**Abstract**

Using oxide compositions is a promising method of increasing the sensitivity and selectivity of semiconductor gas sensors on the basis of SnO₂, In₂O₃, WO₃ and other oxides. We have studied nanocrystalline tungsten oxide (WO₃), indium oxide (In₂O₃), cobalt oxide (Co₃O₄) and mixed oxide compositions with different WO₃/In₂O₃ and WO₃/Co₃O₄ ratios synthesized using the sol-gel method after xerogel annealing at 400–600 °C. The morphology, phase composition and structure of the materials have been studied using X-ray diffraction, infrared spectroscopy, scanning electron microscopy and transmission electron microscopy. We showed that stable structures can be produced in WO₃–In₂O₃ and WO₃–Co₃O₄ nanoheterogeneous compositions. The growth of grain size in WO₃ and In₂O₃, WO₃ and Co₃O₄ during heat treatment of mixed compositions occurs slower than in simple oxides. An increase in the gas sensitivity of the compositions in comparison with simple oxides can be accounted for by smaller grain sizes and hence larger specific surface area, as well as by the dependence of grain surface state on material composition. Both compositions exhibit the greatest nitrogen dioxide response at 130–150 °C and the greatest carbon oxide response at above 230 °C. We have produced low-power nitrogen dioxide sensors with a sensitivity of << 1 ppm and power consumption of ≤ 85 mW.

**Keywords**

tungsten oxide, indium oxide, cobalt oxide, semiconductor gas sensor

**1. Introduction**

Using oxide compositions is a promising method of increasing the sensitivity and selectivity of semiconductor gas sensors on the basis of SnO₂, In₂O₃, WO₃ and other oxides [1]. Earlier [2–5] the structure and morphology of WO₃–In₂O₃ and WO₃–Co₃O₄ oxide compositions synthesized using the sol-gel method were studied. Xerogel annealing at 400 and 600 °C for 2 h in the WO₃–In₂O₃ system led to the formation of a heterogeneous two-phase material consisting of a monoclinic WO₃ phase and a cubic In₂O₃ phase. Annealing at 800–850 °C led to the synthesis of In₃(WO₄)₂ [2]. Annealing at 400 °C for 2 h in the WO₃–Co₃O₄ system led to the formation of a heterogeneous two-phase material consisting of a monoclinic WO₃ phase and a cubic Co₃O₄ phase and annealing at 600–650 °C led to the synthesis of CoWO₄ [3]. The studies were carried out using thermogravimetry, differential thermal analysis, infrared spectroscopy, X-ray phase analysis and low-temperature nitrogen adsorption. The gas sensitivity of the WO₃–In₂O₃ and WO₃–Ga₂O₃ compositions to reducing (CO) and oxidizing (NO₂) gases increased due to strong structural disordering and grain size reduction in the compositions in comparison...
2. Experimental

Tungsten oxide WO₃ was obtained from a 1.23M water solution of Na₂WO₄·2H₂O by drop-by-drop addition to a 12M nitric acid solution with permanent stirring and the residual electrolyte was removed by decanting. Indium oxide In₂O₃ was obtained from a 0.78M water solution of In(NO₃)₃·4.5H₂O by adding 0.24M ammonia water solution. Similarly, cobalt oxide CoO₂₃ was obtained from a 2.3M water solution of CoSO₄·7H₂O by adding 0.24M ammonia water solution.

For physicochemical analysis the specimens were dried of prepared sols at room temperature, mixing of xerogels in different weight ratios and heat treatment of the resultant composites at 200–600 °C for 2 h in air. The electrical resistivity of the specimens was measured during heating and cooling with a B7-40 digital multimeter and the temperature was controlled with an aluminum thermocouple located near the specimen.

X-raying was carried out on a DRON-3 diffractometer in CαKα radiation. The size of coherent scattering regions, i.e., the grain size in polycrystalline specimens, was determined from diffraction peak broadening (the Scherrer method) using the formula

\[ D = \frac{0.9λ}{β \cdot \cos θ} \]  

where \( λ \) is the monochromatic X-ray wavelength, \( b \) is the peak width at half height and \( θ \) is the diffraction angle [6].

The infrared spectra of the specimens dried at 20, 300 and 600 °C were taken with an AVATAR 330 (ThermoNicolet) spectrometer at wavenumbers \( ν = 400–700 \text{ cm}^{-1} \). The diffuse scattering spectra were recorded with a Smart Nicolet spectrometer at wavenumbers \( ν = 400–700 \text{ cm}^{-1} \).

The specific surface area of the powders was determined from low-temperature nitrogen adsorption on a Klyatchko–Gurvich instrument [7].

The specimens were prepared in the form of pellets 10.0 mm in diameter and 3.0 mm in thickness weighing 0.7–0.8 g pressed from preliminarily annealed powdered oxides (400 °C, 2 h) with an organic binder (colophony) under a hydraulic press at a 150 kPa pressure and sintered at 450 °C for 5 h in air. Silver electrodes were applied at both sides of the specimens for improving the quality of the electric contact. Two-electrode sensors were produced by depositing WO₃ and WO₃–CoO₂₃ compositions onto 1.3 × 1.3 mm² anodized aluminum microplates with platinum electrodes by photolithography followed by annealing at 450 °C for 12 h in air.

The sensor response \( S \) (rel. units) was determined using the formula

\[ S = \frac{R_a}{R_g}, \]

where \( R_a \) and \( R_g \) are the electrical resistances of the pellet (the sensor) in air and NO₂ gas oxidizing, respectively, or using the formula

\[ S = \frac{R_{a}}{R_{g}}, \]

where \( R_s \) and \( R_{o} \) are the electrical resistances in air and CO reducing gas, respectively. The gas sensitivity of the compositions was studied using carbon oxide containing test gas mixtures produced by Minsk Research Institute for Radio Engineering Materials. The gas mixtures for nitrogen dioxide sensitivity study of the compositions in the form of gas permeable pellets were prepared as described earlier [8].

3. Results and discussion

Xerogel of hydrated tungstic acid H₂WO₄·H₂O (PDF 87-2404) was obtained from sodium tungstate. Then the xerogel lost water during annealing and crystallized in the form of a monoclinic WO₃ modification (PDF 43-1035). Annealing of tungstic acid xerogel at 300–900 °C for 2 h in the air led to the formation of tungsten oxide. The size of coherent scattering regions increased with annealing temperature from 70 nm at 200 °C to 100 nm at 600 °C. The lattice parameters of the WO₃ monoclinic structure were found almost constant during annealing at 200–800 °C and equal to \( a = 7.299–7.328 \text{ nm}, b = 7.527–7.537 \text{ nm}, c = 7.698–7.732 \text{ nm}, \) and \( β = 90.90–91.40 \text{ deg.} \)

Xerogel obtained from indium nitrate after drying at 20 °C is amorphous In(OH)₃. Comparison of X-ray powder diffraction patterns after In(OH)₃ annealing at 200–800 °C showed that In₂O₃ is the predominant phase after annealing at 200 °C for 2 h. Its sintering leads to an increase in the coherent scattering region size from 10–12 nm after annealing at 200 °C, to 20 nm after annealing at 300 °C, 35 nm after annealing at 600 °C and 50 nm
after annealing at 850 °C. The lattice parameter \( a \) of \( \text{In}_2\text{O}_3 \) did not change after annealing at 200–800 °C, remaining 1.008–1.015 nm.

Cobalt sulfate xerogel consisted of a mixture of \( \text{Co(OH)}_2 \) (PDF 45-31) and \( \text{Co(OH)}_2 \) (PDF 2-925). These compositions decomposed at 200–800 °C to form \( \text{Co}_3\text{O}_4 \) in a cubic structure. The coherent scattering region size of the \( \text{Co}_3\text{O}_4 \) specimen was 80 nm after annealing at 200 °C, 160 nm after annealing at 400 °C and 250 nm after annealing at 600 °C. The lattice parameter \( a \) of \( \text{Co}_3\text{O}_4 \) did not change after annealing at 200–800 °C, remaining 0.8064–0.8084 nm.

X-ray phase analysis showed that the \( \text{WO}_3–\text{In}_2\text{O}_3 \) (20 °C) and \( \text{WO}_3–\text{Co}_3\text{O}_4 \) (20 °C) xerogel powders containing 5.0, 25.0, 50.0 and 75.0 wt.% of \( \text{In}_2\text{O}_3 \) or \( \text{Co}_3\text{O}_4 \) were amorphous. Annealing at 200–450 °C for 2 h did not change the two-phase composition of the \( \text{WO}_3–\text{Co}_3\text{O}_4 \) and annealing at 600 °C led to the formation of a third by-phase \( \text{CoWO}_4 \). Annealing of the \( \text{WO}_3–\text{In}_2\text{O}_3 \) samples (5InW, 25InW, 50InW and 75InW) at 600 °C led to the formation of a heterogeneous two-phase composition with a coherent scattering region size of ~30–35 nm. Annealing of the \( \text{WO}_3–\text{Co}_3\text{O}_4 \) samples (5CoW, 25CoW, 50CoW and 75CoW) at 400 °C led to the formation of a heterogeneous two-phase composition with a coherent scattering region size of ~50 nm. Figure 1 shows X-ray diffraction patterns of the \( \text{WO}_3–\text{In}_2\text{O}_3 \) and \( \text{Co}_3\text{O}_4 \) samples and the test compositions 5InW, 25InW and 75InW, annealed at 600 °C, and 5CoW, 25CoW and 75CoW, annealed at 400 °C.

Annealing of the \( \text{WO}_3–\text{In}_2\text{O}_3 \) system at 800–850 °C for 2 h triggered a solid-state reaction producing a heterogeneous material the main phase of which was \( \text{In}_2(\text{WO}_4)_3 \) (PDF 49-0337). The \( \text{WO}_3–\text{In}_2\text{O}_3 \) specimens for gas absorption tests were annealed at 450 and 650 °C. It was founded, the \( \text{In}_2(\text{WO}_4)_3 \) phase did not form upon annealing. The coherent scattering region sizes of \( \text{WO}_3 \) in the \( \text{WO}_3–\text{In}_2\text{O}_3 \) specimen containing 25.0 wt.% \( \text{In}_2\text{O}_3 \) after annealing at 400 and 500 °C for 2 h were ~25 and ~35 nm, respectively, which is significantly smaller than those of the \( \text{WO}_3 \) powders (~100 and ~110 nm, respectively) annealed under the same conditions.

The X-ray diffraction patterns of the specimens annealed at 400 °C did not contain \( \text{CoWO}_4 \) peaks (Fig. 1b). The size of coherent scattering region of the 25CoW specimen is ~50 nm which is also smaller than for simple tungsten oxide specimens (~100 nm) and cobalt oxide specimens (~200 nm) annealed under the same conditions. This can be caused by the formation of grains with distorted uneven faces impeding their growth in complex oxide systems with different crystalline structures [10].

Figure 1. Spectra of X-ray phase analysis of samples of oxides of tungsten, indium and cobalt, as well as their compositions, obtained under various conditions of annealing: (a) 600 °C, 2 h, (b) 400 °C, 2 h.
Thus joint annealing of tungstic acid and indium or cobalt hydroxide xerogels suppresses grain growth in comparison with simple oxides. A decrease in coherent scattering region size usually increases the gas sensitivity of gas sensors and lowers their operation temperature [1].

Figure 2 shows scanning electron microscopy (SEM) images of (a) WO₃, (b) In₂O₃, (c) 25InW and (d) 15CoW mixed compositions. The WO₃ powder (Fig. 2a) is a mixture of homogeneous spherical particles locally forming agglomerations on the surfaces of which the boundaries of individual particles could be well resolved. The amount of particles with sizes less than 250 nm is 706 per 1000 particles with a surface distribution density of ≈ 3.3 µm². Within the fraction of particles sized 0–250 nm one can easily resolve irregularly shaped particles 50+ nm in diameter. Large particles (up to 2.5 µm) are agglomerations of planar plates with smooth or sharp edges. One can clearly see the step-like structure of the agglomerations formed by single thin plates. The shapes and sizes of WO₃ particles are similar to those described in the literature [10–14].

In₂O₃ powder (Fig. 2b) is a mixture of particles with different shapes and sizes. The fraction of particles sized less than 250 nm is 348 per 1000 particles, with the surface distribution density of ≈ 3.06 µm². Within the fraction of particles sized 0–250 nm one can easily resolve irregularly shaped particles 50+ nm in diameter. Unlike WO₃ and Co₃O₄, In₂O₃ powder has a smaller particle size scatter and a larger fraction of bigger particles.

SEM image of the 25InW sample (Fig. 2c) shows that the powdered mixture of irregularly shaped nanosized particles (50–150 nm) consists of relatively homogeneous grains sometimes forming agglomerations. The fraction of particles with a size of less than 250 nm is 925.72 per 1000 particles with a surface distribution density of ≈ 25.21 µm². Within the fraction of particles sized 0–250 nm one can easily resolve irregularly shaped par-

| Sample    | Heat treatment conditions | S, m²/g |
|-----------|---------------------------|--------|
| WO₃·2H₂O  | 20 °C                     | 32.0   |
| WO₃       | 200 °C, 2 h               | 51.5   |
| WO₃       | 400 °C, 2 h               | 24.0   |
| WO₃       | 600 °C, 2 h               | 3.2    |
| 5InW      | 400 °C, 2 h               | 45.5   |
| 15InW     | 400 °C, 2 h               | 12.5   |
| 50InW     | 400 °C, 2 h               | 9.5    |
| Co₃O₄     | 400 °C, 2 h               | 17.8   |
| 5CoW      | 400 °C, 2 h               | 40.5   |
| 15CoW     | 400 °C, 2 h               | 19.5   |

Table 1. The specific surface area of the studied samples.
Particles 50+ nm in diameter. Large individual particles (to 2.0 µm) are agglomerations of planar plates. The fraction of particles sized less than 500 nm is 982.63 per 1000 particles with the surface distribution density of ≈ 10.67 µm².

The 15CoW powder (Fig. 2d) contains significantly smaller particles and has a high value of specific surface area (0.2–0.3 µm and 12.4 m²/g for 15CoW and 0.2–2 µm and 3.2 m²/g for WO₃, respectively). Thus, according to SEM analysis, the sizes of the WO₃, In₂O₃ and Co₃O₄ particles after heat treatment of mixed compositions are less than the size of simple oxide powders.

Analysis of the SEM images showed a decrease in the particle sizes in the compositions which agrees with the greater specific surface area of mixed compositions in comparison with simple oxide powders (Table 1).

Figure 3 shows TEM images of 25InW and 25CoW powders. The TEM micrographs clearly resolve individual phases of heterogeneous compositions where the grey contrast regions refer to the In₂O₃ (Fig. 3a, b) and Co₃O₄ (Fig. 3c, d) phases and dark contrast regions are the WO₃ phase (Fig. 3a–d). The particles are needle-shaped and have a size from 0.32 to 3 µm. We believe this particle shape determines a large specific surface area of the materials.

IR spectra of WO₃, In₂O₃ and Co₃O₄ powders heat-treated at 200–600 °C were obtained and analyzed earlier [2, 3, 5]. For higher annealing temperatures the band of W–O valence oscillations (500–900 cm⁻¹) is more intense and better resolved due to WO₃ dehydration. The strong absorption band in the 450–900 cm⁻¹ region is commonly attributed to W–O oscillations in
The respective bands are present in the spectra of the samples dried at 20 °C (tungstic acid) and 300 °C. The spectrum of the unannealed specimen had an absorption band in the 3100–3550 cm⁻¹ region caused by the O–H oscillations (symmetrical and asymmetrical) of coordination bound water. The 1600 cm⁻¹ band seems to refer to the HOH bonds in H₂O and the 914.7, 939.9 and 1003.6 cm⁻¹ bands are also related to coordination water (the W–OH₂ bond). The WO₃ specimens treated in a gas and air atmosphere containing NO₂ had a different absorption pattern in the 1200–1700 cm⁻¹ region. They contained bands at 1253.0, 1446.3 and 1498.4 cm⁻¹ which seem to refer to the valence and deformation oscillations of adsorbed NO₂ (there are no available literary data for comparison). Figure 4a shows an IR spectrum of WO₃ annealed at 600 °C for 2 h and Fig. 4b shows an IR spectrum of the same WO₃ specimen heat-treated in a gas and air atmosphere containing NO₂ (T = 187 °C, t = 30 min.). Absorption near 1500 cm⁻¹ is caused by In–O oscillations. The absorption bands at 1385 and 1640 cm⁻¹ should be attributed to bond oscillations of nitrate ions and deformation oscillations in water, respectively [15–17]. The In₂O₃ specimens treated in a gas and air atmosphere containing 3.6 ppm NO₂ (Fig. 4d) has a wide absorption band in the 900–1000 cm⁻¹ region. There are also bands at 904.8 and 998.5 cm⁻¹ which seem to refer to valence and deformation oscillations of adsorbed NO₂.

The Co₃O₄ spectra have peaks at 500–900 cm⁻¹ corresponding to Co–O oscillations. Absorption in the 900–2500 cm⁻¹ region is associated with Co–OH oscillations. The spectrum is shown in Fig. 4d also has a band in the 3100–3550 cm⁻¹ region caused by O–H oscillations (symmetrical and asymmetrical) of coordination bound water. The 1600 cm⁻¹ band refers to HOH bonds in H₂O and the bands at 914.7, 939.9 and 1003.6 cm⁻¹ are related to oscillations of coordination water. Valence and deformation oscillations of adsorbed NO₂ cause the wide and intense bands in the 800–1100 cm⁻¹ region (peaks at 854.6, 1018.3 and 1089.7 cm⁻¹ in Fig. 4e [18–20].
Figure 5. IR spectra of samples of compositions WO$_3$–In$_2$O$_3$ and WO$_3$–Co$_3$O$_4$: (a) 25InW, (b) 50InW, (c) 75InW, (d) 15CoW, (e) 25CoW, (f) 50CoW.

The cubic structure of Co$_3$O$_4$ contains Co$^{2+}$ ($3d^7$) and Co$^{3+}$ ($3d^6$) located in tetrahedral and octahedral sites, respectively, and has the $Fd3m$ space symmetry group. The bands at 556.1–655.7 cm$^{-1}$ are related to valence oscillations of Co–O bonds and are typical of cubic Co$_3$O$_4$, but also could belong to impurities of CoO and Co$_2$O$_3$ which are hard to detect with IR spectroscopy [21].

The shapes, intensities and locations of the two narrow bands at 664.69 and 568.74 cm$^{-1}$ correspond to the mono-disperse fcc structure of Co$_3$O$_4$ [22].

There are no literary data available on the origin of the absorption band at 826 cm$^{-1}$. Since this band does not show for the specimen annealed at 600 °C it can probably be attributed to adsorbed precursor ion decomposition products. For the same reason (high-temperature desorption) the bands in the 1300–2500 cm$^{-1}$ region can be associated with oscillations of carboxyl and carboxylate forms of C–O bonds in adsorbed carbon oxide.

The spectra of the 25InW, 50InW and 75InW specimens (Fig. 5a–c) do not exhibit strong absorption in the 900–3700 cm$^{-1}$ region, by analogy with the WO$_3$ and In$_2$O$_3$ specimens annealed under the same conditions. The 900–3700 cm$^{-1}$ region refers to symmetrical and asymmetrical O–H bond oscillations in coordination bound water, O–H bond oscillations in water molecules, W–OH$_2$ bond oscillations and other oscillations relating to coordination bound water. However, absorption in this region becomes more intense with an increase in the In$_2$O$_3$ content suggesting the presence of some In–OH bonds even after annealing at 600 °C. This phenomenon is untypical to tungsten oxide, which usually loses all hydroxyl groups.

Absorption in the 450–900 cm$^{-1}$ region is related to W–O oscillations in WO$_3$ and H$_2$WO$_4$ as well as In–OH and In–O oscillations in (InOH)$_2$ and In$_2$O$_3$. The ν [In-O] oscillations near 410 cm$^{-1}$ that are typical of In$_2$O$_3$ observe in the spectra of the 50InW and 75InW specimens but absent in the 25InW.

Bands referring to W–O bond oscillations in the WO$_3$–In$_2$O$_3$ composition spectra are slightly shifted to the left. For example, the band at 706.9 cm$^{-1}$ in the WO$_3$ spectrum is observed at 725.4 cm$^{-1}$ in the 25InW specimen spectrum and 747.7 cm$^{-1}$ in the 75InW spectrum. This fact may point to a small mutual solubility of the oxides, e.g. probability of indium atom incorporation into the WO$_3$ lattice [23].

Absorption in the 3200–3700 cm$^{-1}$ region (oscillations of surface OH groups or bonds in adsorbed water molecules) and at 1626 cm$^{-1}$ (deformation water oscillations) in the IR spectrum of WO$_3$ annealed at 600 °C is almost absent. However, indium oxide annealed under the same conditions has strong absorption bands in that region. An increase in the In$_2$O$_3$ content in the WO$_3$–In$_2$O$_3$ composition from 25.0 to 75.0 wt.% leads to an increase in the absorption band intensity in that region. The intensity of
Figure 6. IR spectra of the compound CoWO₃ and samples of the composition WO₃–CoO₂: (a) CoWO₃, synthesis 650 °C, 2 h, (b) CoWO₃, synthesis 650 °C, 2 h, after exposure to a gas-air mixture containing 3.6 ppm NO₂ (T = 187 °C, t = 30 min.), (c) 5 wt.% Co₂O₃, 450 °C, 2 h, (d) 15 wt.% Co₂O₃, 450 °C, 2 h.

The absorption bands in the 75InW specimen is the same as for the In₂O₃ specimen. Thus materials with different WO₃ to In₂O₃ content ratios have different surface properties. Analysis of the IR spectra suggests a higher adsorption capacity of the WO₃–In₂O₃ composition as compared to that of the source oxides due to the retained high concentration of surface OH groups (close or equal to that of In₂O₃).

Analysis of the IR spectra confirms the conclusions made from the X-ray phase analysis data concerning the formation of CoWO₃ as a result of joint annealing of tungstic acid and cobalt hydroxide sols at 600–650 °C for 2 h. Usually, there are characteristic bands of metal oxides at low-frequency region (500–600 cm⁻¹) (in our case Co₂O₃ bands band are absent). The absorption bands near 1000 cm⁻¹ can be attributed to oscillations of deformed Co–O, W–O and W–O–W bonds. The most clearly seen is the band at 500 cm⁻¹ correspondings to W–O bonds in WO₃ octahedra. Moreover, the bands at 821 and 620 cm⁻¹ are directly related to valence oscillations of O–W–O and W–O–W bonds. The bands at 1635 and 3300 cm⁻¹ refer to O–H bond oscillations and adsorption of coordination bound water molecules, W–OH bond oscillations and other oscillations has more intense absorption than for the WO₃ and Co₂O₃ specimens annealed under the same conditions. This can be caused by slower WO₃ and Co₂O₃ dehydration and crystallization in compositions than in simple oxides. The higher concentration of surface OH groups may favor the higher adsorption capacity of the composition in comparison with the source oxides.

Absorption in the 450–900 cm⁻¹ region is caused by W–O oscillations in WO₃ and H₃WO₄ as well as Co–OH and Co–O oscillations in Co(OH)₂ and Co₂O₃. There were no new absorption bands related to the possible formation of chemical compounds including CoWO₃ during annealing at 450 °C found. This result is in agreement with the X-ray phase analysis data.

The ν [In–O] and ν [Co–O] oscillations at 656–659 and 553–557 cm⁻¹ typical of cobalt oxide are present in the 15InW specimen spectrum at 559.3 and 656.0 cm⁻¹. This indicates that there is no shifting typical of Co₂O₃ base solid solution formation. The bands of W=O and W–O
bond oscillations were at 636.8, 809.3, 967.8 and 1038.9 cm$^{-1}$ in the WO$_3$ spectrum and at 620.1, 811.3, 972.1 and 1079.7 cm$^{-1}$ in the 15CoW spectrum. This is another indication of the significant dissolution of cobalt oxide in the tungsten oxide structure. Stronger low-frequency shifts are typical of absorption bands for ν [W–OH$_2$] bond oscillations (1038.9, 1409.8, 1452.0 and 1624.2 cm$^{-1}$), and the higher intensity of these bands, especially the one at 1635 cm$^{-1}$ testifies to a higher concentration of the respective surface bonds (chemisorbed water).

Figure 7 shows sensor response of WO$_3$–In$_2$O$_3$ and WO$_3$–Co$_3$O$_4$ to several air-based gas mixtures as a function of composition (In$_2$O$_3$ or Co$_3$O$_4$ contents, Fig. 7a, b) and temperature (ratio of specimen resistivity in a gas atmosphere to specimen resistivity in the air for NO$_2$, and ratio of specimen resistivity in the air to specimen resistivity in the air in the case of CO, Fig. 7c, d).

The highest sensor response to CO was observed in the 180–240 °C range for the WO$_3$–In$_2$O$_3$ composition specimens and in the 190–240 °C range for the WO$_3$–Co$_3$O$_4$ composition (Fig. 7a). For NO$_2$ containing gas and air mixture, the ratio of specimen resistivity in the gas and air atmosphere to that in the air for specimens of both compositions is the highest at 140–150 °C.

The expressed temperature dependence of semiconductor gas sensor response is primarily accounted for by the fact that CO molecules with insufficient thermal energy enter into reaction with oxygen adsorbed on the sensor surface, this reaction being well-known as follows: CO + 1/2O$_2$ → CO$_2$. An increase in the operating temperature increases the thermal energy of adsorbed CO molecules to a level sufficient for overcoming the activation energy barrier and reaction with adsorbed oxygen.

Furthermore, the conductivity of oxides increases with temperature due to high electron mobility. Further increase in temperature may reduce the sensitivity due to a transformation of adsorbed oxygen particles which will trap more electrons from the sensor material and reduce its gas adsorption capacity.

Gas pore containing tungsten oxide pellets showed a somewhat higher sensitivity to both CO and NO$_2$ containing gas mixtures than indium oxide specimens. However, the mixed specimens have higher sensitivities.

The 25InW specimen has the highest sensor response but further increase in the content of the addition reduces the sensitivity of the material. Sensor response may increase for several reasons. Along with an increase in the specific surface area of mixed compositions (Table 1) which leads to an increase in the number of adsorbed molecules, it also should be taken into account the more complex defect structure of the two oxides in the mixed composition as confirmed by IR spectroscopy. The formation of defects of different origins may significantly change the type of conductivity due to the greater number of free
or delocalized electrons and hence a higher effective carrier concentration on the surface of sensitive materials.

The response of the 5InW specimen is the highest after exposure to a gas and air mixture containing nitrogen dioxide. Along with the above-mentioned factors controlling the CO sensitivity of the material, for NO, one should also take into account the presence of highly charged states $W^{3+}$-$W^{5+}$ which presumably exhibit specific adsorption to nitrogen oxides. This may cause a shift of the sensitivity maximum due to a decrease in the number of these centers with an increase in indium oxide content.

Figure 7a also shows that the addition of Co$_2$O$_4$ increased the CO sensor response in the entire addition concentration range, with the 5CoW specimen having the highest sensitivity. The tungsten oxide specimens had an $n$-type response to CO containing gas mixtures, the cobalt oxide specimens had a $p$-type response, the mixed 5CoW, 15CoW and 25CoW specimens had an $n$-type response to this gas mixture and the 50CoW specimen had a $p$-type response.

The increase in CO sensitivity is probably caused by the catalytic activity of cobalt oxides during oxidation of CO, H$_2$, and hydrocarbons [17–19]. Authors of [17] suggested that the exceptionally high sensitivity of the SnO$_2$–Co$_2$O$_4$ compositions to CO and hydrogen is caused by a change of the oxidation/reduction state of Co$_2$O$_4$.

Unlike the WO$_3$–In$_2$O$_3$ composition, for WO$_3$–Co$_2$O$_4$, one should also take into account possible formation of $p$–$n$ heterojunctions which favor dissociation of gas molecules. Partial electron transfer between $p$ and $n$-type semiconductors changes the electrical conductivity of the material. In the case considered conductivity electrons transfer from WO$_3$ grains to Co$_2$O$_4$ ones at the WO$_3$/Co$_2$O$_4$ heterojunctions thus increasing the electrical resistivity of the composition in air, as was observed in the experiment.

If reducing gases are present in gas and air mixtures (H$_2$, CO and hydrocarbons) the decrease in the electrical conductivity of Co$_2$O$_4$ is higher than that for WO$_3$. Thus conductivity electrons mainly return to the catalytically active oxide Co$_2$O$_4$ thus increasing its sensitivity (electron sensitization) [25]. An increase in the Co$_2$O$_4$ additive to $> 5$ wt.% the sensitivity of the material decreased. This can be accounted for by an increase in the fraction of highly reactive regions that impede gas diffusion in bulk specimens and thin-film sensitive elements.

The sensitizing effect of Co$_2$O$_4$ in the WO$_3$–Co$_2$O$_4$ composition can be attributed to the activation of gas adsorption reactions which cause Co$_2$O$_4$ reduction and $p$–$n$ junction destruction.

The sensor response to NO is the highest for the composition containing 5.0 wt.% Co$_2$O$_4$ and with a further increase in its concentration, the sensor response decreases monotonically (Fig. 7b). It can be seen from Fig. 7d the temperature maximum of the NO$_2$ sensitivity of the composition is at 140 °C and the temperature maximum of the CO sensitivity is at 230 °C.

The reduction of the sensitivities to CO and NO$_2$ can also be caused by the formation of large amounts of CoWO$_4$ (WO$_3$–Co$_2$O$_4$ annealing at 600 °C or higher) or In$_x$(WO$_{3-y}$)$_2$ (WO$_3$–In$_2$O$_3$ annealing at 800 °C or higher).

The high gas sensitivity of the test oxide compositions allows fabricating two-electrode NO$_2$ sensors with a low sensitivity threshold (less than 1.0 ppm), with a working temperature of $< 200$ °C and an acceptable response and recovery time [4, 26]. The Minsk Research Institute for Radio Engineering Materials has developed low-power NO$_2$ sensors with a detection threshold of $< 1$ ppm for gas and air mixtures [2, 3]. The power consumption of the WO$_3$ + 3 wt.% In$_2$O$_3$ sensors on Si substrates is less than 30 mW at a heating current of 51 mA and that of the WO$_3$ + 5 wt.% Co$_2$O$_4$ sensors on Al$_2$O$_3$ substrates is 85 mW at a heating current of 31 mA. An important distinctive feature of the WO$_3$–Co$_2$O$_4$ sensors is the noticeably smaller recovery time (10–20 s) in permanent heating mode for 2–11 ppm NO$_2$ detection in comparison with that of the WO$_3$–In$_2$O$_3$ sensors (30–300 s) and tungsten oxide systems known from the literature. For detection of reducing gases the WO$_3$–In$_2$O$_3$ sensor recovery time was within 20 s.

4. Conclusion

Experiments showed that stable microstructure can be achieved in nanoheterogeneous WO$_3$–In$_2$O$_3$ and WO$_3$–Co$_2$O$_4$ compositions. An increase in WO$_3$, In$_2$O$_3$, WO$_3$ and Co$_2$O$_4$ grain sizes during heat treatment of mixed compositions is slower than in simple oxides.

Joint annealing of tungsten and indium xerogel powders produced by the sol-gel method leads to the formation of In$_x$(WO$_{3-y}$)$_2$ at 800–850 °C. WCoO$_4$ forms in the WO$_3$–Co$_2$O$_4$ system at 600–650 °C. Indium tungstate is not as active as the sensitive element of gas sensors. Indium tungstate localization on the surface or in the superficial layer impedes electron interaction between tungsten oxide and indium oxide and reduces the gas adsorption capacity (CO and NO$_2$ sensitivity) of the WO$_3$–In$_2$O$_3$ oxide composition. The formation of the third CoWO$_4$ phase impedes electron interaction between tungsten oxide and cobalt oxide and reduces the gas adsorption capacity (CO and NO$_2$ sensitivity) of the WO$_3$–Co$_2$O$_4$ oxide composition.

All the experimental WO$_3$–In$_2$O$_3$ compositions containing 3.0–50.0 wt.% In$_2$O$_3$ or Co$_2$O$_4$ have greater CO and NO$_2$ sensitivity than the source oxides. The highest NO$_2$ response was at ~140 °C and the highest CO response, at ~230 °C. Cobalt oxide addition to tungsten oxide more effectively increases the CO response of tungsten oxide, and indium oxide addition more effectively increases the NO$_2$ response. The increase in the gas sensitivity and the reduction of the working temperature of the sensors based on oxide compositions in comparison with the sensors based on the source oxides can be accounted for by structural disordering during heat treatment of the compositions, reduction of grain sizes, an increase in the specific surface area and, for the WO$_3$–Co$_2$O$_4$ composition, the formation of $p$–$n$ junctions.
References

1. Barsan N., Koziej D., Weimar U. Metal oxide-based gas sensor research: How to? Sensors and Actuators B: Chemistry, 2007; 121: 18–35. https://doi.org/10.1016/j.snb.2006.09.047

2. Haiduk Y.S., Lomonosov V.A., Savitsky A.A. Physico-chemical properties of oxide composition WO$_3$–In$_2$O$_3$ prepared by the sol-gel method. Vestnik BGU. Ser. 2, Khimiya. Biol. Geogr., 2016; (3): 36–44 (In Russ.). http://elib.bsu.by/handle/123456789/171465

3. Haiduk Yu.S., Lomonosov V.A., Savitsky A.A. Physico-chemical properties of oxide composition WO$_3$–Co$_3$O$_4$ prepared by the sol-gel method. Izvestiya National’noi Akademii nauk Belarusii. Seriya khimicheskikh nauk, 2015; (2): 9–13. (In Russ.). https://vestichem.blnauka.by/journal/article/viewFile/148/148

4. Haiduk Y.S., Savitsky A.A., Reutskaya O.G., Taratyn A.A. Semiconducting gas sensors based on the composition of tungsten oxide and indium oxide. Nano- i mikrosistennaya tekhnika, 2018; (4): 232–242. https://doi.org/10.17587/nmst.20.232-242 (In Russ.)

5. Haiduk Yu.S., Khort A.A., Lapchuk N.M., Savitsky A.A. Study of WO$_3$–In$_2$O$_3$ nanocomposites for highly sensitive CO and NO gas sensors. J. Solid State Chemistry, 2019; 273: 25–31. https://doi.org/10.1016/j.jssc.2019.02.023

6. Iveronova V.I., Revkievich G.P. Theory of X-ray scattering. Moscow: Izdatelstvo Mokovskogo universiteta, 1978, 278 p. (pp. 136–139). (In Russ.)

7. Klyachko-Gurvich A.L. A simplified method for determining the surface by air adsorption. Izvestiya Akademii Nauk SSSR. Seriya khimicheskikh nauk, 1961; (10): 1884–1886. (In Russ.)

8. Krichmar S.I., Bezpal’chenko V.M., Mishukin A.A. A simple method for obtaining calibration gas mixtures. Zavodskaya laboratoriya. Diagnostika materialov, 2008; 74(1): 21–22. (In Russ.)

9. Kang S.-J.L. Sintering: densification, grain growth and microstructure. Butterworth-Heinemann, 2005, 279 p.

10. Kumar V.Bh., Mochanta D. Formation of nanoscale tungsten oxide structures and colouration characteristics. Bulletin of Material Science, 2011; 34(3): 435–442. https://doi.org/10.1007/s12034-011-0117-1

11. Noguera H., Cavalerio A., Rocha J., Trindade T., Pedrosa de Jesus J. Synthesis and characterization of tungsten trioxide powders prepared from tungstic acids. Materials Research Bulletin, 2004; 39: 683–693. https://doi.org/10.1016/j.materresbull.2003.11.004

12. Shi J., Hu G., Cong R., Bu H., Dai N. Controllable synthesis of WO$_3$–nH$_2$O microcrystals with various morphologies by a facile inorganic route and their photocatalytic activities. New J. Chemistry, 2013; 37(5): 1538–1544. https://doi.org/10.1039/c3nj41159a

13. Ştefan M., Bica E., Muresan L., Grecu R., Indrea E., Trîf M., Poppovici E. J. Synthesis and characterisation of tungsten trioxide powder prepared by sol-gel route. J. Optoelectronics and Advanced Materials, 2010; 2(1): 115–118.

14. Noguera H., Cavalerio A., Rocha J., Trindado T., Pedrosa de Jesus J. Synthesis and characterization of tungsten trioxide powders prepared from tungstic acids. Materials Research Bulletin, 2004; 39: 683–693. https://doi.org/10.1016/j.materresbull.2003.11.004

15. Shimizu Y., Matsuanga N., Hyodo T., Egashira M. Improvement of SO$_2$ sensing properties of WO$_3$ by noble metal loading. Sensors and Actuators B: Chemical, 2001; 77: 35–45. https://doi.org/10.1016/S0925-4005(01)00669-4

16. Sobotta H., Neumann H., Küch N., Riede V. Infrared lattice vibrations of In$_2$O$_3$. Crystal Research and Technology, 1990; 25(1): 61–64. https://doi.org/10.1002/crat.2170250112

17. Liu G. Synthesis, characterization of In$_2$O$_3$ nanocrystals and their photoluminescence property. Int. J. Electrochem. Sci., 2011; (6): 2162–2170. http://www.electrochemsci.org/papers/vol6/6062162.pdf

18. Salavati-Niasari M., Mir N., Davar F. Synthesis and characterization of Co$_3$O$_4$ nanorods by thermal decomposition of cobalt oxalate. J. Phys. Chem. Solids, 2009; 70(5): 847–852. https://doi.org/10.1016/j.jpcs.2009.07.023

19. Sharifi S.L., Shaker H.R., Mirzaei A., Hosseini M.H. Characterization of cobalt oxide Co$_3$O$_4$ nanoparticles prepared by various methods: effect of calcination temperatures on size, dimension and catalytic decomposition of hydrogen peroxide. Int. J. Nanosci. Nanotechnol., 2013; 9(1): 51–58. http://www.ijnjonline.net/article_3880_cfe6933b7ba98dbd646c4ae4ec3c88de.pdf

20. Wöllenstein J., Burgmair M., Plescher G., Sulima T., Hildenbrand J., Böttner H., Eisele I. Cobalt oxide based gas sensor on silicon substrate for operation at low temperatures. Sens. Actuators B: Chem., 2003; 93(1–3): 442–447. https://doi.org/10.1016/S0925-4005(03)00168-0

21. Devadatha D., Raveendran D. Structural and dielectric characterization of nickel-cobalt oxide nanocomposite. J. Material Sci. Eng., 2013; S11: 003. https://doi.org/10.4172/2169-0022.S11-003

22. Tang Ch.-W., Wang Ch.-B., Chien Sh.-H. Characterization of cobalt oxides studied by FT-IR, Raman, TPR and TG-MS. Thermochimica Acta, 2008; 473(1–2): 68–73. https://doi.org/10.1016/j.tca.2008.04.015

23. Khato V., Lloret E., Vilanova X., Brezmes J., Hubalek J., Malysov K., Corrieg X. Gas sensing properties of nanoparticle indium-doped WO$_3$ thick films. Sens. Actuators B: Chem., 2005; 111–112: 45–51. https://doi.org/10.1016/j.snb.2005.06.060

24. Pierson R.H., Fletcher A.N., Clair Gantz E.St. Catalog of infrared spectra for qualitative analysis of gases. Analytical Chemistry, 1956; 28(8): 1218–1239. https://doi.org/10.1021/ac60116a002

25. Choi J.-S., Sakai Go, Shimano K., Yamazoe N. Sensing properties of SnO$_2$–Co$_3$O$_4$ composites to CO and H$_2$. Sens. Actuators B: Chem., 2004; 98: 66–173. https://doi.org/10.1016/j.snb.2003.09.033

26. Haiduk Yu.S., Taratyn I.A. Nitrogen dioxide sensor. Application for the invention of the Republic of Belarus. МПК G01N 27/407; No. a 20140371; appl. 08.07.2014; publ. 28.02.2016. Aficyjni biuletyn Nacjonalnej centry dla intelektualnej ulaszczy Respubliki Bielarus, 2016; (1): 44. (In Russ.)