High Gas Sensitivity to Nitrogen Dioxide of Nanocomposite ZnO-SnO₂ Films Activated by a Surface Electric Field

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Abstract: Gas sensors based on the multi-sensor platform MSP 632, with thin nanocomposite films based on tin dioxide with a low content of zinc oxide (0.5–5 mol.%), were synthesized using a solid-phase low-temperature pyrolysis technique. The resulting gas-sensitive ZnO-SnO₂ films were comprehensively studied by atomic force microscopy, Kelvin probe force microscopy, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, scanning transmission electron microscopy, energy dispersive X-ray spectrometry, and X-ray photoelectron spectroscopy. The obtained films are up to 200 nm thick and consist of ZnO-SnO₂ nanocomposites, with ZnO and SnO₂ crystallite sizes of 4–30 nm. Measurements of ZnO-SnO₂ films containing 0.5 mol.% ZnO showed the existence of large values of surface potential, up to 1800 mV, leading to the formation of a strong surface electric field with a strength of up to 2 × 10⁵ V/cm. The presence of a strong surface electric field leads to the best gas-sensitive properties: the sensor’s responsivity is between two and nine times higher than that of sensors based on ZnO-SnO₂ films of other compositions. A study of characteristics sensitive to NO₂ (0.1–50 ppm) showed that gas sensors based on the ZnO-SnO₂ film demonstrated a high sensitivity to NO₂ with a concentration of 0.1 ppm at an operating temperature of 200 °C.

Keywords: ZnO; SnO₂; nanocomposite thin film; solid-phase pyrolysis; NO₂ gas sensor; surface electric field

1. Introduction

Gas sensors based on thin-film semiconductor oxide materials are widely used due to their high sensitivity to toxic gases [1–3]. Metal oxides, such as tin dioxide [4], zinc oxide [5], titanium dioxide [6], cobalt oxide [7], iron oxide [8], indium oxide and others [9] are used as gas-sensitive sensor materials for monitoring the concentration of pollutants (NOₓ, CO [10]) or process gases (H₂S, H₂, C₃H₈, C₂H₅OH, CH₃COCH₃, etc. [11]). Currently of great scientific interest are the gas-sensitive properties of metal oxide nanostructure (nanotubes, nanorods, nanofilms, nanowires, etc.) materials [12–14].

However, despite the good gas-sensitive properties of these materials, nanostructure synthesis technology is quite difficult to apply widely in the production of gas sensors. On the other hand, thin films of nanocomposite materials are used to determine low concentrations of gases (fractions and ppm units). Excellent results are shown by thin films based
on tin dioxide, with the addition of other oxides in small concentrations [9,15–18] or heterostructures [19,20]. In this case, the nature, the oxidation degree, the crystallites size, and the modifying agents’ concentration are the controlling factors of the density of surface defects and the surface area of oxide nanomaterials [21], as well as the concentration of surface oxygen [15,22]. In such materials, ZnO-ZnO, SnO\textsubscript{2}-SnO\textsubscript{2} homostructures, and ZnO-SnO\textsubscript{2} heterojunctions, as well as Schottky barriers, are formed [23]. The resulting heterojunctions lead to an improvement in the gas-sensitive properties of nanocomposite materials [24].

Nanocomposite materials based on SnO\textsubscript{2} are obtained by various methods [22], such as magnetron sputtering methods [25], chemical technologies [26–28], atomic layer deposition [29], the microwave hydrothermal method [30,31], magnetron sputtering [32], spray [33–35] or solid-phase [36,37] pyrolysis, etc. During the preparation of this article, the authors analyzed the available publications devoted to the study of the gas-sensitive and physicochemical properties of composite materials based on SnO\textsubscript{2} with a small concentration of ZnO. A literature review shows that changes in the physicochemical and gas-sensitive properties of the obtained materials are significantly influenced by the concentration of the introduced additives.

The most important measuring results for nanocomposite ZnO-SnO\textsubscript{2} films are shown in Table 1. It was found that better sensitive properties are recorded when the particle size of the gas-sensitive material is below 20–30 nm [23,29,38–42]. If crystallite size is higher, the sensitivity is usually lower [43–45]. On the other hand, the best gas-sensitive properties are shown for materials with the one component concentration equal to 10% or lower [15,29,46]. The first case can be explained by the existence of a depletion–enrichment zone comparable to the size of nanoparticles. In the second case, the situation is not fully explained. The authors of these publications, as a rule, explain a sensitivity increase by citing the presence of ZnO-SnO\textsubscript{2} heterojunctions, the nanocrystalline structure, and the synergistic effect.

Additionally, there is an insufficient number of studies concerned with the influence of small concentrations of some metal oxides. The mechanism of gas sensitivity in such cases should be investigated comprehensively using X-ray photoelectron spectroscopy (XPS) [47] and high-resolution transmission electron microscopy (TEM, HRTEM).

Thus, the aim of the present work was to study the effect of small concentrations of zinc oxide (0.5–5 mol.%) on the physicochemical, electrophysical, and gas-sensitive properties of ZnO-SnO\textsubscript{2} thin films. A new method of solid-phase pyrolysis was used to obtain gas-sensitive materials based on ZnO-SnO\textsubscript{2} thin films. The characteristics of a gas sensor with ZnO-SnO\textsubscript{2} films deposited on the MSP 632 multi-sensor platform (Heraeus Sensor Technology, Hanau, Germany) were also investigated.
| №  | Material (Composition, Structure) | Technology                  | Particle Size, nm | The Formula for Response Calculation (Gas Concentration) | Operating Temperature, °C | Response Value | Response/Recovery Time, s | Reference |
|----|---------------------------------|-----------------------------|-------------------|---------------------------------------------------------|---------------------------|----------------|--------------------------|-----------|
| 1  | SnO$_2$-ZnO (0.9:0.1)           | Electrospinning method      | 15                | $R_a/R_g$ (0.1–10 ppm)                                  | 300                       | 168.6          | $10^3/10^3$               | [23]      |
| 2  | Sn-ZnO                          | Spray pyrolysis             | 8–14              | $\Delta R/R_g$ (500 ppm) $$(R_a - R_g) \times 100\%$$ | 400                       | 200            | 50/80                    | [38]      |
| 3  | ZnO-SnO$_2$                     | Chemical synthesis          | 50–90             | $R_a/(10,000 \text{ ppm})$                             | 150                       | 90%            | 60/80                    | [39]      |
| 4  | SnO$_2$-ZnO                     | Pulse laser deposition      | 10–20             | $R_g/R_a$ (3.2 ppm)                                    | 180                       | 100            | 240/480                  | [40]      |
| 5  | SnO$_2$-ZnO (5:95)              | Chemical technologies       | 5–10              | $R_g/R_a$ (0.5–1.0 ppm)                                | 150                       | 48             | 100/101                  | [41]      |
| 6  | 7% Sb-SnO$_2$/ZnO               | Microwave hydrothermal      | 10                | $R_g - R_a/R_a (1000 \text{ ppb})$                      | 300                       | 9.5            | 16/-                     | [29]      |
| 7  | ZnO-SnO$_2$ (1:1)               | Wet chemical method         | 11–17             | $R_a$ (500 ppm)                                        | 20                        | 13.4           | 420/480                  | [42]      |
| 8  | ZnO-SnO$_2$                     | Magnetron sputtering        | 10                | $R_g/R_a$ (5 ppm)                                      | 100                       | 26.4           | 20/45                    | [30]      |
| 9  | SnO$_2$-ZnO (1:99)              | Solid phase pyrolysis       | 13–14             | $R_g/R_a (5 \text{ ppm})$                              | 200                       | 4.5            | 300/400                  | [15]      |
| 10 | SnO$_2$-ZnO (1:1)               | Combined deposition, ethanol| 20–40             | $R_g/R_a (200 \text{ ppm})$                            | 300                       | 4.69           | 72/-                     | [43]      |
| 11 | Au-doped SnO$_2$-ZnO (1:0.5; 1:1:0.5:1) | Electrospinning method         | 5–10              | $R_g/R_a (100 \text{ ppm})$                           | 300                       | 90             | 130/-                    | [44]      |
| 12 | SnO$_2$/ZnO= (3:1; 1:1; 1:3)    | Chemical coating            | 2800              | $R_a$ (24 ppm)                                         | 275                       | 53%            | 150/-                    | [45]      |
| 13 | SnO$_2$/ZnO core/shell          | The thermal evaporation SnO$_2$ NWs and the spray-coating of ZnO | 150                | $R_a/R_g (100 \text{ ppm})$                            | 450                       | 15.9           | 215/-                    | [46]      |
2. Materials and Methods

2.1. Chemicals for Synthesis of ZnO-SnO$_2$ Thin Films

Zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O), stannic chloride pentahydrate (SnCl$_4$·5H$_2$O), an abietic acid (C$_{19}$H$_{29}$COOH), and 1,4-dioxane as a solvent were used as precursors for the synthesis of SnO$_2$-ZnO thin films. The reagents were purchased from “ECROS”, Saint Petersburg, Russia. All chemicals used were of analytical grade or of the highest purity available.

2.2. Synthesis of ZnO-SnO$_2$ Thin Films

The synthesis was carried out in two stages. In the first stage, synthesis was carried out in a melt of abietic acid. The necessary amounts of zinc and tin salts were added to the melt, after which the melt was cooled and crushed. In the second stage, the necessary amounts of organic salts were dissolved in 1,4-dioxane so that the molar ratios of tin and zinc were Zn:Sn = 0:100 (sample 0ZnO), 0.5:99.5 (sample 0.5ZnO), 1:99 (sample 1ZnO), and 5:95 (sample 5ZnO) mol.%, respectively. The resulting solution was applied three times onto polycor substrates and a multi-sensor platform. The precursor solution was deposited on the multi-sensor platform using a mechanical pipette. Each layer was dried in air and in a drying cabinet at a temperature of 100 °C. Heat treatment was carried out at 500 °C for two hours (Figure 1). The synthesis technique is described in more detail in previous studies [15,36].

![Figure 1. Gas sensor formation scheme.](image)

To make gas sensors based on ZnO-SnO$_2$ thin films, precursor was applied over a Pt counter-pin structure multi-sensor platform, MSP 632, and dried at 100 °C. Annealing at a temperature of 500 °C for two hours in air- and temperature-controlled conditions was carried out directly, using a heater and a temperature sensor MSP 632.

2.3. Characterization

The resulting gas-sensitive ZnO-SnO$_2$ films were comprehensively studied by atomic force microscopy (AFM), Kelvin probe force microscopy (KPFM), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray spectrometry (EDS), and XPS.

Electrophysical (volt-ampere characteristics; temperature dependences of electrical conductivity) and gas sensitivity measurements were estimated using an automated installation for determining the parameters of gas sensors [16]. In addition, the activation energy of conductivity ($E_a$) was estimated using the Arrhenius equation (Equation (1)) [48]:

$$G = G_0 \exp\left(-\frac{E_a}{k \cdot T}\right)$$  

(1)

where $k$ is the Boltzmann constant, and $G_0$ the coefficient taking into account the bulk material conductivity.
Next, the temperature-stimulated conduction measurements [16,49,50] method was used to evaluate the “effective” value of the energy barrier between the grains of a nanocrystalline material.

The gas response of sensors was measured with 5–50 ppm nitrogen dioxide (NO\textsubscript{2}) balanced with synthetic air at operating temperatures of 200–250 °C. In the experiments, cylinders with test synthetic air and a mixture of synthetic air and NO\textsubscript{2} (Monitoring LLC, Saint Petersburg, Russia) were used. The gases were injected at a flow rate of 0.3 dm\textsuperscript{3}/min using a gas mixture generator (Microgaz F, Moscow, Russia) [16]. The response of sensor elements based on ZnO-SnO\textsubscript{2} films was calculated using the following formula (Equation (2)):

\[ S = \frac{R_g}{R_0} \]  

where \( R_0 \) and \( R_g \) are the sensors resistance in synthetic air and in a mixture of synthetic air and NO\textsubscript{2}, respectively. Subsequently, the gas sensor, which showed the best gas-sensitive properties, was tested for exposure to NO\textsubscript{2} with a concentration of 0.1 to 1 ppm.

3. Results

The XRD spectra of pure and ZnO-SnO\textsubscript{2} thin films are shown in Figure 2. All of the diffraction peaks are well indexed to the tetragonal structure of SnO\textsubscript{2} typical for cassiterite (JCPDS: 41–1445), regardless of the amount of modifying agents. Moreover, no additional diffraction peaks of ZnO were observed, which may be due both to the small amount of it in the system and to the small size of the crystallites. No other impurity phases are observed in the XRD pattern. The XRD patterns for pure and ZnO-SnO\textsubscript{2} materials show that the films have a polycrystalline microstructure.

![Figure 2. XRD patterns of synthesized film materials 0ZnO, 0.5ZnO, 1ZnO, 5ZnO.](image)

The degree of material crystallinity was determined by XRD according to the method described in the paper [49,50]. It was found that an increase in the content of the introduced additives leads to an increase in the degree of materials’ crystallinity (57.2, 66.0, 67.0 and 67.4% for 0ZnO, 0.5ZnO, 1ZnO, and 5ZnO materials, respectively).

Cross-sectional and top-view SEM images of 0ZnO (a), 0.5ZnO (c), 1ZnO (e), and 5ZnO (g) thin films are presented in Figure 3. It was found that the films are cracked, homogenous, and uniform, with a continuous distribution of grains. The type of coating obtained is an area with adjacent grains, and the thickness of the three-layer films is 160–240 nm; statistical processing of the results of the SEM analysis is shown in the histograms below. However, in SEM images, as a rule, it is difficult to determine the dimensions of agglomeration of observed nanocrystallites. Therefore, the sizes of nanocrystallites measured may, in this case, be partly overestimated.
Figure 3. SEM microphotographs and particle size distribution of materials 0ZnO (a, b), 0.5ZnO (c, d), 1ZnO (e, f), 5ZnO (g, h).

The 0.5ZnO thin film was investigated using the TEM method. The synthesized film material consists of many nanocrystallites with particles ranging in size from 4.5–11.5 nm (Figure 4a, e–h). Where the film is thin, SnO$_2$ nanocrystallites are visible in large quantities; between these, separate ZnO nanocrystallites are located. Studies conducted using the EDX method showed that the proportion of zinc in the material, by weight, does not exceed 1% of the mass (Figure 4a–f). The mapping of the elements Zn, O, and Sn in one film’s area is shown in Figure 4b–d. It can be seen that the elements Sn, Zn, and O are evenly distributed throughout the material, without local agglomeration. The content of the elements Sn, Zn, and O is consistent with the relative amount of the elements Sn, Zn, and O in the initial solution. The TEM images show that ZnO crystallites make contact with SnO$_2$ crystallites. To prove this, high resolution photos were taken; areas 1 and 2 are highlighted in Figure 4e, f. Area 2 comprises SnO$_2$ nanocrystallites, which is confirmed by the EDX analysis. Area 1 consists of nanocrystallites of SnO$_2$ and ZnO, which are uniformly distributed throughout the area. Moreover, since there are significantly more SnO$_2$ nanocrystallites, ZnO nanocrystallites make contact with SnO$_2$ nanocrystallites.
Figure 4. TEM characterization results of ZnO-SnO$_2$ materials: (a,e,g) TEM images with different magnifications; (b–d,f) EDS elemental mapping images; (h) HRTEM image and insert to the right at the top—SAED images.

To observe the planes of the crystal structure, images with high magnification were obtained for some sections of the film. One particle with a lattice fringe of 0.264 nm corresponds to the plane (002) of the ZnO hexagonal structure: it is shown in Figure 4h. Additionally, on this site there are areas in which it is possible to distinguish a lattice fringe of 0.334 nm, which corresponds to the plane (110) of the SnO$_2$ rutile structure. Thus, it can be concluded that nanoparticles consist of ZnO and SnO$_2$ crystals. Selected area electron diffraction (SAED) circles correspond to the (110), (101), (200), (211), and (112) crystal planes of SnO$_2$.

AFM and KPFM images of 0ZnO, 0.5ZnO, 1ZnO, and 5ZnO films are presented in Figure 5.
AFM studies showed that the films have a granular structure, with a height difference of $S_{q}$ of 10–35 nm (Figures 5 and 6). In general, with a decrease in the content of ZnO in the film, the roughness decreases from 34 to 11 nm. However, the 0.5ZnO film surface has a higher roughness than the surface of the 0ZnO and 1ZnO films—see Figure 6 (curve 2).
KPFM studies have shown that a lowest average value of the surface potential (Figure 6 (curve 1)) of about 4 mV is characteristic of SnO₂ film (Figure 5h). 1ZnO and 5ZnO films have similar average values of surface potential, equal to 15–30 mV (Figure 5b,d).

However, for 0.5ZnO film, a peak value of the surface potential is observed, the average value of which reaches 845 mV, and at some points on the surface the maximum value is 1824 mV; the difference between the maximum and minimum values of $V_b$ could be 1642 mV (Figure 5f and Figure S2).

The samples’ surface composition (Table 2) was also calculated from high-resolution XPS spectra using relative sensitivity factors from the Scofield Library. The high-resolution spectra of Zn2p, Sn3d and the valence band are presented in Figure 7. It can be seen from Figure 7b that the photoelectronic line Sn 3d for the sample 0ZnO (red curve) corresponds to SnO₂.

Figure 6. The dependence of the average values of the surface potential $V_b$ (curve 1) and the roughness parameters $S_q$ (curve 2) on the content of ZnO in the film.

Figure 7. High-resolution XPS spectra of Zn2p (a), Sn3d (b), and the maximum valence band (c) in ZnO-SnO₂ films.
Table 2. The surface composition of ZnO-SnO\textsubscript{2} films.

| Materials | C 1s  | O 1s  | Sn3d5 | Zn2p3 |
|-----------|-------|-------|-------|-------|
| 0ZnO      | 34.15 | 44.85 | 21.00 | 0     |
| 0.5ZnO    | 27.36 | 45.64 | 26.53 | 0.47  |
| 1ZnO      | 33.35 | 40.73 | 24.47 | 1.45  |
| 5ZnO      | 33.39 | 41.05 | 22.55 | 3.01  |

Minor changes in the maximum positions of the Sn\textsubscript{3d} photoelectronic lines for samples containing ZnO suggest the formation of a special interface at the nanocomposite oxides’ surface, which leads to a decrease in the work function. Analysis of the XPS spectra valence band edge makes it possible to evaluate and determine in more detail both the change in the maximum of the valence band (VBM), and the band gap and the Fermi level position at the phase boundary \([51–54]\). The formation of this interface in the ZnO-SnO\textsubscript{2} system can be confirmed by analysing the high-resolution Zn2p spectra (Figure 7a). At zinc concentrations of 0.5% and 1%, the shapes of the Zn2p photoelectronic lines are very different from the case of bulk ZnO (Figure S1). In the region of binding energies of 1033.5 eV, plasmon losses, which are inherent in metallic zinc, are visible; however, the position and shape of the Zn2p\textsubscript{3} peak exclude the presence of metallic zinc. The ratio of peak intensities of Zn2p\textsubscript{3} photoelectronic lines’ plasmon losses for the obtained samples, as well as a comparison for pure metallic and ZnO crystalline, is shown in Figure 8a. Thus, the presence of a gap between the Fermi level and the edge of the valence band on the one hand, and the features of Zn2p photoelectronic lines on the other, completely exclude the presence of metallic zinc in the synthesized nanocomposites. The peculiarity of the Zn2p photoelectronic lines here can be linked to the formation of an interface enriched with charge carriers at the phase boundary, which leads to inelastic scattering of photoelectrons on them, and the appearance of an intense peak of plasmon losses in the region of 1033.5 eV.

\[
\Delta E = (E_{\text{Sn3d}}^{\text{SnO}_2} - E_{\text{VBM}}^{\text{SnO}_2}) - (E_{\text{Zn2p}}^{\text{ZnO}} - E_{\text{VBM}}^{\text{ZnO}}) + \Delta E_{\text{CL}} \tag{3}
\]

Figure 8. The ratio of peak intensities of zinc photoelectronic lines Zn2p\textsubscript{3} plasmon losses (a), and the distribution of changes in the valence band level at the interface (b), in ZnO-SnO\textsubscript{2} films.

The values of the valence band edge from high-resolution XPS spectra close to the Fermi level are determined using a linear approximation of the background line and the useful signal. The intersection of the obtained lines determines the value of the valence band edge, shown in Figure 7c.

From the analysis of the valence band edge, the values of the change in the valence band maximum for each sample are obtained according to the well-known formula (Equation (3))\([55]\):
where \( \Delta E_{\text{CL}} = E_{\text{ZnO}} - E_{\text{SnO}_2} \)

\( E_{\text{SnO}_2} \) – binding energy of 3d5 electrons in SnO2;

\( E_{\text{VBM}} \) – valence band edge value in SnO2

\( E_{\text{ZnO}} \) – binding energy of 2p3 electrons in ZnO

\( E_{\text{VBM}} \) – valence band edge value in ZnO

Valence band edge values and the binding energy of core levels for ZnO2p3/2 and SnO2 3d5/2 are presented in Table 3.

Table 3. Valence band edge values and binding energy of core levels.

| Materials | VBM, (eV) | Zn2p3, (eV) | Sn3d5, (eV) | \( \Delta E \), (eV) | \( \Delta E_{\text{CL}} \), (eV) |
|-----------|-----------|-------------|-------------|-----------------|-----------------|
| 0ZnO      | 3.49      | -           | 486.65      | 0               | -               |
| 0.5ZnO    | 2.95      | 1021.54     | 486.55      | -0.55           | 534.99          |
| 1ZnO      | 2.77      | 1015.50     | 486.45      | -0.73           | 535.05          |
| 5ZnO      | 2.74      | 1021.48     | 486.43      | -0.76           | 535.05          |

The distribution of the change in the valence band level at the interface for each sample is presented below in Figure 8b.

The dependence of reverse resistance on reverse temperature for all samples has a characteristic form for metal oxide semiconductors (Figure 9).

![Figure 9](image)

Figure 9. (a) Temperature dependence of gas sensors’ reverse resistance and (b) dependences of the activation energy of the conductivity \( E_a \) (curve 1) and the potential barrier (curve 2) of ZnO-SnO2 films on the content of ZnO.

The activation energy of conductivity (\( E_a \)), calculated by the Arrhenius equation (Figure 9b, curve 1), shows a sharp (by 2–2.5 times) decrease in the \( E_a \) and the potential barrier \( \Phi_B \) for 0.5ZnO films. The \( E_a \) decreases from 0.51 eV to 0.2 eV, and the \( \Phi_B \) from 1.1 eV to 0.54 eV.

The results of the gas sensitivity study of ZnO-SnO2 films at 200 °C and 250 °C are shown in Figure 10. The typical response of gas sensors when exposed to NO2 with concentrations of 5, 10, and 50 ppm is shown in Figure 10c.
when exposed to NO (Table 4) that for this sensor, when exposed to 5 ppm NO
Table 4. Response time of ZnO-SnO films to NO exposure.

| Materials of Gas Sensor | t_{resp} (s), When Exposed to NO2 Gas by Working Temperature |
|-------------------------|------------------------------------------------------------|
|                         | 200 °C | 250 °C | 200 °C | 250 °C | 200 °C | 250 °C |
| 0ZnO                    | 67     | 60     | 58     | 87     | 70     | 86     |
| 0.5ZnO                  | 144    | 144    | 240    | 80     | 86     | 244    |
| 1ZnO                    | 151    | 126    | 108    | 85     | 90     | 162    |
| 5ZnO                    | 394    | 388    | 87     | 126    | 170    | 552    |

It is shown (Figure 10c) that, when exposed to NO2 concentrations of 5, 10, and 50 ppm, a gas sensor based on a 0.5ZnO-99.5SnO2 film is approximately 1.5–9 times more sensitive to NO2 compared to gas sensors based on ZnO-SnO2 films with other compositions. For exposure to NO2 with a concentration of 50 ppm and an exposure temperature of 200 °C, the sensor’s response S is equal to 146. The evaluation of the response time t_{resp} shows (Table 4) that for this sensor, when exposed to 5 ppm NO2, t_{resp} is 144 s and 80 s at operating temperatures of 200 and 250 °C, respectively.

A gas sensor based on a 0.5ZnO-99.5SnO2 film has a higher sensitivity; it was therefore investigated for exposure to NO2 with concentrations from 0.1 to 1 ppm. The sensor response of this gas sensor is shown in Figure 10d. The response value, when exposed to NO2 with a concentration of 1.0 ppm, is 3.9, and, when exposed to NO2 with a concentration of 0.1 ppm, is 1.1.
Thus, gas sensors based on a ZnO-SnO$_2$ film, synthesized using a solid-phase pyrolysis technique with a ratio of 0.5ZnO, have a range of measured concentrations of NO$_2$ equal to 0.1–50 ppm, with a response time of 80–144 s, and an operating temperature of 200 °C.

To test the selectivity of the sensor based on a 0.5ZnO-99.5SnO$_2$ film to other gases, studies were conducted with acetone, ethanol, ammonia, and water molecules, with a concentration of 200 ppm at an operating temperature of 200 °C. The sensor response was 1.1 for acetone, 1.25 for ethanol, 1.76 for ammonia, and 1.1 for water. It can be seen that, in comparison with the response value for nitrogen dioxide with a concentration of 50 ppm (146), these values do not exceed 1.2%.

4. Discussion

It is known that the valence band edge for pure SnO$_2$ is 3.5 eV [54,55]. This is also confirmed by our measurements for the material ZnO:SnO$_2$ = 0:100 (Figure 8, Table 3). For 0.5ZnO film materials or for other ZnO-SnO$_2$ materials, the energy level of the valence band edge decreases to 2.95 eV. Further decrease in the valence band edge value is slower—up to 2.77 and 2.74 eV for 1ZnO and 5ZnO materials, respectively. Thus, the energy of the valence band edge in ZnO-SnO$_2$ films decreases with an increase in the ZnO concentration.

Potential barriers are formed at the interface of SnO$_2$-SnO$_2$ homostructures and the ZnO-SnO$_2$ heterojunction. Measured by temperature-stimulated conduction measurements, the value of the potential barrier $\Phi_B$ for the SnO$_2$ film was 0.80 eV (Figure 9b). This potential barrier is formed due to the adsorption of oxygen molecules on the surface of SnO$_2$ nanocrystals, and their subsequent ionization with the formation of O$_2^-$ ions [33,56–60].

The contact of two SnO$_2$ nanocrystallites is shown in Figure 11a. It is well known that, because of this contact, a depletion region is formed in SnO$_2$ nanocrystallites [59–61].

![Figure 11. Flat band scheme of crystallite contacts for SnO$_2$-SnO$_2$ (a) and SnO$_2$-ZnO-SnO$_2$ (b).](image)

The study of the gas sensor based on the film material 0.5ZnO-99.5SnO$_2$ showed that the value of $\Phi_B$ sharply decreases to 0.47 eV (Figure 9b). With a further increase in the ZnO concentration (1ZnO and 5ZnO), $\Phi_B$ becomes significantly higher—1.1 and 1.0 eV, respectively. The mechanism of a sharp decrease in $\Phi_B$ in the gas sensor based on the 0.5ZnO-99.5SnO$_2$ film is shown in Figure 11b. It is known that the work function of ZnO (5.2–5.3 eV) [62,63] is higher than that of SnO$_2$ (4.8–4.9 eV) [61,64]. In addition, the Fermi level of SnO$_2$ is closer to the vacuum level, in relation to the Fermi level of ZnO. When ZnO and SnO$_2$ crystallites are in contact with each other, electrons will transfer from tin dioxide to zinc oxide (Figure 11). The value of the potential barrier at the SnO$_2$-ZnO-SnO$_2$ heterojunction will decrease in this case (Figure 9b). According to TEM studies (Figure 4c), individual ZnO crystallites come into contact with SnO$_2$ crystallites, so ZnO becomes highly enriched with charge carriers. This fact is also confirmed by XPS studies: plasmon losses are observed on Zn2p3 zinc photoelectronic lines (Figure 7a). The same effect leads to the appearance of regions with large local surface potential $V_b$. This is confirmed by our KPFM measurements (Figures 5c and 6b). On the surface of the 0.5ZnO film, the average value of the surface potential is 845 mV, and in some places reaches values of 1824 mV (Figure 5c). For film materials with a higher content of zinc oxides (1ZnO and 5ZnO), the concentration of ZnO crystallites becomes higher, which leads to a decrease in the average value of the surface potential to 15–30 mV. The existence of high values of the $V_b$ in 0.5ZnO-99.5SnO$_2$
films leads to the formation of a strong surface electric field. The electric field contributes to the reduction of the $\Phi_B$ between nanocrystallites. In this regard, $E_a$ also decreases in the 0.5ZnO-99.5SnO$_2$ film. In addition, it can be noted that the surface potential affects the morphology of the film’s surface (Figure 6).

As can be seen from Figure 10, gas sensors based on the film material 0.5ZnO-99.5SnO$_2$ show a peak response to NO$_2$ exposure, compared to other samples.

The reason for this sharp increase in response may, on the one hand, be a decrease in the potential barrier $\Phi_B$ [65]. On the other hand, however, the reason for the sharp increase in the response of gas sensors based on film material 0.5ZnO-99.5SnO$_2$ is, in our opinion, the high surface potential formed due to the contact of ZnO and SnO$_2$ crystallites. The analysis of TEM images (Figure 4) shows that the distance between the crystallites is no more than 0.1 nm. At such values, distances, and potentials, there is a surface electric field with a strength of $2 \times 10^7$ V/cm. It is known that an electric field with a strength of up to $3 \times 10^7$ V/cm can exist in oxide materials if their thickness is up to 4 nm [66,67]. The presence of a surface electric field is supported by the response decreasing from 200 °C to 250 °C (Figure 10a,b), since it is well known that an increase in temperature leads to a decrease in the influence of the electric field. The effect of the electric field influence on the atoms’ diffusion over the surface, and in the volume of solids, has been well studied [68,69].

As shown in [70], the surface electric field of this magnitude, created by charged adsorption centers, significantly affects the mechanism of the interaction of polar gas molecules with the gas-sensitive material’s surface.

It is known that the NO$_2$ molecule has a dipole moment 0.29–0.33 D [71–73]. In this case, the interaction energy of the polar adsorbate molecule with the charged adsorption center ($Q_{aa}$) can be estimated using the following formula (Equation (4)) [74]:

$$Q_{aa} = -N_a \times \frac{e \times V \times \mu}{z_0^2}$$  \hspace{1cm} (4)

where $e$ is the electron charge; $V$ is the valence of the adsorbent ion; $\mu$ is the dipole moment of the adsorbate molecule; $z_0$ is the equilibrium distance between the adsorbate molecule and the charged adsorption centre; and $N_a$ is the Avogadro constant.

Calculations show that if $z_0$ is equal to 0.2 nm, the $Q_{aa}$ for the NO$_2$ molecule is 31–35 kJ/mol.

At the same time, we have shown that a sufficiently strong surface electric field ($E_s$), of magnitude (1–2) $\times 10^7$ V/cm, is created at the crystallite boundary of tin and zinc oxides. The processes of adsorption and dissociation of NO$_2$ molecules are activated by a strong surface electric field. NO$_2$ molecules receive an additional field-induced dipole moment ($\mu_i$), the magnitude of which depends on the polarizability of the $\alpha$ molecule. It is known that the NO$_2$ molecule has a high polarizability ($\alpha$), equal to $1.8 \times 10^{-24}$ cm$^3$ [67].

When the amount of polarizability increases, the surface electric field effect on the molecule also increases. The energy of the adsorbate–adsorbent interaction ($Q_{aa}$) increases by the value of the induction component ($Q_i$) associated with the occurrence of the induced dipole moment. The value of $\mu_i$ can be estimated using the formula (Equation (5)) [75].

$$\mu_i = \alpha \times E_s.$$  \hspace{1cm} (5)

Calculation of the total dipole moment ($\mu' = \mu + \mu_i$) shows that $\mu'$ can be equal to 0.47–0.51 D.

In addition, the adsorbate molecule will be affected by orientation polarization, in accordance with the direction of the electric field, which depends on the magnitude of the molecule’s dipole moments [75]. The energy of the orientation influence ($Q_{or}$) of the field is equal to (Equation (6)):

$$Q_{or} = 0.5 \times \mu' \times E_s.$$  \hspace{1cm} (6)
The total energy of the adsorbate adsorbent ($Q_{aa'}$) interaction between the adsorption centre and the NO$_2$ molecule is calculated by the formula (Equation (7)):

$$Q_{aa'} = (Q_{aa} + Q_i + Q_{ir}). \quad (7)$$

The calculation results show that, for an NO$_2$ molecule with high polarizability, the $Q_{aa'}$ can increase to 57–60 kJ/mol, that is, almost twofold. Such energy may already be enough to initiate the process of dissociation of gas molecules, since the activation energy of the molecule’s dissociation is half of the molecule dissociation energy [76,77]. The latter circumstance means that dissociation of the NO$_2$ molecule is possible. These arguments do not contradict previously published works [78,79]. Thus, adsorption of NO$_2$ molecules, with their subsequent dissociation, can occur (Equation (8)):

$$NO_2_{gas} + e \rightarrow NO_2^-_{ads} \rightarrow O^-_{ads} + NO_{gas}. \quad (8)$$

A strong surface electric field is a powerful activating factor, as is ultraviolet radiation. In the presence of these factors, forced ionization of adsorbed molecules can occur (Equation (9)) [80]:

$$NO_2_{gas} + O^-_{ads} + 2e \rightarrow NO_2^- + 2O^- \quad (9)$$

As can be seen, these reactions can lead to a stronger response to NO$_2$ molecules.

A comparative analysis of the gas sensitivity to NO$_2$ of nanocomposite ZnO-SnO$_2$ structures presented in Table 1 and in this paper shows that the size of nanostructures (nanocrystallites) is essential for high gas sensitivity to low concentrations of NO$_2$ in the air. In all works, the nanostructures of the gas-sensitive material are formed by different technologies, and have sizes from 5 to 17 nm [15,29,30,40–42]. In addition, when the operating temperature of the gas sensor decreases, the response and recovery times increases [30,81]. The optimal value of the operating temperatures for sensors with low concentrations of nitrogen dioxide is, in our opinion, in the range of 150–250 °C, in order to achieve the optimal value of response times of 80–140 s. When analyzing these articles, the gas-sensitive properties of sensors based on ZnO-SnO$_2$ films are similar.

The characteristics of NO$_2$ sensors based on other materials are presented in Table 5.
Table 5. Gas-sensitive characteristics of NO\textsubscript{2} sensors based on other materials.

| Material | Method | Gas Concentration, ppm | Operating Temperature, °C | Sensitivity | Response/Recovery Time | Reference |
|----------|--------|------------------------|---------------------------|-------------|------------------------|-----------|
| Single wall carbon nanotubes—Mn-porphyrin WS\textsubscript{2} | Chemical technologies and Langmuir–Blodgett technique | 2.5 | 100 | 38% | 9 min/– | [82] |
| Zn\textsubscript{0.5}Fe\textsubscript{0.5}O\textsubscript{4} | Drawing on paper Method of sol–gel auto combustion | 0.8 | Room temperature | 42% | 5.2 min/19 min | [83] |
| MoS\textsubscript{2}/ZnO | Wet chemical method | 5 | Room temperature | 0.54% | 100 s/100 s | [84] |
| Thioglycolate- capped CdS quantum dots | Electrochemical method | 0.011 | Room temperature | 3050% | 211 s/1000 s | [85] |
| WO\textsubscript{3} nanofiber | Electrospinning Solvothermal process | 3 | 90 | 0.54% | 100 s/100 s | [86] |
| Au/pr-In\textsubscript{2}O\textsubscript{3} | Ultrasonic-Spray Pyrolysis | 5 | 100 | 125 s/231 s | 30 min/doesn’t recover | [87] |
| Al-doped NiO | RF-sputtered | 0.2 | 200 | 2.7 | 20 min/40 min | [88] |
| voltage activation rGO porous polythiophene (PTh) films | Chemically reducing GO water dispersion Plasma jets polymerization technique One-step hydrothermal technique Solid-phase low-temperature pyrolysis | 0.05 | Room temperature | 5 | 2.1 min/28 min | [89] |
| polypyrrole/Fe\textsubscript{2}O\textsubscript{3} | | 0.25 | Room temperature | 21% | 1250 s/2500 s | [90] |
| 0.5ZnO-99.5SnO\textsubscript{2} | | 0.5 | 200 | 2.5 | 80 s/90 s | This work |
Sensors operating at room temperature have long response/recovery times [82–84,89–93]. The advantage of such sensors is that there is no need for heating to operating temperature, and they can be used indoors. Since gas sensors are used for NO$_2$ monitoring outside, in a wide temperature range, sensors operating at 200 °C are recommended for analysis unification. Sensors with response/recovery times in the range of 30–180 s have a more complex technology for forming a gas-sensitive layer [86–88,93]. Some gas-sensitive materials are unstable over time, in particular metal sulfides [83,85,86].

Thus, it can be seen that many materials used in gas sensors of the resistive type have similar gas-sensitive characteristics. The choice of gas-sensitive materials is determined by the following requirement: “simple technology—high-quality, reproducible and fast response to a given concentration.” The solid-phase pyrolysis method proposed in this work and in our other works [15,36] satisfies this requirement. Using the described method, it is possible to obtain composite nanoscale materials of various compositions with high values of gas-sensitive characteristics. In this case, by selecting the composition of mixed ZnO-SnO$_2$ oxides, this technology allows for the formation of heterostructures with a strong surface electric field, thereby “fine-tuning” the gas-sensitive properties.

5. Conclusions

Nitrogen dioxide gas sensors were formed on the MSP 632 multi-sensor platform. The gas-sensitive element of the sensor is a ZnO-SnO$_2$ film with thickness 60–200 nm. The film materials were formed using a new low-temperature pyrolysis technique; the zinc oxide content was from 0.5 to 5 mol.%. Comprehensive studies of the materials’ physicochemical, structural, electrophysical, and other properties were carried out using modern research methods. It was shown that all ZnO-SnO$_2$ films are composite with crystallite sizes of 4–30 nm and have a cassiterite structure. Zinc oxide nanocrystallites are evenly distributed in the structure of ZnO-SnO$_2$ films.

This leads to the creation, in the 0.5ZnO-99.5SnO$_2$ film, of a surface potential of up to 1800 mV. This is because of the existence of a strong surface electric field with a strength of (1–2) $\times$ 10$^7$ V/cm.

When NO$_2$ molecules approach the surface of the ZnO-SnO$_2$ film, a strong surface electric field promotes the induction of a dipole moment in the molecule. As a result, this leads to an increase in the energy of the adsorbate–adsorbent interaction between the adsorption center and the NO$_2$ molecule, and an activation of the molecules’ dissociation process. The response of the gas sensor based on 0.5ZnO film is 1.5–9 times higher compared to sensors based on other ZnO-SnO$_2$ films.

Thus, it was shown that the gas sensor based on film material 0.5ZnO-99.5SnO$_2$ is very promising for the detection of NO$_2$ gas at concentrations of 0.1–50 ppm; it has a response time equal to 80–144 s and an operating temperature of 200 °C.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/nano12122025/s1, Figure S1: The XPS spectra of pure zinc and its oxide, Figure S2: Distribution of the surface potential on the film surface 0.5ZnO.

Author Contributions: V.V.P.: conceptualization, investigation, methodology, writing—review and editing, project administration, funding acquisition. A.P.I.: SEM, electrophysical and gas sensitive properties. M.G.V.: material synthesis, analysis of the XRD data, writing the Introduction. V.Y.S.: material synthesis. I.A.G.: AFM and KPFM analysis and gas sensitive properties. I.V.P.: TEM and STEM analysis. V.A.V.: sample preparation for TEM, TEM analysis. S.A.K.: XPS analysis. E.M.B.: analysis of the data, investigation, methodology, writing the manuscript, review, and editing. The corresponding author, V.V.P., ensured that the descriptions are accurate and agreed by all authors. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the RFBR, project 20-07-00653.

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.
Data Availability Statement: Not applicable.

Acknowledgments: Electrophysics and gas sensitivity measurements were conducted using equipment from the Centre for Collective Use, Microsystems and Integral Sensors, Southern Federal University (SFedU). The XPS analyses were carried out at the Nanophysics and Nanotechnology Research Center (CCU SOGU). We also thank the staff of the Laboratory for the Technology of Functional Nanomaterials at the Institute of Nanotechnologies, Electronics, and Equipment Engineering and SEC Nanotechnology (SFedU), Ageev O.A., Ilyin O.I. and Ilyina M.V., for providing the opportunity to conduct SEM, AFM, and KFPM research. The authors are grateful to the Shared Use Center’s High-Resolution Transmission Electron Microscopy (SFedU), which was used to conduct the TEM studies.

Conflicts of Interest: The authors declare no conflict of interest.

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