Xerogels of ammonium polyvanadatomolybdate as starting material for ammonia gas sensors

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1. INTRODUCTION

The various gas sensors were designed for detection of different gases in the air using different oxides and impurities [1- 3]. For example the manufacturing of ammonia sensors on the basis of Cu_xS-micro-porous-Si structure includes manufacture of micro-porous silicon, drawing on it of SiO₂ isolating layer, and then the Cu_xS layer [4, 5]. The special equipment for all these processes is needed. More usable method for sensor production is so-called soft chemistry or sol-gel synthesis [6, 7].

Sol-gel process can be used to produce a wide range of various compounds (usually oxides) including their thin films, nanopowders, fibers, glasses, ceramics, organic-inorganic hybrids, and so on. The sol-gel process can be characterized by a series of discrete steps. Step 1: formation of the "sol" i.e. colloidal suspension of solid particles (usually salts of necessary materials) in a liquid (solvent for necessary materials). Step 2: gelation resulting from the formation of an oxide network (the gel) by a polycondensation that results in a dramatic increase in the viscosity of the solution. This network structure may result from physical or chemical bonds, as well as crystallites or other junctions that remain intact within the extending fluid. Step 3: formation of a xerogel - a solid formed from a gel by drying usually in air atmosphere. As a result all solvent components that are not bonded with oxide network abandon the gel. A lot of various vanadium hydrated compounds were synthesized by using this simple method [8]. The sol-gel technology is also widely used for the production of the humidity sensors based on the vanadium hydrated compounds [9, 10].

The chemical composition of produced materials was investigated using the X-ray photoelectron spectroscopy (XPS) method. XPS is known as the surface analysis method which provides the direct information on the species concentration and their valence states. So we use these features of the method for studies of the surface composition of investigated xerogels.

In the present paper, we introduce the ammonia gas sensor based on the vanadium-molybdenum-ammonium oxide hydrate that could operate at the room temperature area.

2. Experimental

The ammonium polyvanadatomolybdate xerogels were synthesized using V₂O₅, NH₄VO₃, 40% H₂O₂, and Mo powder. V₂O₅, Mo powders and NH₄VO₃ in a suitable proportion were dissolved in H₂O₂ to form mixed solutions of pervanadic (molybdic) acids. Slow heating up to 333 K initiates the decomposition of the peroxide compounds, followed by gelation. The reactions with the participation of V₂O₅ are following:

The reaction (3) represents polymerization of the neutral precursor, resulting in a hydrous V_2O_5 gel, which can be regarded as the polyvanadic acid $H_2V_{12}O_{31\pm\delta}\cdot nH_2O$. Decomposition of the peroxide solution of vanadium containing only NH_4^+ ions is not accompanied by gelation, whereas, in the presence of molybdenum, $(NH_4)HV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ gels are formed [11]. Obtained gels were deposited on Ni substrates by screen printing method and dried in air. The thickness of prepared films was about 10 μm . The films have layered structure where NH_4^+ ions and H_2O are incorporated between the V-O-Mo layers [10]. Such structure causes anisotropy of physical properties of the produced films along and across the V-O-Mo layers that is peculiar to the other hydrated vanadium compounds [11].

Surface chemical composition was inspected using the XPS method. XSAM 800 (Kratos Analytical, UK) was used to record the X-ray photoelectron spectra. A nonmonochromatized Mg $K\alpha_{1,2}$ (1253.6 eV) radiation source excited the photoelectrons at 15 kV, 300 W. During the spectrum analysis the working pressure was below 10^{-7} Pa in the analysis chamber. The analyzer used with an energy resolution $\Delta E/E = 0.08\%$ in steady retarding mode. Using KRATOS DS800 data system the photoemission data has been collected and processed. The multiple photoelectron spectra were separated into several peaks setting the peak position: binding energy (BE), area (A), width (FWHM), and Gaussian/Lorentzian (G/L) 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 the BE of which should have been equal to 284.6 eV was used for the correction of the charging effects. After the Mg $K\alpha_{1,2}$ source satellites and Shirley background [12] subtraction, 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 samples was cleaned using Ar^+ ions bombardment at 3 kV and current density of $10 \mu A \cdot cm^{-2}$ for 3 min. The energy scale was calibrated using the Au 4 $f_{7/2}$ peak (84.0 eV).

Electrical contacts of the sensitive films were manufactured by a dc-magnetron sputtering in Ar atmosphere from a metallic In target. The contacts were deposited in two configurations as shown in Fig. 1. These configurations of the contacts allow to investigate physical properties of the films across (a) and along (b) 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. The resistance of the films was calculated by measuring output voltage on the resistance connected in series with the sample as a time function during the tests.

3. Results and Discussion

The successful synthesis of the $(NH_4)HV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ xerogel was confirmed using XPS spectra study where presence of NH_4^+ , Mo^{6+} , V^{4+} , V^{5+} ions, oxygen ions O^{2-} connected with molybdenum and vanadium ions, and oxygen in water molecules were captured. Figure 2 shows the XPS spectrum of $(NH_4)HV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ xerogel in the vanadium - oxygen region (points are experimental data). V 2p and O 1s peaks are composed of several components. V 2p_{3/2} and V 2p_{1/2} peaks consists of two components and O 1s peak consists of three components. It is possible to subsume that the V 2p_{3/2} peak components with binding energies 516.03 eV and 517.53 eV corresponds to the quadrivalent [13] and quinquivalent [14] vanadium ions in the xerogel, respectively. The same can be said about the V 2p_{1/2} peak components with binding energies of 523.5 eV and 524.98 eV [15]. From V 2p_{3/2} peak components' areas one can calculate the vanadium ions reduction ratio $C = C_{V4+} / (C_{V5+} + C_{V4+})$ where C_{V5+} and C_{V4+} are the concentrations of the corresponding ions. In our case $C = 0.043$, i. e. quadrivalent vanadium constitutes just 4.3 % of vanadium ions content similar as in other vanadium hydrates [8]. The O 1s peak has three components (see Fig. 2). The first one, a more intensive component, with binding energy 530.48 eV matches the O^{2-} ions [16] linked with vanadium and molybdenum ions. The second one, less intense (531.4 eV), is possible to assign to the relations with carbon [16]. And the last and weakest component with binding energy at 533.01 eV matches the oxygen linked with hydrogen in water

molecules [17]. In Fig. 3 the XPS spectrum of molybdenum (Mo 3p_{3/2}) and nitrogen region is shown. The fact that Mo 3p_{3/2} and N 1s binding energies are close to each other makes the analysis of this spectrum more complex, whereas the neglect of nitrogen presence in the gel makes the interpretation of this spectrum quite difficult. The component with binding energy 398.68 eV matches Mo⁶⁺ ions [18] and the component with binding energy 401.76 eV matches nitrogen which is in NH₄⁺ ions [19]. Mo 3d emission comprises the pair of spin - orbit doublets with Mo 3d_{3/2} and Mo 3d_{5/2} binding energies of ~ 236 eV and ~ 233 eV respectively that was observed in other vanadium hydrates containing molybdenum [20].

(NH₄)HV₉Mo₃O_{31±6}·nH₂O xerogel was tested as a possible material for ammonia gas sensor. Fig. 4 shows the resistance response to ammonia gas injection ("In" on Fig. 4) and removal ("Off" on Fig. 4) versus time measured across (contacts configuration - Fig. 1b) V – O – Mo layers. In this case the resistance response of the sample increases after ammonia injection then decreases and practically does not change with time even after removing the gas from the chamber ("Off" on Fig. 4). It is clear that "across" configuration of the samples contacts is unusable for the gas sensors production. Figure 5 shows the resistance response to ammonia gas injection ("In" on Fig. 5) and removal ("Off" on Fig. 5) versus time measured along (contacts configuration - Fig. 1a) V – O – Mo layers. In this case after gas injection the resistance response at first three seconds increase, then practically do not changes about 5 – 6 seconds (region A on Fig. 5), then decrease and after that do not changes with time (region B on Fig. 5). After gas removal from the testing chamber the resistance response increase and then do not depends on the time. So, by measuring the resistance response in regions A and B (Fig. 5) we can determine the ammonia gas presence in the testing chamber. Figure 6 presents the resistance response dependence on gas concentration measured in region A. The experimental results (points in Fig. 6) can be described as linear function

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

where α and β are some constants and NH₃ – the concentration of ammonia gas in chamber. Solid line in Fig. 6 presents the calculation results using (5) and $\alpha = 1.01253 \pm 0.01418$, $\beta = (0.02337 \pm 0.00141) \%^{-1}$. The value of constant β specifies the sensitivity of the xerogel to ammonia gas concentration.

The resistance response dependence on gas concentration measured in region B is shown on Fig. 7. The experimental results (points on Fig. 7) can be described as exponential function

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

where NH₃ – the concentration of ammonia gas, $(R/R_0)_0 = 0.7731 \pm 0.01509$, $C = 0.2286 \pm 0.02521$, and $t = (0.348 \pm 0.0949) \%^{-1}$ (calculation results are shown on Fig. 7 - solid line). In this case the resistance response exponentially decreases with gas concentration and practically does not changes at the large values of the ammonia concentration. So, this concentration measurement method in region B in Fig. 7 is not usable.

4. Conclusions

The ammonium polyvanadatomolybdate (NH₄)HV₉Mo₃O_{31±6}·nH₂O xerogels were synthesized from V₂O₅, NH₄VO₃, 40 % H₂O₂, and Mo substances using sol–gel technology method. Heating up to 333 K mixed solutions of pervanadic (molybdic) acids and NH₄VO₃ K initiates the decomposition of the peroxide compounds. Decomposition of the peroxide solution of vanadium containing only NH₄⁺ ions is not accompanied by gelation, whereas, in the presence of molybdenum, (NH₄)HV₉Mo₃O_{31±6}·nH₂O gels are formed. Obtained xerogels have layered structure where among the V – O – Mo layers NH₄⁺ ions and H₂O are incorporated.

The resistance response versus ammonia concentration after ammonia injection in the testing camera was studied for two samples configurations – planar, when resistance response was measured along V – Mo – O layers and sandwich – across layers. It was shown that “across” configuration of the samples contacts is unusable for the gas sensors production because the resistance response of the sample practically does not change with time even after removing the gas from the testing chamber. More usable is planar sample configuration when resistance response versus ammonia concentration was measured along V – Mo – O layers. In this case, after gas injection, the resistance response at first increased, then practically do not change about 5 – 6 seconds, later decreased and after that did not change with time. After gas removal from the testing chamber the resistance response increased and later did not change on time. The resistance response after gas injection can be described by the linear function $(R/R_0) = \alpha + \beta \cdot \text{NH}_3$ where $\alpha = 1.01253 \pm 0.01418$, $\beta = (0.02337 \pm 0.00141) \%^{-1}$, and NH_3 is the concentration of ammonia gas in the chamber. The value of constant β specifies the sensitivity of the xerogel to ammonia gas concentration.

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Fig. 1. Configuration of electrodes for resistance measurements across (a) and along (b) V – O – Mo layers.

Fig. 2. XPS V – O region spectra of $(\text{NH}_4)\text{HV}_9\text{Mo}_3\text{O}_{31\pm\delta} \cdot n\text{H}_2\text{O}$ xerogel.

Fig. 3. XPS spectra of molybdenum (Mo 3p) and nitrogen (N 1s) region.

Fig. 4. The time dependence of the resistance response to ammonia measured across (contacts configuration - Fig.1b) V – O – Mo layers.

Fig. 5. The time dependence of the resistance response to ammonia measured along (contacts configuration - Fig.1a) V – O – Mo layers.

Fig. 6. Resistance response dependence on ammonia concentration measured in region A in Fig.5.

Fig. 7. Resistance response dependence on ammonia concentration measured in region B in Fig.5.

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