

VILNIUS GEDIMINAS TECHNICAL UNIVERSITY
STATE SCIENTIFIC RESEARCH INSTITUTE
CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY

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SYNTHESIS OF THE VANADIUM OXIDE COMPOUNDS AND INVESTIGATION BY X-RAY PHOTOELECTRON SPECTROSCOPY METHOD

SUMMARY OF DOCTORAL DISSERTATION

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VANADŽIO OKSIDINIŲ JUNGINIŲ
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Introduction

Formulation of the problem

Rapid development of molecular devices is determined by the existing light-emitting diodes, solar photochemical batteries, electrochromic devices and in the future – molecular computers. To gain the knowledge about the molecular systems and their electronic, photonic, magnetic and spintronic properties is an important goal of modern science to solve which require the active chemical systems and processes to be used in molecular devices. One of the challenges that will help to solve the problem is the synthesis and analysis of new molecular blocks, nanometer materials, molecular conductors, etc.

Conventional chemical-technological methods used in the synthesis of new materials, generally require special equipment (high vacuum, temperature, pressure, etc). The synthesis of new materials using sol-gel technology is mostly under normal conditions (low temperatures and pressures, synthesis is usually in the air atmosphere). The materials obtained using sol-gel process are used in various industrial fields such as electronics and active optical elements, IR radiation detectors, sensors of humidity and gas production, etc. The opportunities of inserting the biomolecules in sol-gel matrices are intensively examined.

Topicality of the work. The thin films of vanadium pentoxide, β -phase of vanadium-sodium oxide bronze and xerogel, molecular oxide bronzes and xerogels of vanadium-hydroquinone, vanadium-titanium-hydroquinone and hydrated compounds of vanadium-ammonium were synthesized by sol-gel technology method. The chemical composition of mentioned compounds was investigated using XPS method in order to determine the valence of metal ions.

The object of investigations

The object of investigations is the synthesis and study of the vanadium oxide thin films and bronzes.

Aim and tasks of the work. The aim of dissertation is to synthesize the thin films of vanadium oxide, and vanadium molecular xerogels and bronzes using sol-gel technology and to study the chemical composition of these films using X-ray photoelectron spectroscopy (XPS) method. The following tasks were formulated:

1. To synthesize vanadium pentoxide xerogel and thin film using sol-gel technology method.
2. Using sol-gel technology method synthesize β -phase of vanadium-sodium xerogel and bronze, vanadium-ammonium oxide xerogels,

vanadium-hydroquinone and vanadium-titanium-hydroquinone molecular oxide's xerogels and bronzes.

3. Determine the binding energies of mixed valence vanadium ions in various hydrated compounds using XPS method.
4. To investigate the possibilities on practical application of hydrated vanadium compounds.

Methodology of the investigations. The sol-gel technology method was used to synthesize the thin films and bronzes of the vanadium oxide compounds. The X-Ray photoelectron spectroscopy method was used to determine the valence states of synthesized compounds.

Scientific novelty. The thin films of vanadium pentoxide, β -phase of vanadium-sodium oxide xerogel bronze, molecular oxide bronzes of vanadium-hydroquinone, vanadium-titanium-hydroquinone and hydrated compounds of vanadium-ammonium was synthesized using sol-gel technology for the first time. The valence states of metals in mentioned compounds are determined.

Practical value. It is shown that it is possible to produce the thin films of vanadium oxide bronzes using simple methods. The possibility to use vanadium-ammonium oxide hydrated compounds as materials for producing the ammonium sensors is shown in the dissertation.

Defended propositions

1. Using the sol-gel technological method it is possible to produce vanadium oxide xerogels intercalated with metal ions (in our case – sodium) as well as molecular xerogels (hydroquinone, ammonium) without much difficulty. The thin films of vanadium pentoxide, vanadium-sodium oxide bronze, vanadium-hydroquinone and vanadium-titanium-hydroquinone oxide bronzes can be prepared from xerogels heating them up to 580 K.
2. The binding energy of V $2p_{3/2}$ line of V^{4+} ions in V_2O_5 based xerogels is shifted by about 1.3 eV to the lower energy side compared to the basic V^{5+} line. The chemical shift for V_2O_5 and V_2O_4 xerogels is about 0.6 eV. The V $2p_{3/2}$ line width in xerogels for four-valence vanadium is the same as for five-valence vanadium.
3. The vanadium ions in $(NH_4)_{2-x}H_xV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ ($x = 0, 1$) xerogels are in V^{5+} and V^{4+} states with reduction ratio 0.04 independent on the x value. Molybdenum ions are in the stable Mo^{6+} states. N 1s peak position indicates that nitrogen is connected with hydrogen in NH_4^+ ions.
4. In $V_{1.67}Ti_{0.33}O_{4.85}\cdot nH_2O/2HQ$ and $V_{1.67}Ti_{0.33}O_{4.85}\cdot nH_2O/HQ$ (HQ – hydroquinone, chemical formula $C_6H_4(OH)_2$) xerogels titanium ions are

in the stable 4+ states independent on the hydroquinone intercalation degree (one or two HQ). Vanadium ions in all cases (one or two HQ) are in V^{3+} , V^{4+} and V^{5+} valence states. The increase of quantity of hydroquinone in the gels leads to the growth of relative concentration of V^{3+} and V^{4+} ions.

5. $(NH_4)_{2-x}H_xV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ ($x = 0, 1$) xerogels can be used as starting materials for ammonium sensors production.

The scope of the scientific work. The dissertation consists of introduction, five chapters, conclusions, the list of 168 references, the list of 15 publications related to the theme of the dissertation and appendix. The total scope of the dissertation – 112 pages (13 of them include contents, abstract, abbreviation, the first and the last pages of the dissertation), 52 pictures and 19 tables.

The aim of the dissertation, topicality of the work, solved problems, the novelty of the results, practical importance and the statements presented for the defense of the thesis are presented in **Introduction**.

1. The Properties of the Hydrated Vanadium Oxide Compounds, X-Ray Photoelectron Spectroscopy and Sol-Gel Technology Methods

X-Ray diffraction spectroscopy study of hydrated vanadium pentoxide was first described by Aldebert in 1981. The structure has a layered character where V_2O_5 layers are formed by cross-linked fibers separated by water molecules. The interlayer distance is from 8.75 Å up to 11.55 Å depending on the water content in the hydrate.

The binding energy of the photoelectrons depends on the energetic level from which the electron is emitted as well as on the degree of oxidation of atom and chemical-physical environment. The differences between the peak positions of photoelectron spectra are arising because of the above mentioned reasons are called chemical shifts. The ions with higher oxidation states has higher binding energy and using X-Ray photoelectron spectroscopy (XPS) method it is possible to determine the valence of single ion of investigated compound.

XPS is routinely used for surface analysis of inorganic compounds, metal alloys, semiconductors, glasses etc. X-ray photoelectron spectrometer is universal equipment designed for surface chemical and quantitative analysis of any structure. XPS detects all elements except hydrogen and helium. The depth of the obtained information is up to 10 nm.

The sol-gel process is the system transition from a liquid phase to the gel-like phase. Colloidal system is such disperse system when the large aggregates, consisting of large amount of molecules (up to hundreds or thousands), compose the system but not of the separate molecules or ions. These aggregates are called disperse phase and the environment in which they are – dispersion medium. Sol is colloidal solution and gel is such colloidal solution in which the large

aggregates of the disperse phase are bonded to each other, i. e. the formation of such jellylike material which is rather solid than liquid. The gel from which are removed all volatile components of disperse medium and which are unconnected with disperse phase is named xerogel.

The main feature of this process is that the obtained products (thin films, ceramics, superconductors etc.) are synthesized by means of so called soft chemistry (chimie douce) methods. The precursors of “soft chemistry” are various solutions and most widely used are alkoxides. The main advantage of this process is the obtaining materials which chemical composition will match the wanted one.

2. The Methodology of Synthesis and Investigation of the Hydrated Vanadium Compounds

In this chapter the synthesis methods vanadium-hydroquinone and vanadium-titanium-hydroquinone xerogels and bronzes are also presented. The synthesis of molecular ammonium-polyvanadate-molybdate xerogels is described. The measurement method of XPS spectra is discussed.

When investigating the system of $\text{Na}_2\text{O}-\text{V}_2\text{O}_5$ it is shown that three sodium vanadate compounds NaVO_3 , $\text{Na}_4\text{V}_2\text{O}_7$ and Na_3VO_4 exists when Na_2O concentration is from 50% to 100%. The structure of β phase vanadium-sodium oxide bronze can be imagined like the chains of V–O between which the ions of sodium are located.

The synthesis of hydrated vanadium compounds can be separated into four stages. The first one – production of sol. The powders of vanadium pentoxide are mixed with proper material in the suitable proportion and placed to the test-tube which. Then the 30% of H_2O_2 was poured into test-tube continually mixing the solution.

The second stage is the production of gel. The obtained solution was sustained at 333 K temperature for the dissociation of the peroxide complexes of vanadium.

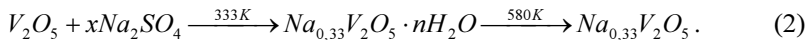
The third stage – the production of xerogel. The obtained gel was applied on the glass or Ni substrate and dried in the air at room temperature for one day. The result of this is the removal of the volatile component of the disperse medium and the xerogel of wanted composition is obtained.

The fourth stage is the production of bronze. The xerogel was exposed at 580 K temperature for four hours for the removal of chemically bonded water.

The gel of vanadium pentoxide was prepared using the powders of vanadium pentoxide and the 30% hydrogen peroxide according to the first stage of above mentioned scheme. Then obtained sol was exposed at 333 K temperature for two hours. The obtained gel was deposited on the clean metal substrate (Ni) and dried in the air at room temperature for one day. The synthesized xerogel was heated up to 580 K temperature and exposed at this

temperature for 4 hours for the removal of chemically bonded water, i. e. to form the thin film of V_2O_5 .

The powders of vanadium pentoxide, Na_2SO_4 , hydrogen peroxide from which the solution of 30 % hydrogen peroxide were used for β -phase of vanadium-sodium oxide bronze synthesis. The process of bronze production can be written as



The production of molecular vanadium-hydroquinone xerogel and bronze process can be described by the following steps: the synthesis of vanadium pentoxide gel, intercalation of hydroquinone to the gel structure and production of the bronze by heating the gel up to the temperature ensuring the removal of all water (absorbed and chemically bonded) from the gel.

The molecular xerogels of vanadium-titanium-hydroquinone were synthesized as well as the molecular bronzes of vanadium hydroquinone. The vanadium pentoxide and titanium dihydride were taken in molar ratio 1.67:0.33 and dissolved in hydrogen peroxide at 273 K temperature. Then the solution was heated up to 333 K and exposed at this temperature until the peroxide complexes of vanadium and titanium fully decomposed and $V_{1.67}Ti_{0.33}O_{5\pm\delta} \cdot nH_2O$ gel was formed. An aqueous solution of hydroquinone was mixed with the formed gel in molar ratio 0.33:1 and 0.17:1 respectively. In this way the $V_{1.67}Ti_{0.33}O_{5\pm\delta} \cdot nH_2O$ / 2HQ and $V_{1.67}Ti_{0.33}O_{5\pm\delta} \cdot nH_2O$ / HQ gels were synthesized. These gels were applied on the Ni substrate and dried in the air.

The V_2O_5 , NH_4VO_3 , 40 % H_2O_2 and Mo powders was used as starting materials to synthesize molecular xerogel of ammonium polyvanadomolybdate. V_2O_5 and Mo powders in the suitable proportion were dissolved in hydrogen peroxide to form pervanadic (molybdic) acids. Slow heating up to 333 K initiates the decomposition of the peroxide compounds followed by gelation. Mo ions replace the V^{5+} ions in the resulting compounds. Decomposition of the peroxide solution of vanadium containing NH_4^+ is not accompanied by gelation, whereas, in presence of molybdenum, $(NH_4)_{2-x}H_xV_9Mo_3O_{31\pm\delta} \cdot nH_2O$ ($x = 0, 1$) gels are formed. The obtained gels were deposited on the Ni substrates and dried in the air. The films have layered structure where NH_4^+ ions and H_2O are incorporated between V-O-Mo layers. XSAM 800 (Kratos Analytical, UK) and ESCALAB MK II (VG Scientific) spectrometers were used to record XPS spectra.

A non-monochromatized Mg K_α (1253.6 eV) or Al K_α (1486.6 eV) radiation source of XSAM 800 spectrometer excited the photoelectrons at (15 kV, 300 W). The spectrometer is equipped with the hemispherical analyzer which was set to 20 eV pass energy. During the spectrum analysis the working pressure was below 10^{-7} Pa. The analyzer used with an energy resolution

$\Delta E/E = 0.08 \%$ in steady retarding mode. Using the KRATOS DS800 data system the photoemission data has been collected and processed.

A non-monochromatized Mg K_{α} (1253.6 eV) or Al K_{α} (1486.6 eV) radiation source of ESCALAB MK II spectrometer excited the photoelectrons. The spectrometer is equipped with five-channeltron detection system and a hemispherical analyzer which was set to 20 eV pass energy. The working pressure in the analyzer chamber was maintained below 10^{-7} Pa during the spectrum analysis. The energy scale was calibrated using the Au $4f_{7/2}$ peak (84.0 eV). Photoemission data have been collected and processed using a VGX-900 data system.

The multiple photoelectron spectra were separated into several peaks setting the peak position: binding energy (BE), width (FWHM) and Gaussian/Lorentzian ratio. The accuracy of the relative intensities and BE of the measured lines were about 10 % and 0.1 eV respectively. The random C 1s line which BE should be equal to 284.6 eV was used for the correction of the charging effects. After Shirley background subtraction and the removal of satellites, a non-linear least squares curve fitting routine with a Gaussian/Lorentzian product function was used for the analysis of XPS spectra. Before the measurements the surface of the samples they were cleaned using Ar^{+} ions (3 kV, $10 \mu A \cdot cm^{-2}$).

3. The Results of the Investigation Vanadium Oxide Compounds

The identification of mixed valence metal species in solid oxides is not a trivial task. The chemical analytical methods often fail owing to the relative instability of the various oxidation states of metals in common dissolution media. XPS is a very useful technique for determining such important parameters as the chemical state of different metal species and their relative concentration. By using XPS analysis, the species of elements at the surface are identified from XPS spectra and the oxidation states of the elements are determined from the chemical shift (CS) defined as the BE difference of the electron concerned

$$CS_{ij} = BE_i - BE_j, \quad (3)$$

where i and j denotes the different valence states, BE – binding energy.

The analysis of distribution of BE spectrum has been performed by using a curve-fitting procedure in order to distinguish the vanadium species in different oxidation states. The distribution function of BE of V $2p_{3/2}$ line may be separated into three Gaussian peaks centered at 517.3 eV, 516.6 eV and 515.6 eV. These peaks may be attributed to V^{5+} , V^{4+} and V^{3+} species in V_2O_5 , VO_2 and V_2O_3 oxides respectively. Therefore, it may be concluded that the use of the data reported in literature for the main valence vanadium oxides permits separation of vanadium species in different oxidation states.

The accuracy of CS determination from BE analysis is insufficient to use these data for the accurate separation of the multicomponent V 2p_{3/2} XPS peak envelope. Only the BE data obtained by means of the same equipment employed under the same conditions were used for further statistical analysis of CS in order to minimize the uncertainty related with the equipment calibration and the charge correction procedure.

The chemical composition of (NH₄)_{2-2x}H_xV₉Mo₃O_{31±δ}·nH₂O (x = 0, 1) xerogels synthesized by the sol-gel technology were determined by XPS method. The vanadium ions are in the V⁵⁺ and V⁴⁺ states with reduction ratio of about 0.04 independent on the x value. The investigation of the Mo 3p and Mo 3d spectra shows that the molybdenum ions are in the stable Mo⁶⁺ states. Figure 1 presents the XPS spectra of V-O region.

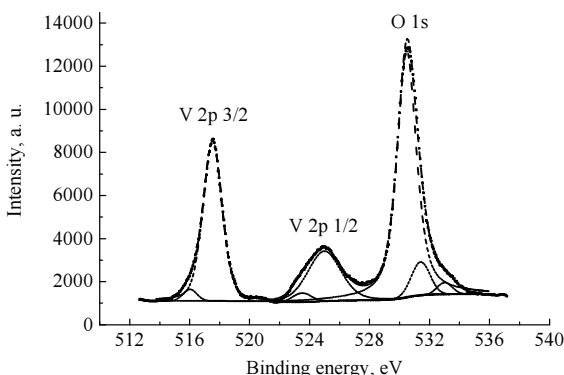


Fig. 1. XPS spectra of V-O region of (NH₄)₂V₉Mo₃O_{31±δ}·nH₂O xerogel (points – experimental data)

The O 1s peak consists of three components, where the first one is connected with vanadium and molybdenum ions, the second is possible to subsume under relations with carbon, and the third belongs to oxygen linked with hydrogen in water molecules. The position of the N 1s peak indicates that the nitrogen is connected with hydrogen in NH₄⁺ ions.

XPS spectra of V_{1.67}Ti_{0.33}O_{4.85}·nH₂O/2HQ and V_{1.67}Ti_{0.33}O_{4.85}·nH₂O/HQ (HQ is hydroquinone) gels produced by using sol-gel technology methods, are presented. The valences of vanadium and titanium ions in the investigated compounds are studied by means of XPS before and after etching the samples with Ar⁺ ions for 15 min (3 keV, current density 10 μA·cm⁻²). Figure 2 show typical XPS spectrum of titanium region for V_{1.67}Ti_{0.33}O_{4.85}·nH₂O/HQ xerogel before Ar⁺ ion etching. XPS spectra for V_{1.67}Ti_{0.33}O_{4.85}·nH₂O/2HQ xerogel are similar.

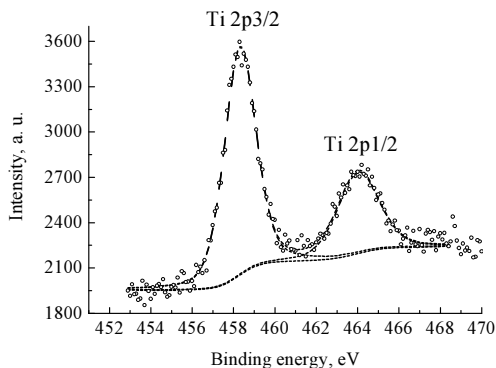


Fig. 2. XPS spectra of $V_{1.67}Ti_{0.33}O_{4.85} \cdot nH_2O/HQ$ gel titanium region before the etching

Titanium peaks consists of two $Ti\ 2p_{3/2}$ and $Ti\ 2p_{1/2}$ components. For both gels (with one and two hydroquinone), before as well as after the Ar^+ ion bombardment, the binding energies of $Ti\ 2p_{3/2}$ and $Ti\ 2p_{1/2}$ peaks are 458 eV and 464 eV respectively. The values of BE are typical of titanium dioxide. This fact shows that independent of the hydroquinone intercalation degree and Ar^+ ion etching the ions of titanium are in stable $4+$ states.

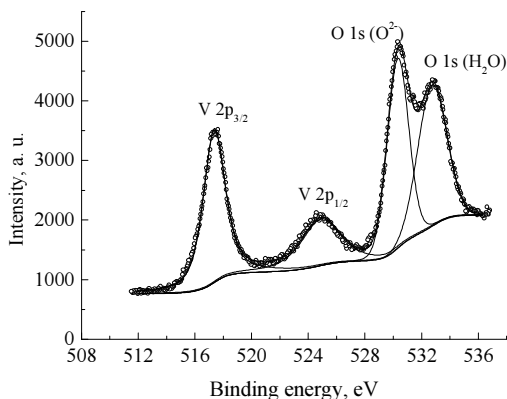
In all cases (with one or two HQ) the V 2p peaks consist of three pairs of lines. The binding energies of three V $2p_{3/2}$ peak components are about 517 eV, 516 eV and 515 eV that correspond to $5+$, $4+$, and $3+$ valence states of vanadium.

The V^{3+} ions exist in all investigated compounds before as well as after the Ar^+ ion bombardment. It is necessary to notice that in vanadium-titanium hydrated compounds the V^{3+} ions appear only after the Ar^+ ion etching of the samples. From the relative area of the V $2p_{3/2}$ peak V^{3+} , V^{4+} and V^{5+} components, we can calculate the reduction ratio of various valence states of vanadium ions. These concentrations are proportional to the relative area of corresponded fitting components. The concentrations of lower valence vanadium ions increase after the Ar^+ ion etching of the samples. Thus it is possible to say about vanadium-oxygen bonding lessening when the hydroquinone is intercalated in the vanadium-titanium hydrates.

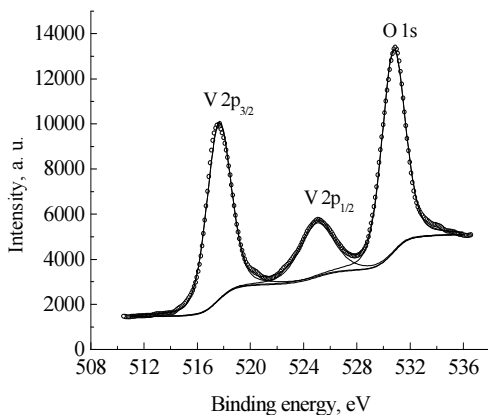
4. The Investigation of the Vanadium Oxide Bronzes

The thin films of the vanadium pentoxide can be produced from the vanadium pentoxide xerogels annealing them up to 580 K temperature, i.e. to obtain the thin films it is not necessary to use the difficult technique. The XPS

spectrum of vanadium pentoxide xerogel is shown in Figure 3. a) before the heat treatment and b) after the removal of water. From a comparison of Figure 3 a) and b) it follows that the main changes in the XPS data are in the O 1s peak. The changes can be assigned to the effect of a water removal from the xerogel after the heat treatment. The XPS data allow us to conclude that sol-gel processed thin films are pure vanadium pentoxide.



a)



b)

Fig. 3. The XPS spectrum of vanadium pentoxide xerogel before the heat treatment (a) and of vanadium pentoxide thin film (b)

The XPS spectra of materials used for synthesis (Na_2SO_4 and V_2O_5) were measured in order to better understand the synthesis processes producing

the vanadium-sodium oxide bronze. These spectra were measured for xerogel as well as for bronze (annealed xerogel). From comparison the XPS spectrum of bronze and xerogel (Fig. 4) it can be seen that oxygen is in one state in bronze that corresponds to the bond of vanadium-oxygen.

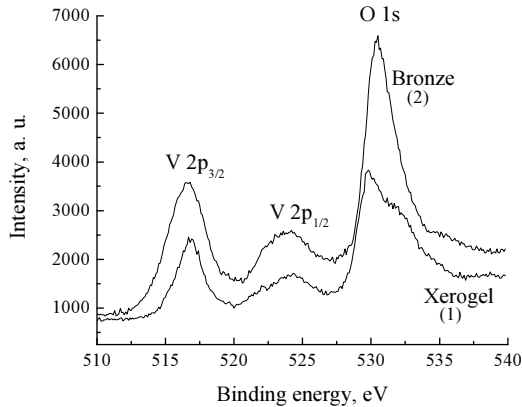


Fig. 4. The overlap of XPS spectra of vanadium-oxygen region for xerogel (1) and bronze (2)

So we removed all water – absorbed and chemically bonded from xerogel structure during the heat treatment. The XPS spectra of sodium region (the interval of binding energy is 1060–1080 eV) for xerogel and bronze are similar.

The sulphur region of XPS spectra showed that there is no S 2p_{3/2} peak at about 168 eV in bronze that means after the xerogel heat treatment at 580 K the bonds of S-O compounds resolves and evaporates from the sample.

The summary of XPS spectra parameters resumptive the above mentioned results are shown in Table 2.

Table 2. The binding energies of main V₂O₅, Na₂SO₄, xerogel and bronze peaks of XPS spectra (eV).

Sample	V 2p _{3/2}		V 2p _{1/2}		O 1s	Na 1s	S 2p _{3/2}
	V ⁴⁺	V ⁵⁺	V ⁴⁺	V ⁵⁺			
V ₂ O ₅	–	517.1	–	524.9	530.8	–	–
Na ₂ SO ₄	–	–	–	–	531.6	1071.5	168.8
Xerogel	516.2	516.98	522.8	524.6	529.8	1071.34	?
					531.7		
					533.5		
Bronze	515.7	516.9	522.8	524.6	530.6	1071.35	–

The XPS spectra of V_{1.67}Ti_{0.33}O_{5±δ}·nH₂O/HQ xerogel and bronze were analyzed. Figure 5 shows the XPS spectrum of vanadium-oxygen region for xerogel.

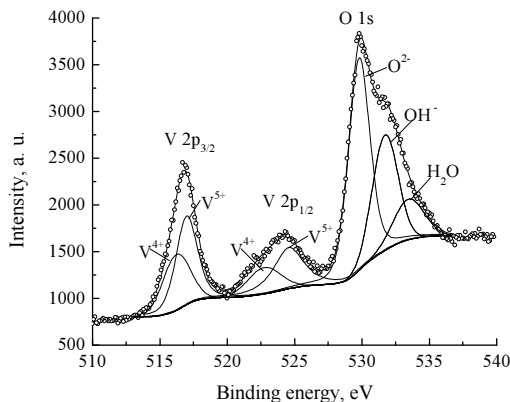


Fig. 5. The XPS spectra of vanadium-oxygen region for xerogel

The V $2p_{3/2}$ and V $2p_{1/2}$ peaks consists of two components. The binding energies of the components of V $2p_{3/2}$ peak are 516.23 eV and 516.98 eV that corresponds to V^{4+} and V^{5+} ions. The same is possible to say about the components of V $2p_{1/2}$ peak with binding energies 522.79 eV and 524.57 eV. The oxygen peak consists of three components with binding energies 529.79 eV, 531.71 eV and 533.47 eV i.e. we have the ions of oxygen O^{2-} which are connected to vanadium ions, oxygen from hydroxyl group (OH^-) and oxygen from water molecules.

Figure 6 shows the XPS spectrum of vanadium-oxygen region for bronze where the all components of peaks are abstracted.

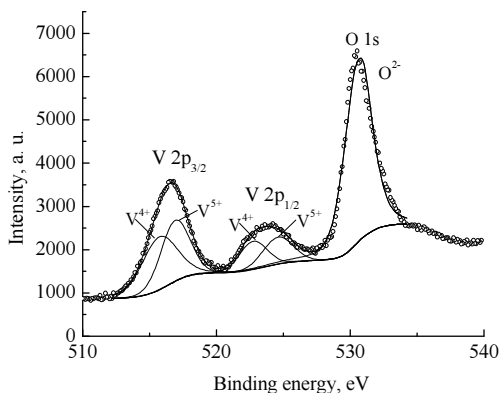


Fig. 6. The XPS spectrum of vanadium-oxygen region for bronze

The V 2p_{3/2} and V 2p_{1/2} peaks consists of two components. The binding energies of the components of V 2p_{3/2} peak are 515.74 eV and 516.92 eV that corresponds to V⁴⁺ and V⁵⁺ ions. The same is possible to say about the components of V 2p_{1/2} peak with binding energies 522.75 eV and 524.61 eV. The peak of oxygen consist only of one component with binding energy 530.61 eV which corresponds to oxygen ions O²⁻ and which are connected to vanadium ions.

From the comparison of XPS spectra for xerogel and for bronze it can be seen that oxygen is only in one state in bronze which correspond vanadium-oxygen bonding. It means that during the heat treatment all water – absorbed and chemically bonded in xerogel structure was removed.

The XPS spectra of C 1s region for xerogel and for bronze are similar. C 1s peak consists of three components with binding energies 284.6 eV (C-C bonding), 284 eV (C-H bonding) and 287.6 eV (C-O bonding).

These results confirm that the vanadium-hydroquinone oxide bronze is synthesized.

5. Possible Practical Applications of the Hydrated Vanadium Compounds

In dissertation, we introduce the ammonia sensor based on vanadium hydrate that could operate at the room temperatures. The synthesis process of produced (NH₄)HV₉Mo₃O_{31±8}·nH₂O gels in details is described in chapters 2 and 3. Obtained gels were deposited on Ni substrates and dried in air. The thickness of prepared films was about 10 μm. The films have layered structure where between the V-O-Mo layers are incorporated NH₄⁺ ions and H₂O.

The contacts were deposited in two configurations which allow investigating the physical properties of the films along and across V-O-Mo layers.

DC-electrical resistance was measured for the samples in clean air and air contaminated with the target gas (ammonia). For this, the sensors were situated in a test chamber with ambient air. The chamber was equipped with special inlets for injection of the target gas and for purging the gas out with clean air.

After the ammonia injection the resistance increases after 3 s when measuring across the V-O-Mo layers, then decreases and practically stays constant even after the ammonia gas removal from the test chamber (Fig. 7, curve 1). It is clear that such configuration of electrodes is not suitable for the production of sensors. When measuring the response of resistance along the V-O-Mo layers the resistance after 3 s increases then after 5–6 s stays constant (Fig. 7 curve 2, region A) and during the 5 s decreases up to constant value (Fig. 7 curve 2, region B). After the removal of gas from the test chamber the resistance increases rapidly during 1–2 s.

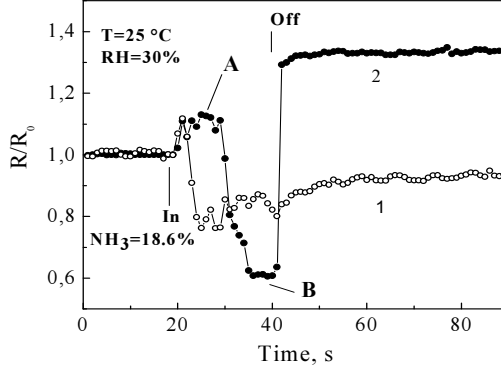


Fig. 7. The time dependencies of the resistance response to ammonia measured across (1) and along (2) V-O-Mo layers

The response of resistance dependence to the ammonia concentration in the region A can be written as linear function

$$\frac{R}{R_0} = \alpha + \beta \cdot NH_3, \quad (4)$$

where $\alpha = 1.01253 \pm 0.01418$ and $\beta = (0.02337 \pm 0.00141) \%^{-1}$, NH_3 is the ammonia concentration (%). Coefficient β is the sensitivity of the sample to the ammonia gas.

The experimental results of response of resistance measured in the region B dependence to ammonia concentration can be written by exponential function

$$\frac{R}{R_0} = \left(\frac{R}{R_0} \right)_0 + C \cdot \exp((-NH_3) \cdot t), \quad (5)$$

where NH_3 is the ammonia concentration, $(R/R_0)_0 = 0.7731 \pm 0.01509$, $C = 0.2286 \pm 0.02521$, $t = (0.348 \pm 0.0949) \%^{-1}$.

In this case when the concentration of ammonia gas increases the response of resistance exponentially decreases and practically stays constant when concentrations are high. This means that it is not suitable to use the response of resistance in the region B for manufacturing the sensors.

It is necessary to use the resistance changes with ammonia concentration in the region A for producing the sensors developing such electrical scheme that could act in response to the maximum resistance change after the gas inlet to the test chamber.

General Conclusions

The molecular oxide gels of vanadium-sodium, vanadium-hydroquinone and oxide bronzes of vanadium-hydroquinone are synthesized using sol-gel synthesis method for the first time and the XPS spectra of these compounds are analyzed. It is determined that:

1. The binding energy of V 2p_{3/2} peak is shifted to lower energy region about 1.3 eV of V⁴⁺ ions in V₂O₅ based xerogels compared to the main V⁵⁺ peak.
2. The vanadium ions are in V⁵⁺ and V⁴⁺ states with reduction ratio of about 0.04 independent on the x value and the molybdenum ions are in Mo⁶⁺ states in (NH₄)_{2-x}H_xV₉Mo₃O_{31±δ}·nH₂O ($x = 0, 1$) gels. The position of the N 1s peak indicates that the nitrogen is connected with hydrogen in NH₄⁺ ions.
3. In V_{1.67}Ti_{0.33}O_{4.85}·nH₂O/2HQ and V_{1.67}Ti_{0.33}O_{4.85}·nH₂O/HQ (HQ – hydroquinone) xerogels the ions of titanium are in stable 4+ states independent of the hydroquinone intercalation degree (one or two HQ). Vanadium ions in all cases (one or two HQ) are in V³⁺, V⁴⁺ and V⁵⁺ valence states. The increase in quantity of hydroquinone leads to the growth of relative concentration of V³⁺ and V⁴⁺ ions.
4. The sol-gel method allows embed the molecules of ammonia into the matrix of vanadium pentoxide and that allows use the obtained oxide xerogels of vanadium-ammonium as initial material for manufacturing the ammonia gas sensors.
5. Using the sol-gel technological method it is possible to produce vanadium oxide xerogels intercalated with metal ions (in our case – sodium) as well as molecular xerogels (hydroquinone, ammonium) without much difficulty. The thin films of vanadium pentoxide, vanadium-sodium oxide bronze, vanadium-hydroquinone and vanadium-titanium-hydroquinone oxide bronzes can be prepared from xerogels heating them up to 580 K.

List of Published Works on the Topic of the Dissertation In the reviewed scientific periodical publications

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Bondarenka, V.; Kačiulis, S.; Martūnas, Z.; Réza, A.; Babonas, G. J.; Pašiškevičius, A. 2008. XPS and optical properties of sol-gel processed vanadium pentoxide films, *Lithuanian Journal of Physics* 48(4): 341–348. ISSN 1648-8504 (ISI Master Journal List).

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Bondarenka, V.; Tvardauskas, H.; Grebinskij, S.; Senulis, M.; Pašiškevičius, A. 2009. $V_{1.67}Ti_{0.33}O_{5\pm\delta}\cdot nH_2O$ kserogelių, interkaliuotų hidrochinonu, tyrimas Rentgeno fotoelektronų spektroskopijos metodu, iš *Puslaidininkų fizikos XX mokslinės konferencijos*, Vilnius, p. 109–112.

Pasiskevicius, A.; Bondarenka, V. 2006. Palydovinių smailių įtaka Rentgeno fotoelektronų spektrų analizei, iš *Fizika ir fizinė kompiuterija, IX jaunųjų mokslininkų konferencijos "Mokslas – Lietuvos ateitis" medžiaga*, Vilnius: Technika, 156–158. ISBN 9986-05-989–5.

Pašiškevičius, A.; Bondarenka, V. 2008. Oksidinių vanadžio-titano-hidrochinono nanodarinų rentgeno fotoelektronų spektroskopija, iš *Fizika ir fizinė kompiuterija, XI Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis“ medžiaga*, Vilnius: Technika, 65–72. ISBN 978-9955-28-301-0.

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VANADŽIO OKSIDINIŲ JUNGINIŲ SINTEZĖ IR TYRIMAS RENTGENO FOTOELEKTRONŲ SPEKTROSKOPIJOS METODU

Problemos formulavimas. Sparčiai vystomą molekulių prietaisų tematiką lemia jau dabar egzistuojantys organiniai šviesą spinduliuojantys diodai, fotocheminės saulės baterijos, elektrochrominiai ekranai, o ateityje lems ir molekuliniai kompiuteriai. Žinių praplėtimas apie molekulinės sistemos bei jų elektronines, fotonines, magnetines ir spintronines savybes yra svarbus šiuolaikinio mokslo uždavinys, kurį sprendžiant reikia sukurti aktyvias chemines sistemas ir procesus, kuriuos galima panaudoti molekulinuose prietaisuose. Vienas iš uždavinių, padėsiančių išspręsti iškeltą problemą, yra naujų molekulių blokų, nanometrinių medžiagų, molekulių laidininkų ir t. t. sintezė ir tyrimas.

Įprasti cheminiai-technologiniai metodai, naudojami naujų medžiagų sintezei, paprastai reikalauja gana sudėtingos įrangos (aukšto vakuumo, temperatūros, slėgio ir pan.). Sintetinant naujas medžiagas zolis-gelis technologijos pagalba, visi procesai vyksta dažniausiai esant įprastinėms sąlygoms (nedidelės temperatūros ir slėgiai, sintezė paprastai vyksta oro atmosferoje). Zolis-gelis proceso pagalba gaunamos medžiagos naudojamos įvairiose pramonės srityse, tokiose kaip aktyviųjų elektronikos ir optikos elementų, IR spinduliuotės detektorių, drėgmės ir dujų jutiklių gamyboje ir t. t. Intensyviai nagrinėjamos biomolekulių įterpimo į zolis-gelis matricas galimybės.

Darbo aktualumas. Šiame darbe panaudojant zolis-gelis technologiją, susintetinti plonieji vanadžio pentoksido sluoksniai, vanadžio-natrio β fazės oksidinės bronzos plonieji sluoksniai, vanadžio hidrochinono molekulinės oksidinės bronzos plonieji sluoksniai ir vanadžio amonio hidratuoti junginiai. Visų minėtų medžiagų cheminė sudėtis ištirta panaudojant Rentgeno fotoelektronų spektroskopijos (RFS) metodą siekiant nustatyti metalų jonų valentines būsenas.

Tyrimų objektas – vanadžio oksidinių junginių plonųjų sluoksnių ir bronzų sintezė ir tyrimas.

Darbo tikslas ir uždaviniai. Disertacinio darbo tikslas – panaudojant zolis-gelis technologiją susintetinti plonuosius vanadžio oksidinių bei vanadžio molekulinį kserogelių ir bronzų sluoksnius ir ištirti jų cheminę sudėtį panaudojant RFS metodą. Disertacinio darbo metu spręsti šie uždaviniai:

1. Panaudojant zolis-gelis technologijos metodą, susintetinti vanadžio pentoksido kserogelį ir plonąjį sluoksnį.
2. Zolis-gelis technologijos pagalba susintetinti vanadžio-natrio β fazės kserogelį ir bronzą, vanadžio-amonio oksidinių kserogelį bei vanadžio-hidrochinono ir vanadžio-titano-hidrochinono molekulinį oksidų kserogelius ir bronzas.
3. Nustatyti įvairaus valentingumo vanadžio jonų ryšio energijas įvairiuose hidratuotuose junginiuose panaudojant RFS metodą.
4. Išanalizuoti hidratuotų vanadžio junginių praktinio pritaikymo galimybes.

Tyrimų metodika. Darbe panaudota sintezė zolis-gelis technologijos metodu. Vanadžio oksidinių junginių plonųjų sluoksnių bei bronzų valentinės būsenos nustatytos Rentgeno fotoelektronų spektroskopijos metodu.

Mokslinis naujumas – pirmą kartą panaudojant zolis-gelis technologijos metodus susintetinti vanadžio-natrio β fazės oksidinės bronzos, vanadžio-hidrochinono ir vanadžio-titano-hidrochinono molekulinį bronzų plonieji sluoksniai bei vanadžio-amonio hidratuoti oksidiniai junginiai. Nustatytos minėtų junginių metalų valentinės būsenos

Praktinė reikšmė. Parodyta, kad:

1. Panaudojant zolis-gelis technologiją, galima gana paprastais metodais, nenaudojant sudėtingos technologinės įrangos, gaminti vanadžio oksidinių bronzų plonuosius sluoksnius.
2. Vanadžio amonio hidratuoti oksidiniai junginiai gali būti naudojami kaip medžiagos amoniako dujų jutikliams gaminti.

Ginamieji teiginiai

1. Panaudojant zolis-gelis technologijos metodą galima gauti ne tik vanadžio oksidinius kserogelius, interkaluotus metalo jonais (mūsų atveju – natrio), bet ir molekulinis kserogelius (hidrochinonas, amonis). Iš kserogelių, atkaitinant juos ~ 580 K temperatūroje, galima pagaminti vanadžio pentoksido, vanadžio-natrio oksidinės bronzos, vanadžio-hidrochinono ir vanadžio-titano-hidrochinono oksidinių bronzų plonuosius sluoksnius.
2. V^{4+} jonų, kurių pagrindą sudaro V_2O_5 kserogeliai, $V 2p_{3/2}$ smailės ryšio energija pasislinkusi apie 1,3 eV į mažesnių energijų sritį lyginant su pagrindine V^{5+} smaile. V_2O_5 ir V_2O_4 oksidų cheminis poslinkis

kserogeliuose yra apie 0,6 eV. Keturvalenčio vanadžio $V\ 2p_{3/2}$ smailės plotis kserogeliuose yra toks pats kaip ir penkiavalenčio vanadžio.

3. $(NH_4)_{2-x}H_xV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ ($x = 0, 1$) kserogeliuose vanadžio jonai yra V^{5+} ir V^{4+} būsenose, kurių redukcijos santykis – 0,04, nepriklausomai nuo x reikšmės. Molibdeno jonai yra stabiliose Mo^{6+} būsenose. N 1s smailės padėtis rodo, jog azotas yra surištas su vandeniliu NH_4^+ jonuose.
4. $V_{1,67}Ti_{0,33}O_{4,85}\cdot nH_2O/2HQ$ ir $V_{1,67}Ti_{0,33}O_{4,85}\cdot nH_2O/HQ$ (HQ – hidrochinonas) kserogeliuose, nepriklausomai nuo hidrochinono įterpimo laipsnio (vienas ar du HQ), titano jonai yra stabilioje $4+$ būsenoje. Vanadžio jonai visais atvejais (vienas ar du HQ) yra V^{3+} , V^{4+} ir V^{5+} valentinėse būsenose. V^{3+} ir V^{4+} jonų santykinė koncentracija didėja, didėjant HQ kiekiui geliuose.
5. $(NH_4)_{2-x}H_xV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ ($x = 0, 1$) kserogelius galima naudoti kaip pradines medžiagas amoniako jutiklių gamyboje.

Darbo apimtis. Darbą sudaro bendra darbo charakteristika, 5 skyriai, išvados, literatūros sąrašas, publikacijų sąrašas ir priedas. Bendra disertacijos apimtis – 112 puslapiai (iš jų 13 psl. – turinys, reziumė, santrumpos, pirmieji bei paskutiniai darbo puslapiai), 52 iliustracijos, 19 lentelių ir 1 priedas.

Pirmajame disertacijos skyriuje apžvelgtos hidratuotų vanadžio oksidinių junginių savybės. Trumpai aprašyti zolis-gelis technologijos bei RFS metodo pagrindai.

Antrajame disertacijos skyriuje aprašyti vanadžio pentoksido ir vanadžio-natrio oksidinės bronzos plonųjų sluoksnių sintezės metodai bei metalų valentingumo nustatymas panaudojant RFS metodą. Taip pat pateikti vanadžio-hidrochinono ir vanadžio-titano-hidrochinono molekulinį kserogelių bei jų bronzų sintezės metodai. Pateiktas amonio-polivanadato-molibdato molekulinio kserogelio sintezės aprašymas. Aptarta RFS spektro matavimo metodika.

Trečiajame disertacijos skyriuje aprašomas vanadžio jonų valentingumo nustatymas įvairiuose vanadžio oksidiniuose junginiuose. Pateikti amonio-polivanadatų-molibdatų bei vanadžio oksidinių kserogelių, interkaluotų hidrochinonu, RFS spektrų tyrimo rezultatai.

Ketvirtajame disertacijos skyriuje pateikti vanadžio pentoksido plonųjų sluoksnių, vanadžio-natrio oksidinės bronzos plonųjų sluoksnių ir vanadžio-hidrochinono oksidinių molekulinį bronzų plonųjų sluoksnių RFS spektrų tyrimo rezultatai.

Penktajame disertacijos skyriuje aptartos vanadžio-amonio hidratuotų junginių taikymo galimybės naudojant juos amoniako dujų jutiklių gamyboje.

Bendrosios išvados

Pirmą kartą zolis-gelis technologijos metodais susintetinti vanadžio-natrio, vanadžio-hidrochinono ir vanadžio-titano-hidrochinono molekuliniai kserogeliai bei minėtų junginių oksidinės bronzos. Ištirti kserogelių ir bronzų RFS spektrai. Nustatyta, kad:

1. V^{4+} jonų, kurių pagrindą sudaro V_2O_5 kserogeliai, $V\ 2p_{3/2}$ smailės ryšio energija pasislinkusi apie 1,3 eV į mažesnių energijų sritį lyginant su pagrindine V^{5+} smaile. V_2O_5 ir V_2O_4 oksidų cheminis poslinkis yra apie 0,6 eV. Keturvalenčio vanadžio $V\ 2p_{3/2}$ smailės plotis kserogeliuose yra toks pat kaip ir penkiavalenčio vanadžio.
2. $(NH_4)_{2-x}H_xV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ ($x = 0, 1$) geliuose vanadžio jonai yra V^{5+} ir V^{4+} būsenose, kurių redukcijos santykis yra 0,04 nepriklausomai nuo x reikšmės, molibdeno jonai yra stabiliose Mo^{6+} būsenose. N 1s smailės padėtis rodo, jog azotas yra surištas su vandeniliu NH_4^+ jonuose.
3. $V_{1,67}Ti_{0,33}O_{4,85}\cdot nH_2O/2HQ$ ir $V_{1,67}Ti_{0,33}O_{4,85}\cdot nH_2O/HQ$ (HQ – hidrochinonas) kserogeliuose nepriklausomai nuo hidrochinono įterpimo laipsnio (vienas ar du HQ) titano jonai yra stabilioje $4+$ būsenoje. Vanadžio jonai visais atvejais (vienas ar du HQ) yra V^{3+} , V^{4+} ir V^{5+} valentinėse būsenose. V^{3+} ir V^{4+} jonų santykinė koncentracija didėja, didėjant HQ kiekiui geliuose.
4. Naudojant zolis-gelis technologijos metodą, amonio molekules galima įterpti į vanadžio pentoksido matricą. Todėl gauti vanadžio - amonio oksidiniai kserogeliai gali būti naudojami kaip pradinė medžiaga amoniako dujų jutiklių gamybai.
5. Panaudojant zolis-gelis technologijos metodą galima gauti ne tik vanadžio oksidinius kserogelius, kuriuose įterpti metalo jonai (mūsų atveju – natrio), bet ir molekulinis kserogelius (hidrochinonas, amonis). Iš kserogelių, atkaitinant juos ~580 K temperatūroje, galima pagaminti vanadžio pentoksido, vanadžio-natrio oksidinės bronzos, vanadžio-hidrochinono bei vanadžio-titano-hidrochinono oksidinių bronzų plonuosius sluoksnius.

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SYNTHESIS OF THE VANADIUM OXIDE
COMPOUNDS AND INVESTIGATION
BY X-RAY PHOTOELECTRON SPECTROSCOPY
METHOD

Summary of Doctoral Dissertation

Physical Sciences,

Physics (02P),

Condensed Matter: electronic structure; electric,
magnetic and optical properties; superconductors;
magnetic resonance; relaxation; spectroscopy (P260)

Audrius PAŠIŠKEVIČIUS

VANADŽIO OKSIDINIŲ JUNGINIŲ
SINTEZĖ IR TYRIMAS
RENTGENO FOTOELEKTRONŲ
SPEKTROSKOPIJOS METODU

Daktaro disertacijos santrauka

Fiziniai mokslai,

Fizika (02P),

Kondensuotos medžiagos: elektroninė struktūra,
elektrinės, magnetinės ir optinės savybės,
superlaidininkai, magnetinis rezonansas, relaksacija,
spektroskopija (P260)

2010 12 17. 1,5 sp. l. Tiražas 70 egz.

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