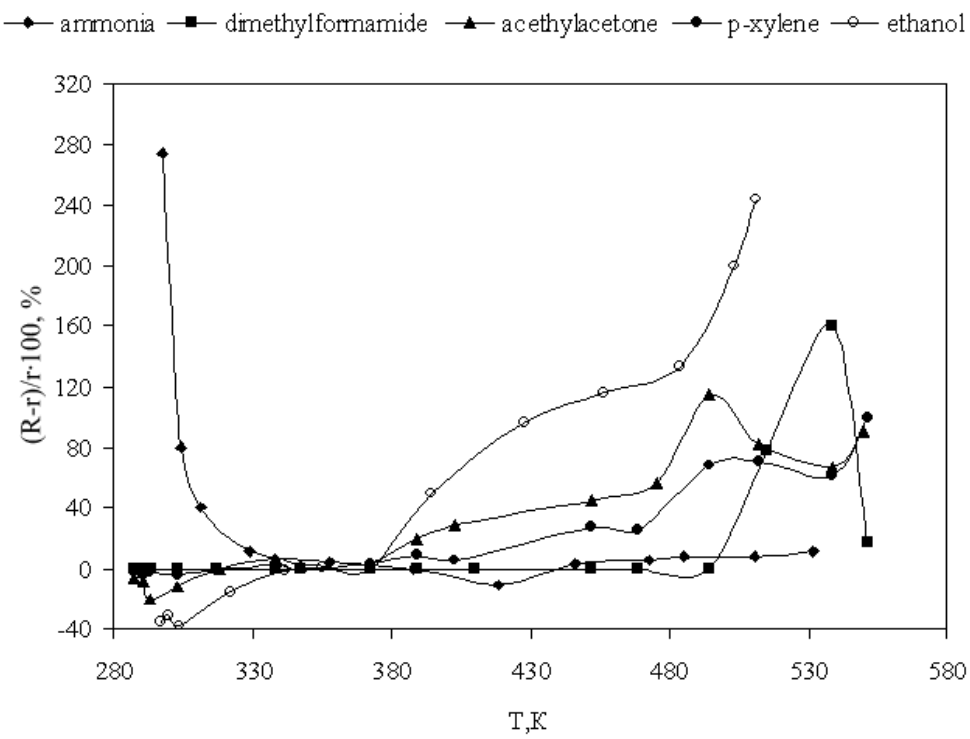


Fig. 13. Sensor properties of $0.98WO_3+0.02V_2O_5$ ceramic layers.

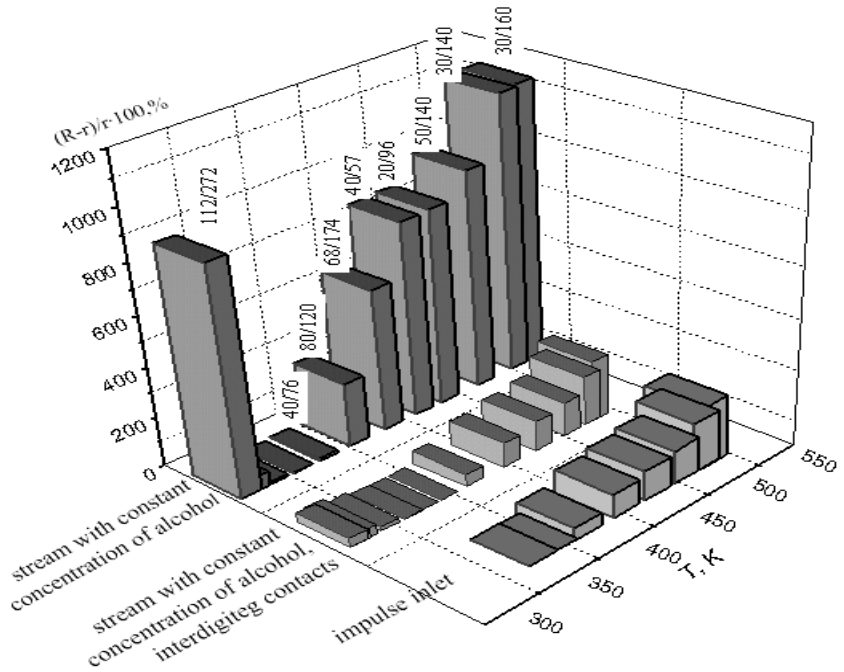


Fig. 14. Influence of sensing element production mode and mode of mixture inlet on responsivity to ethanol of the samples $0,98WO_3+0,02V_2O_5$.

3.3. Catalytic Samples Sensing Properties

The sensing properties of the samples with catalyst were investigated for a number of gases. The responsivity was measured in a pulse regime and static inlet. In contrast to the films without catalytic centres, these films display higher responsivity, and also the response time was improved. So, for example, by inlet of the air - ethanolic mixture the response time was 1-2 s, reduction period 30-40 s,

against 10-20 s and 1-3 min accordingly without the catalyst. A drop of response time was observed for all the gases also. Good sensitivity results were obtained to ethanol and acethylacetone (~ 2000 % and 1700 % resistance change).

The following stage was to prepare sensing elements suitable for industrial construction. We made such elements by sintering on air at 400 K small drop (about 1-2 mm in diameter) of the sample with two gold wires as electrodes. Only external heater was used.

Samples without catalyst ($0{,}98WO_3+0{,}02V_2O_5$) in such construction have high selection responsivity to the presence of ammonia (10-1000 ppm) in air (1700 % at operating temperature 500 K) as contrasted to low responsivity to a number of other gases (Fig. 15). Palladium doped samples ($0{,}99WO_3+0{,}01V_2O_5$ Table 1, pos.3) have high values of responsivity to ethanol and p-xylene (Fig. 16).

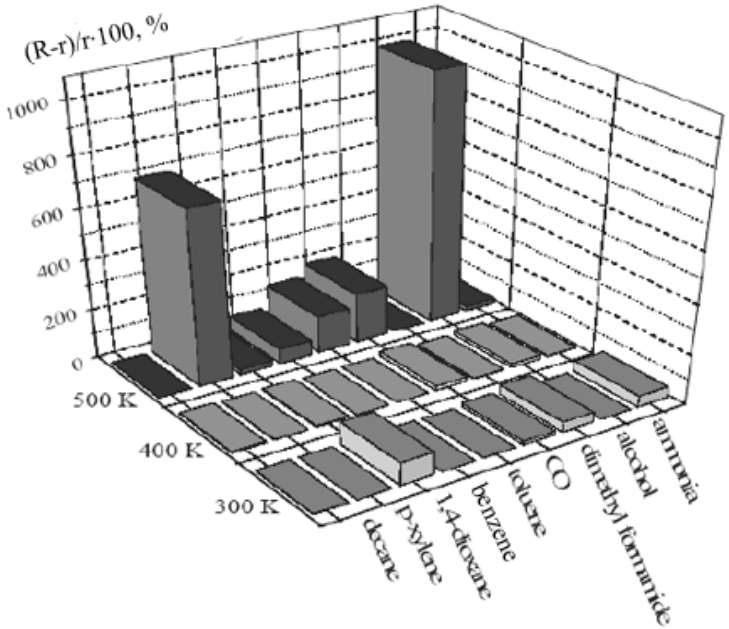


Fig. 15. Responsivity of the samples of $0{,}98WO_3+0{,}02V_2O_5$.

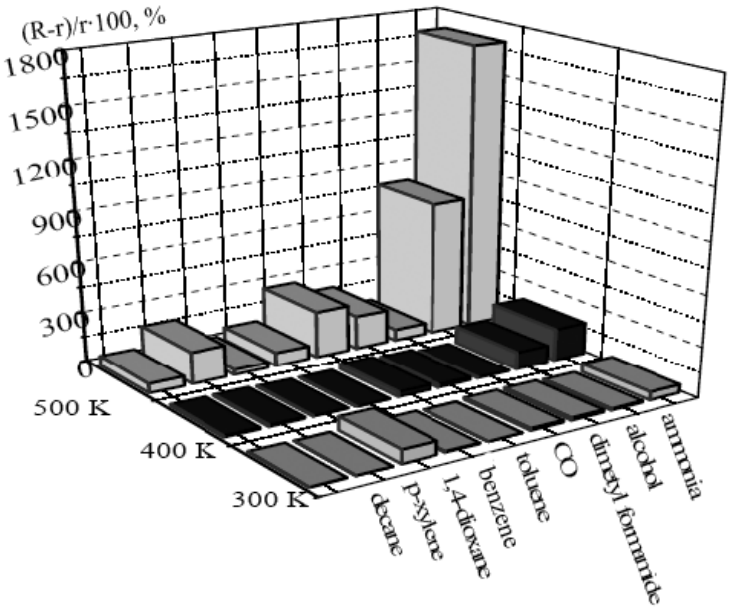


Fig. 16. Sensing element $0{,}99WO_3+0{,}01V_2O_5$ with palladium catalyst responsivity.

3.4. The Result of the Present Investigation

The result of the present investigation is that we cannot utilize low-temperature phase transition (60-90^{o}C) of vanadium doped WO_3 as in that region the sensitivity is very poor. That is explained by dimeric vanadium dioxide formation which is insensitive to external impacts as having molecular bond. This is the reason why we should shift the interest to operating temperatures closer to the next tungsten oxide phase transition (330^{o}C). Unfortunately this temperature is rather high for practical sensor utilization. For this reason, we limited the study to temperatures close to this high-temperature phase transition.

As a subsequent step, the working elements of the chemical sensors were manufactured and their testing was carried out (Fig. 17). The sensors manufactured on the base of doped (by 2 (with catalyst) and 4 % at. of vanadium) tungsten oxide had shown high responsivity to the presence in air admixtures of nitrogen oxides, ammonia, ethanol. The construction of the working element and the sensory device is shown in Fig. 17, Table 4. Tungsten oxide (WO_3) film (NO_2 sensor), this doped with V_2O_5 (NH_3 sensor), then that with catalyst (alcohol sensor) were screen printed on dielectric substrate (SiO_2), supplied with platinum electroheater and one separate platinum electrode. This heater simultaneously served as an electrode for conductance measurements. The thickness of the films was 50-200 microns. Concentration of gas - oxidizing (NO_2) or reduction (NH_3, C_2H_5OH) agent in the stream of air changed in the limits 1 - 10 ppm, temperature of the sensor was 300-600 K. The dependences of response magnitude of the sensor to NO_2 to different concentrations (also time dependences) are represented in Fig. 18. At the temperature of 510 K the response increases linearly when increasing NO_2 concentration from 2 up to 6 ppm. At 480 K such linear dependence is observed for all concentrations. The time dependent resistance change vs. vapors concentration of ethanol (samples without catalyst ($0,98WO_3+0,02V_2O_5$)) is represented in Fig. 19. In Figures 20, 21 the concentration dependences of responsivity to ethanol (samples without catalyst ($0,98WO_3+0,02V_2O_5$)) and ammonia (palladium doped samples ($0,99WO_3+0,01V_2O_5$)) presence in air are presented. The responsivity of the sensors to the presence of toluene, benzene, p-xylene, decane in air up to 100 ppm did not exceed 10 %.

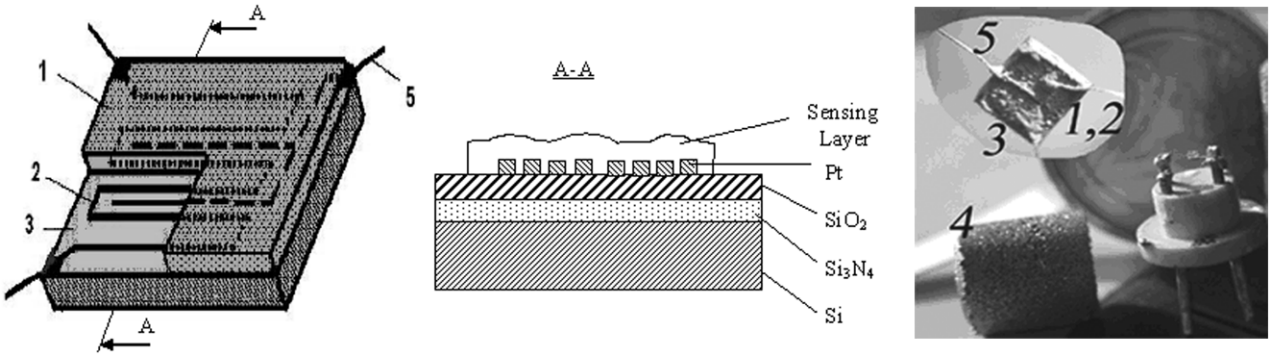


Fig. 17. Sensor construction and photo of the sensor elements (labels in the Table 4).

Table 4. Sensor construction in Fig. 17.

№	Part	Material
1	Sensing layer	Tungsten oxide (6) (or doped with vanadium and palladium)
2	Electroheater (resistance 10-15 Ohms)	Platinum
3	Substrate by a size 1.5x1.5 mm, on which the electroheater and contacts are sputtered and the sensing layer is printed	Silicon oxide, silicon nitride
4	Protective fireproof bell jar	Porous stainless steel
5	Bringing electrode	Platinum

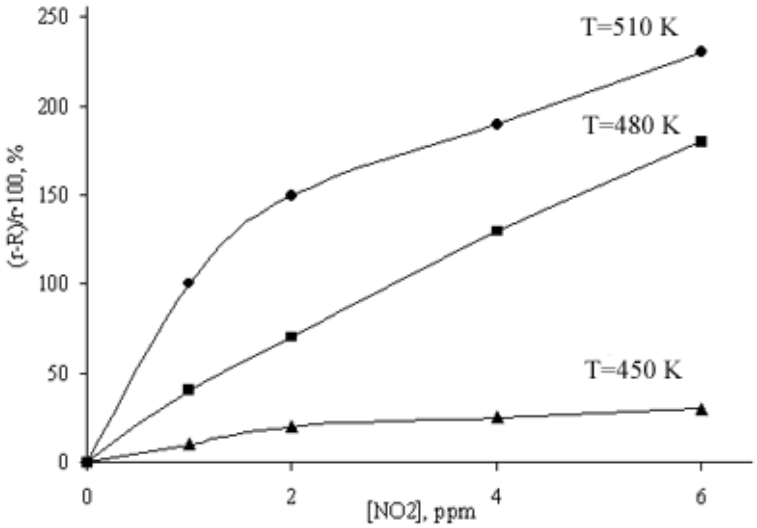


Fig. 18. Sensitivity to nitrogen dioxide of the WO_3 sensors.

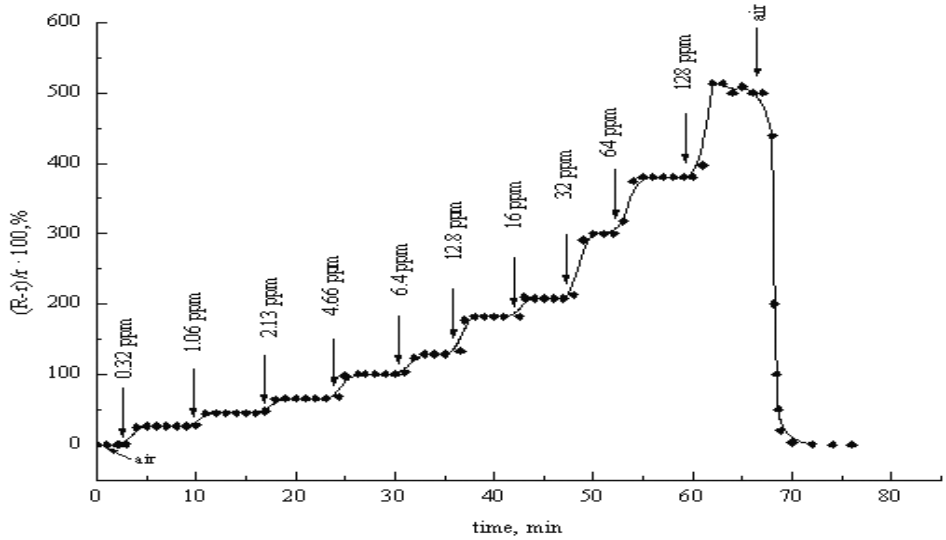


Fig. 19. Resistance change vs. vapors concentration of ethanol (samples without catalyst ($0{,}98WO_3+0{,}02V_2O_5$)), 500 K.

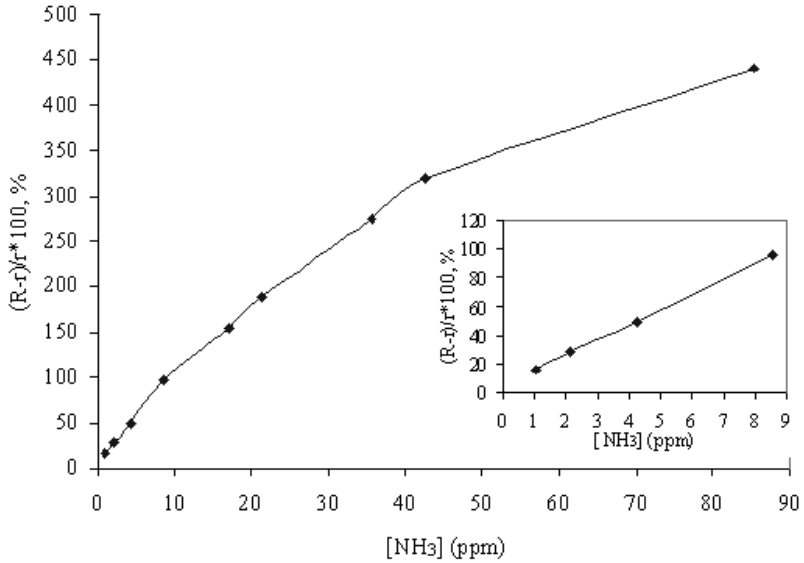


Fig. 20. Sensitivity to ammonia (palladium doped samples ($0{,}99WO_3+0{,}01V_2O_5$) sensor), 500 K.

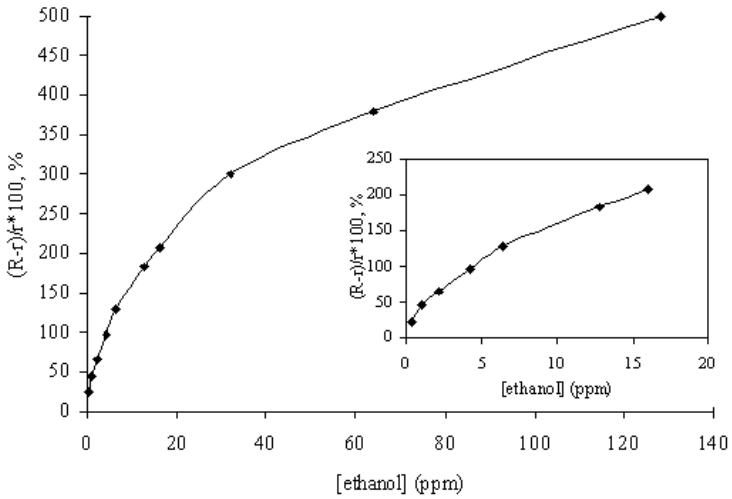


Fig. 21. Sensitivity to ethanol (samples without catalyst ($0{,}98WO_3+0{,}02V_2O_5$) sensor), 500 K.

4. Conclusion

The study of tungsten oxide doped with V_2O_5 bulk samples, films and layers electrical, physical, structural and sensory properties was carried out. New phase transition of the doped material caused by vanadium transformations was observed. The best selectively sensing material to alcohol, ammonia, nitrogen oxide was found to be 2 – 4 at.% V doped tungsten oxide at the temperatures of about 500K. Sensor transducers were manufactured and tested for these gases. The investigated materials are very promising for many electrical physical applications and should be further studied.

References

[1]. N. O. Korolkoff, Survey of toxic gas sensors and monitoring systems, *Solid State Technology*, 32, 1989, pp. 49–64.
[2]. G. Sberveglieri, Radio frequency magnetron sputtering growth and characterization of ITO thin films for NO_2 gas sensors, *Sensors and Actuators, B: Chemical*, 15, 1988, pp. 235–242.
[3]. K. Satake, T. Takeuchi, Titania NO_x sensors for exhaust monitoring, *Sensors and Actuators, B: Chemical*, 20, 1994, pp. 111–117.
[4]. S. Kudo, M. Ippommatsu, NO_x sensor using $YBa_2Cu_3O_{7-\delta}$ thin films, *Sensors and Actuators, B: Chemical*, 23, 1995, pp. 219–222.
[5]. M. Akiyama, N. Yamazoe, Tungsten oxide-based semiconductor sensor highly sensitive to NO and NO_2, *Chemistry Letters*, 1991, pp. 1611–1614.
[6]. S. Sato, Y. Seino, *Electronics and Communications in Japan*, 65-C, 1982, pp. 104.
[7]. S. Hashimoto, H. Matsuoka, H. Kagechika, M. Susa, K. S. Goto, *J. Electrochem. Soc*., 137, 1990, pp. 1300.
[8]. P. K. Shen, J. Syed-Bokhari, A. C. C. Tseung, *J. Electrochem. Soc*., 138, 1991, pp. 2778.
[9]. P. M. S. Monk, S. Chester, *Electrochimica Acta,* 38, 1993, pp. 1521.
[10]. Gottsche, A. Hinsch, V. Wittwer, *Solar Energy Materials and Solar Cells*, 31, 1993, pp. 415.
[11]. S. Hashimoto, H. Matsuoka, *J. Electrochem. Soc*., 138, 1991, pp. 2403.
[12]. M. Moser, R. Lynam, US Patent, No. 4855161, Aug. 8 1989.
[13]. S. Takano, A. Kishimoto, K. Hinokuma, T. Kudo, *Solid State Ionics,* 70/71, 1994, pp. 636.
[14]. W. Zhongchun, C. Xiaofeng, H. Xingfang, *Proc. SPIE,* 3175, 1997, pp. 247.
[15]. K. Tatsumi, M. Hibino, T. Kudo, *Solid State Ionics,* 96, 1997, pp. 35.
[16]. N. Ozer, N. Dogan, *Proc. SPIE,* 3424, 1998, pp. 65.

Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually.

Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

Submission of papers

Articles should be written in English. Authors are invited to submit by e-mail editor@sensorsportal.com 6-14 pages article (including abstract, illustrations (color or grayscale), photos and references) in both: MS Word (doc) and Acrobat (pdf) formats. Detailed preparation instructions, paper example and template of manuscript are available from the journal's webpage: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm Authors must follow the instructions strictly when submitting their manuscripts.

Advertising Information

Advertising orders and enquires may be sent to sales@sensorsportal.com Please download also our media kit: http://www.sensorsportal.com/DOWNLOADS/Media_Kit_2008.pdf