High Sensitivity Low-Temperature Hydrogen Sensors Based on \( \text{SnO}_2/\kappa(\varepsilon)-\text{Ga}_2\text{O}_3:\text{Sn} \) Heterostructure

Aleksei Almaev\(^1,2,\ast\), Nikita Yakovlev\(^1\), Viktor Kopyev\(^1\), Vladimir Nikolaev\(^3,4\), Pavel Butenko\(^3\), Jinxiang Deng\(^5\), Aleksei Pechnikov\(^3\), Petr Korusenko\(^6,7\), Aleksandra Koroleva\(^8\) and Evgeniy Zhizhin\(^8\)

1. Introduction

Sustainable development in terms of preserving the environment requires employment of a great number of sensors: biosensors, image sensors, motion sensors, and chemical sensors for indoor and outdoor as well as for industry-relevant gas surveillance and control. Wide bandgap metal oxide semiconductors tin dioxide (SnO\(_2\)) and gallium oxide (Ga\(_2\)O\(_3\)) are of high interest for the development of gas sensors and transparent contacts, finding applications in a number of devices [1–6]. Heterostructures based on metal oxide semiconductors allow the advantages of each component to be combined in a single structure [7]. Thus, superior gas-sensitive characteristics can be achieved for heterostructures compared to single semiconductors. It is reasonable to combine semiconductors with high catalytic activity and concentration of electrons, involved in the physico-chemical processes at chemisorption of gas molecules on the semiconductor surface.
SnO$_2$ is one of the most studied metal oxide semiconductors for gas sensor applications [1] primarily due to its high catalytic activity, which leads to a high gas sensitivity compared to other metal oxides. Chemisorption of gas molecules on the SnO$_2$ surface occurs with the involvement of free electrons. However, pure SnO$_2$ does not have a high electron concentration. Localization of electrons in this semiconductor can be achieved by forming heterostructures. Ga$_2$O$_3$ with an electron affinity $\chi = 4.0$ eV can be paired with SnO$_2$, which is characterized by $\chi = 5.32$ eV [8], to form such a heterostructure. In turn, Ga$_2$O$_3$ needs to be doped to achieve the required concentration of free electrons. In this case, one can expect an increase in the sensitivity of such heterostructure to gases as compared to pure SnO$_2$ and Ga$_2$O$_3$ films.

Gallium oxide has several polymorphs [9–12] namely $\alpha$, $\beta$, $\gamma$, $\delta$, and $\kappa(\varepsilon)$. Metastable $\kappa(\varepsilon)$-Ga$_2$O$_3$ polymorph is of particular interest for the development of electronic devices due to its fundamental properties [13] such as the thermal stability up to 700 °C; the high bandgap $E_g$ of 4.5–5.0 eV; availability of the ferroelectric properties; the high symmetry of a crystal lattice. $\kappa(\varepsilon)$-Ga$_2$O$_3$ is a novel material in terms of sensors, since its gas sensitivity was researched for the first time in 2022 [14]. We have demonstrated that $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn films grown by the halide vapor phase epitaxy (HVPE) have a low resistance (i.e., high electron concentration), stable characteristics in the temperature range from 20 °C to 500 °C, and exhibit sensitivity to H$_2$ at room temperature (RT) [14]. In addition, the $\kappa(\varepsilon)$-Ga$_2$O$_3$ polymorph meets the conditions of heteroepitaxy on a commercially available (0001) Al$_2$O$_3$ substrate better than monoclinic $\beta$-Ga$_2$O$_3$ [15]. Thus, doped $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn can be chosen to pair with SnO$_2$ to form a heterostructure.

SnO$_2$/$\beta$-Ga$_2$O$_3$ and SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$ heterostructures have previously been investigated for the development of power diodes [16,17] and solar-blind avalanche photodetectors with high sensitivity [8]. $\beta$-Ga$_2$O$_3$ nanostructures covered with ultrathin layers of SnO$_2$ demonstrated high sensitivity to ethanol at $T = 400$ °C [18] and to H$_2$ in the range of $T = 25$–200 °C [19]. The gas-sensitive properties of SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn heterostructures have not been studied before.

The purpose of this work is to gain insight into the gas-sensitive properties of SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn heterostructures.

2. Materials and Methods

The following films were deposited on (0001) single crystal Al$_2$O$_3$ substrates: $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn and SnO$_2$ thin films as well as SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn heterostructure. The process of the $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn films growth was multistage. In the first stage, a 3-µm-thick semi-insulating (SI) GaN layer was deposited on the Al$_2$O$_3$ substrate by gas phase deposition employing a homemade reactor. This layer served as a template for the $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn film growth. In the second stage, a 1-µm-thick $\kappa(\varepsilon)$-Ga$_2$O$_3$ layer in situ doped by Sn was deposited on the SI-GaN layer by HVPE using a hot-wall homemade reactor. Gaseous gallium chloride and oxygen were utilized as precursors. The doping of the $\kappa(\varepsilon)$-Ga$_2$O$_3$ films was carried out during the growth by adding tin. The HVPE growth temperature of the $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn film was 600 °C. The analysis of current–voltage ($I$–$V$) and capacitance–voltage ($C$–$V$) characteristics applied at this stage showed that the effective donor concentration $N_d$ of the films was $5.13 \times 10^{20}$ cm$^{-3}$.

120-nm-thick pure SnO$_2$ thin films were deposited by means of magnetron sputtering of an Sn (5N) target in an oxygen–argon plasma on Al$_2$O$_3$ and $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn. An Edwards A-500 (Edwards, USA) setup was employed. To prepare SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn heterostructures, SnO$_2$ thin films were deposited through a mask with square-shaped slots of 1 mm × 1 mm. The temperature of substrates during the deposition of the film was RT. The working pressure and power were kept at $7 \times 10^{-3}$ mbar and 70 W, respectively. The oxygen concentration in the O$_2$+Ar mixture was 56.1 ± 0.5 vol. %. The as-deposited SnO$_2$ films were annealed ex situ at $T = 600$ °C; for 4 hours in air. The estimates showed that the $N_d$ value of these films was $5.26 \times 10^{17}$ cm$^{-3}$. 
Pt contacts were deposited on the $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn and SnO$_2$ films (see Figure 1) by means of the magnetron sputtering. Pt contacts were chosen on the basis of their high stability at high temperatures and under exposure to various gases, which are of natural surroundings- and industrial relevance.

![Figure 1. Schematic of the SnO$_2$/k(ε)-Ga$_2$O$_3$:Sn heterostructure.](image)

X-ray diffraction (XRD) analysis of the samples was performed at DRON-6 diffractometer (Bourevestnik, Petersburg, Russia) equipped with a copper anode ($\text{CuK}_\alpha$, $\lambda = 1.5406$ Å). The XRD patterns were registered in $\theta$-2$\theta$ scanning mode. The phase composition of the samples was identified by the position of the reflection peaks. XRD $\theta$-2$\theta$ curves were processed using the Scherrer method [20] to determine the characteristic size of the block in the direction perpendicular to the plane of epitaxial growth.

The chemical composition of the samples was studied by X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out using a hemispherical analyzer included in the ESCALAB 250Xi (Thermo Fisher Scientific, Waltham, MA, USA) laboratory spectrometer. The measurements were carried out using a monochromatized AlK$_α$ radiation ($h\nu = 1486.6$ eV). Survey and core (O1s, Sn3d, Ga3d) photoemission (PE) spectra were recorded at the analyzer transmission energy of 100 and 50 eV, respectively. The film’s surface was irradiated with argon ions at an average energy of 3 eV for 60 s before XPS measurements to remove adsorbed atoms and molecules of contaminants. The analysis of the core spectra was processed employing the Avantage Data System software.

Measurement of transmission spectra was carried out using an Ocean Optics (Ocean Insight, Orlando, FL, USA) spectrometric system to determine the $E_g$ of SnO$_2$ in the wavelength range of $\lambda = 300$–600 nm. The transmission spectrum of $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn films was measured using a UV-VIS two-beam SPECORD (Analytik Jena, Jena, Germany) spectrophotometer in the range of $\lambda = 230$–360 nm.

A high-resolution field emission scanning electron microscope (FESEM) Apreo 2S (Thermo Fisher Scientific, USA) operating at an accelerating voltage of 5 kV was employed to study the micrelief of the film surfaces with a high resolution.

Gas sensing measurements of the samples were performed in a dedicated sealed chamber with a volume of 100 cm$^3$, equipped with a micro-probe Nextron MPS-CHH station (Nextron, Busan, Republic of Korea). A ceramic-type heater, installed in the sealed chamber, was used to heat the samples. The accuracy of temperature $T$ control was $\pm 0.1$ °C. The experiments were carried out under dark conditions. Streams of pure dry air or gas mixture of pure dry air + H$_2$ were pumped through the chamber to measure the gas sensing characteristics of the samples. The H$_2$ concentration in the mixture was controlled by a gas mixing and delivery system Microgas F-06 (Intera, Moscow, Russia). A special generator (Khimelektonika SPE, Moscow, Russia) was used to produce pure dry air. The total flow rate of the gas mixtures through the chamber was 1000 sccm. The relative error of the gas mixture flow rate did not exceed 1.5%. A Keithley 2636 A (Keithley, Solon, OH, USA) source meter was utilized to measure the time dependences of the current $I$ and the $I$–$V$ characteristics of the samples. An E4980A RLC-meter (Agilent, Santa Clara, CA, USA) was applied to measure the $C$–$V$ dependences. Additionally, gas sensing measurements of the samples were carried out under exposure to NH$_3$, CH$_4$, CO, NO$_2$, and O$_2$. A mixture of N$_2$ + O$_2$ was used to study the sensitivity of samples to O$_2$. To study the effect of relative humidity (RH) on the response of the samples to H$_2$, the pure dry air in one of the channels was passed through a bubbler with distilled water. Then it entered the homogenizer, where it was mixed with the pure dry air and/or pure dry air + H$_2$ mixture streams from the other channels. Varying the ratio of flows through the channels, we set the desired level of RH in
were subjected to heat treatment at $T = 500 \degree C$ for 90 s in pure dry air to stabilize the contact properties and regenerate the surface.

3. Results and Discussion
3.1. Structural Properties

Figure 2a illustrates the $\theta$-2$\theta$ XRD pattern of the SnO$_2$/Ga$_2$O$_3$ heterostructure deposited on an Al$_2$O$_3$ substrate via a GaN template. The peaks at $2\theta = 41.8^\circ$ and $90.9^\circ$ are associated with the (0006) and (0 0 12) reflections of the Al$_2$O$_3$ substrate (ICDD # 00-042-1468). A series of peaks at $2\theta = 19.2^\circ$, $39.0^\circ$, $60.0^\circ$, $83.6^\circ$, and $112.7^\circ$ correspond to the 002, 004, 006, 008, and 0 0 10 planes of the $\kappa(\varepsilon)$-Ga$_2$O$_3$ phase. (The calculation was made on the basis of the Bragg equation for the case of CuK$_{\alpha 1}$ anode ($\lambda = 1.5406 \AA$). The peaks at $2\theta = 34.7^\circ$, $73.0^\circ$, and $126.1^\circ$ are due to the (0002), (0004), and (0006) reflections of the GaN template (AMCSD # 99-101-0461). Peaks corresponding to SnO$_2$ could not be distinguished due to possible overlapping by neighboring reflections of other phases. Thus, the (101) reflection of SnO$_2$ (AMCSD no. 99-100-8661) is close to the (0002) one of GaN, and the (111) reflection of SnO$_2$ is close to the (004) one of $\kappa(\varepsilon)$-Ga$_2$O$_3$. The auxiliary vertical red lines of equal intensity depicted in Figure 2a are the tabular values of the SnO$_2$ reflection positions. In addition, difficulties in SnO$_2$ peaks identification may be caused by the low film thickness and the developed microrelief of the surface. Finally, the possible low crystallinity of the SnO$_2$ phase may be the reason for the absence of sharp peaks on the XRD pattern. In this case, broad humps of a low intensity may be present.

$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn and SnO$_2$ films are characterized by direct optical transitions according to the analysis of transmission spectra (see Figure 2b), where $\alpha$ is the absorption coefficient.

$E_g$ values were graphically calculated and proved to be equal to $4.61 \pm 0.01 \text{ eV}$ and $3.76 \pm 0.01 \text{ eV}$ for the $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn and SnO$_2$ films, respectively.

According to XPS analysis, the composition of the SnO$_2$ film includes Sn and O elements only. However, carbon (C) as a common contaminant was also observed in the subsurface layer a few nanometers thick. C atoms completely disappear after argon-etching for 60 s. Ga, Sn, O, and C lines were observed in the survey PE spectra of SnO$_2$ films. The Sn concentration in this film appeared to be about 3 at. %, which indicates a high level of doping. Thus, the chemical analysis has shown that there are no third-party impurities in the composition of $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn and SnO$_2$ films, which confirms the high purity of the deposited films.

The analysis of the chemical state of Sn based on the Sn3d$_{5/2}$ PE line revealed the energy position of the main maximum of Sn at 486.5 and 486.3 eV (Figure 2c). The obtained values are in good agreement with the literature data [21,22] and correspond to the higher oxidation state of Sn–Sn$_2$O$_2$ oxide. A lower value of the SnO$_2$ energy position for the $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn film indicates the effect of Ga$_2$O$_3$ on the charge state of SnO$_2$. Previously, we have observed a similar effect of the Sn3d$_{5/2}$ PE line shift to low binding energies of the SnO$_2$ film doped with rare-earth elements and platinum group metals [21,22]. Analysis of the Ga chemical state in the $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn film based on the Ga3d PE line showed that Ga corresponds to the higher Ga$_2$O$_3$ oxide [23] (Figure 2d).

FESEM images of the SnO$_2$ films surface deposited on Al$_2$O$_3$ substrates and $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn film are displayed in Figure 2e,f, respectively. The microrelief of the SnO$_2$ film on Al$_2$O$_3$ (Figure 2e) contains small spherical grains with a diameter of ~35 nm and large agglomerates with a characteristic size of ~300 nm. Whereas the microrelief of the SnO$_2$ film deposited on a $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn one (see Figure 2f) is represented by small grains with a diameter of ~35 nm only. The formation of large agglomerates for these structures was not observed.
Figure 2. Structural characterization of the samples: (a) XRD pattern of the SnO$_2$/Ga$_2$O$_3$ heterostructure grown on GaN/Al$_2$O$_3$; (b) $\alpha^2$ versus the photon energy for $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn and SnO$_2$ films; (c) Sn3d PE spectra of $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn and SnO$_2$ films; (d) Ga 3d, Sn 4d PE lines for $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn; FESEM images of the SnO$_2$ film deposited on Al$_2$O$_3$ (e) and $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn (f).

3.2. **Gas-Sensitive Properties of the SnO$_2$/κ(ε)-Ga$_2$O$_3$:Sn heterostructure**

The $I$–$V$ characteristics of the SnO$_2$ thin films equipped with Pt contacts are linear in the range of applied voltages $U = -40$–$40$ V at RT as well as at higher $T$. Contrary to this, the $I$–$V$ characteristics of the $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn films equipped with Pt contacts are nonlinear. The dependence of $\ln(I)$ on $U^{1/4}$ is linear, indicating the presence of a Schottky barrier at the Pt/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn interface [24]. The I value through the Pt/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn/Pt structures exceeds 0.1 A at $U > 12$ V which leads to the samples self-heating.

The SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn structure equipped with Pt contacts is a $n$-$N$ isotype heterojunction and the Schottky barriers are connected in series. The $I$–$V$ characteristics of such heterostructures are nonlinear and asymmetric as can be seen in Figure 3a. The $I(U = 4$ V)/$I(U = -4$ V) ratio reaches the value of $\sim 2 \times 10^5$ at $T = 25$ $^\circ$C, then drops by half as $T$ increases to 150 $^\circ$C. The increase in reverse current with $T$ rising is significantly higher than the increase in forward current. The forward-bias region of the $I$–$V$ characteristics is approximated by the following function: $I_f = A_1 \times \exp(B_1 U)$, where $I_f$ is a forward current; and $A_1$ and $B_1$ are the constants: $A_1 = (3.0 \pm 0.4) \times 10^{-6}$ A and $B_1 = 0.88 \pm 0.02$ V$^{-1}$ at $T = 25$ $^\circ$C. The reverse-bias region of the $I$–$V$ characteristics can be approximated by a
similar function of \( I_r = A_2 \times \exp(B_2 |U|) \), where \( I_r \) is a reverse current; \( A_2 \) and \( B_2 \) are the constants: \( A_2 = (2.0 \pm 0.4) \times 10^{-9} \) A and \( B_2 = 0.89 \pm 0.04 \) V\(^{-1}\) at \( T = 25^\circ\)C. The forward-bias mode of the structure corresponds to the application of a positive potential to the SnO\(_2\)/Pt interface.

![Graphs](image)

**Figure 3.** \( I-V \) characteristics of the SnO\(_2\)/\( \kappa(\varepsilon) \)-Ga\(_2\)O\(_3\):Sn heterostructure at \( T = 25^\circ\)C in pure dry air in semi-logarithmic coordinates (a), at \( T = 150^\circ\)C under exposure to \( 10^4 \) ppm of H\(_2\) (b). The insertions show these \( I-V \) characteristics in linear coordinates. Dependence of the response to \( 10^4 \) ppm H\(_2\) on the applied voltage at different temperatures (c), the insertion shows the response to \( 10^4 \) ppm H\(_2\) on the applied voltage at \( T = 25^\circ\)C and \( 200^\circ\)C.

Exposure to H\(_2\) leads to a reversible increase in the \( I \) through heterostructures at \( T = 25-200^\circ\)C. Figure 3b shows the change in the \( I-V \) characteristics of the SnO\(_2\)/\( \kappa(\varepsilon) \)-Ga\(_2\)O\(_3\):Sn heterostructure when exposed to \( 10^4 \) ppm of H\(_2\) at \( T = 150^\circ\)C. The type of the functions, approximating the forward and reverse branches of the \( I-V \) characteristics, does not change with increasing \( T \) to \( 200^\circ\)C and under exposure to \( 10^4 \) ppm of H\(_2\). The \( A_1 \) and \( A_2 \) increase, but \( B_1 \) and \( B_2 \) values decrease with \( T \). The \( A_1 \) and \( A_2 \) values increase, whereas \( B_1 \) and \( B_2 \) practically do not change when exposed to H\(_2\). Table 1 shows the \( A_1, A_2, B_1, \) and \( B_2 \) values at \( T = 150^\circ\)C and under exposure to \( 10^4 \) ppm of H\(_2\).

**Table 1.** \( A_1, A_2, B_1, \) and \( B_2 \) at \( T = 150^\circ\)C and under exposure to \( 10^4 \) ppm H\(_2\).

<table>
<thead>
<tr>
<th>Conditions</th>
<th>( A_1 ) (A)</th>
<th>( A_2 ) (A)</th>
<th>( B_1 ) (V(^{-1}))</th>
<th>( B_2 ) (V(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry pure air</td>
<td>((1.1 \pm 0.1) \times 10^{-4})</td>
<td>((1.1 \pm 0.1) \times 10^{-6})</td>
<td>0.65 ± 0.03</td>
<td>0.65 ± 0.02</td>
</tr>
<tr>
<td>Dry pure air + ( 10^4 ) ppm H(_2)</td>
<td>((2.6 \pm 0.3) \times 10^{-4})</td>
<td>((1.3 \pm 0.1) \times 10^{-6})</td>
<td>0.66 ± 0.03</td>
<td>0.63 ± 0.03</td>
</tr>
</tbody>
</table>
To assess the effect of H2 on the I through the SnO2/κ(ε)-Ga2O3:Sn structures, the current response $S_I$ was calculated based on the experimental $I$–$V$ characteristics by the following ratio:

$$S_I = \frac{I_{H_2}}{I_{air}}$$  \hspace{1cm} (1)

where $I_{H_2}$ is the current of the charge carrier through the SnO2/κ(ε)-Ga2O3:Sn heterostructure in the gas mixture of pure dry air + H2; $I_{air}$ is the current of the charge carrier through the SnO2/κ(ε)-Ga2O3:Sn heterostructure in pure dry air. The $S_I$ values calculated on the basis of the experimental $I$–$V$ characteristics and time dependences of currents at a fixed $U$ (see Figure 4a) coincide. The $S_I$ value depends on the magnitude and direction of the applied voltage (see Figure 3c). The highest response in the range of $T = 100$–125 °C was observed at $U = 0.5$ V, whereas the highest $S_I$ was observed at $U = 0.75$ V at $T = 150$ °C. At room temperature, the maximum $S_I$ was also noticed at $U = 0.5$ V (see Figure 3c, insertion). The response decreases exponentially with the applied voltage in the range of $U = 1$–5 V. $S_I$ values are significantly lower at the reverse-bias mode and decrease slightly with an increase in the reverse voltage $|U_r|$ from 0.25 V to 2.5 V. Moreover, the response increases slightly with a further increase in $|U_r|$ to 5 V.

**Figure 4.** Gas-sensitive properties of $n$-$N$ SnO2/κ(ε)-Ga2O3:Sn heterostructure and other samples: (a) time dependences of current upon exposure to $10^4$ ppm of H2; (b) temperature dependences of...
responses to $10^4$ ppm of H$_2$; (c) temperature dependences of response and recovery times upon exposure to $10^4$ ppm of H$_2$ for different samples; (d) time dependence of current upon exposure to different H$_2$ concentration; (e) dependence of response on H$_2$ concentration; (f) time dependence of current upon cyclic exposure to $10^4$ ppm of H$_2$; (g) responses to fixed concentrations of NO$_2$, CH$_4$, NH$_3$, CO, H$_2$, and O$_2$; (h) effect of the relative humidity on responses to $10^4$ ppm of H$_2$; (i) dependences of the capacitive response on applied voltage upon exposure to $10^4$ ppm of H$_2$ at $T = 125 \, ^\circ C$ and different frequencies; (j) effect of $10^4$ ppm of H$_2$ on C-V characteristics at $T = 125 \, ^\circ C$ and different frequencies; dependences in (d–h) were measured at $T = 125 \, ^\circ C$ and $U = 0.5 \, V$.

The temperature dependences of the sample’s response to $10^4$ ppm of H$_2$ are presented in Figure 4b. The $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn films show the highest response to H$_2$ at $T = 25 \, ^\circ C$. The $S_1$ of $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn films exceeds those of SnO$_2$ films in the temperature range of $T = 25$–$50 \, ^\circ C$; meanwhile, the $S_1$ of $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn films decreases and $S_1$ of SnO$_2$ films increases drastically with further increase in $T$. Sensitivity of SnO$_2$ and $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn films is based on reversible chemisorption of H$_2$ molecules on the semiconductor’s surface according to the mechanisms described in refs. [14,25]. High sensitivity to H$_2$ at moderate temperatures ($T = 300 \, ^\circ C$) is characteristic of the SnO$_2$ thin films. Low $S_1$ for the $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn films are caused by a significant influence of the bulk conductivity $\kappa_{BULK}$, which does not depend on the charge state of the surface. The dependence of the SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn heterostructures response to H$_2$ on temperature is characterized by a maximum at $T = 125 \, ^\circ C$. These samples demonstrate the highest $S_1$ in the range of $T = 75$–$125 \, ^\circ C$.

The experimental results displayed in Figure 4c prove that the SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn heterostructures are characterized by the high speed of operation compared to the SnO$_2$ thin films when exposed to H$_2$. The response $t_{\text{res}}$ and recovery $t_{\text{rec}}$ times were calculated to assess the speed of operation by the method described in ref. [9]. The calculated $t_{\text{res}}$ and $t_{\text{rec}}$ values can only be used to compare the speed of sensors operation at similar experimental conditions. $t_{\text{res}}$ and $t_{\text{rec}}$ decrease exponentially with $T$. $t_{\text{rec}}$ and $t_{\text{res}} + t_{\text{rec}}$ of the SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn structures are significantly lower than those of SnO$_2$ thin films at $T = 25$–$200 \, ^\circ C$. SnO$_2$ films are characterized by low $t_{\text{res}}$. The speed of operation for the $\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn films was not evaluated due to their low responses at $T > 50 \, ^\circ C$. These samples are of interest for developing room temperature H$_2$ sensors. The $t_{\text{res}}$ and $t_{\text{rec}}$ of these films under exposure to $10^4$ ppm of H$_2$ at $T = 25 \, ^\circ C$ are 349.2 s and 379.6 s, respectively. Obviously, SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn heterostructures are the most interesting for highly sensitive H$_2$ sensors with high speed of operation and low operating temperatures. Therefore, our further attention will be focused on these structures.

The dependence of the SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn structure response on the H$_2$ concentration $n_{\text{H}_2}$ is linear (Figure 4d,e) in the $n_{\text{H}_2}$ range of 100–30000 ppm. The $I_{\text{air}}$ and $I_{\text{H}_2}$ of the SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn heterostructures decrease by 30% and 28%, respectively (see Figure 4f), during a cyclic exposure to H$_2$ (five cycles). At the same time, the current response decreased by only 17%. The observed decrease in response during cyclic exposure to H$_2$ is caused by the manifestation of chemisorbed hydrogen atoms with high binding energy. The temperature of 125 °C is not sufficient for the complete desorption of these hydrogen atoms from the semiconductor surface. Short-term heating of the structure at high temperatures can be used to regenerate the surface of semiconductors and for full desorption of H atoms [26]. The results of the long-term tests of the SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn heterostructures at $T = 125 \, ^\circ C$ and when exposed to $10^4$ ppm of H$_2$ demonstrated opposite changes of $S_1$. The samples after the experiments were stored in sealed packages. The long-term tests lasted 8 weeks with an interval between the experiments of 7–8 days. Just prior to each measurement the SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn heterostructures were subjected to heat at $T = 500 \, ^\circ C$ for 90 s. There were increases in response from ~30 arb. un. to 47 arb. un. during the long-term tests. Response increases mostly due to a decrease in $I_{\text{air}}$. The most significant changes in response were in the first 4 weeks of testing.

The responses of the SnO$_2$/$\kappa(\varepsilon)$-Ga$_2$O$_3$:Sn heterostructure to NO$_2$, CH$_4$, NH$_3$, CO, and O$_2$ gases at $T = 125 \, ^\circ C$ was measured to evaluate its selectivity (Figure 4g). Noteworthy, is that $I$ through heterostructure increases reversibly when exposed to $10^4$ ppm of CH$_4$. 
NH₃ and CO. The response to these gases has been calculated by equation (1). The $I_{H}$ was replaced by $I_g$, where $I_g$ is the charge carrier current through the $\text{SnO}_2/\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ heterostructure in the gas mixture of pure dry air + reducing gas (CH₄, NH₃, or CO). The responses to CH₄, NH₃, and CO are insignificant compared to the S₁ to H₂, which equates to 29.92–46.98 arb. un. at $T = 125$ °C and $n_{H2} = 10^4$ ppm.

It was found, that the $I$ value of the $\text{SnO}_2/\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ reversibly decreases when exposed to NO₂ and O₂. The responses to NO₂ ($S_{\text{NO}_2}$) and O₂ ($S_{\text{O}_2}$) have been calculated by the following equations, correspondently:

$$S_{\text{NO}_2} = \frac{I_{\text{air}}}{I_{\text{NO}_2}},$$

$$S_{\text{O}_2} = \frac{I_{\text{N}}}{I_{\text{O}_2}},$$

where $I_{\text{NO}_2}$ is the charge carrier current through the $\text{SnO}_2/\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ heterostructure in the gas mixture of pure dry air + NO₂; $I_{\text{N}}$ is the charge carrier current through the $\text{SnO}_2/\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ heterostructure in the nitrogen atmosphere; $I_{\text{O}_2}$ is the charge carrier current through the $\text{SnO}_2/\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ heterostructure in the gas mixture of N₂ + O₂. S₁ ratio when exposed to 100 ppm of H₂ at $T = 125$ °C happened to be 26.7 times lower than those for 100 ppm of NO₂ (Figure 4g). The $\text{SnO}_2/\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ heterostructure also demonstrated relatively high response to O₂. The response to O₂ appears to be higher than to CH₄, NH₃, or CO at same concentration values. Hence, we have shown that $\text{SnO}_2/\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ heterostructure is also attractive for developing highly sensitive NO₂ and O₂ sensors operating at low temperatures.

An increase in RH leads to a drop in the response of the $\text{SnO}_2/\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ heterostructure to H₂ (Figure 4h). The most significant decrease in S₁ occurs when RH increases from 0 to 34 %. In the range of RH = 34–90.0%, the response varies slightly.

Furthermore, the effect of $10^4$ ppm of H₂ on the C-V characteristics of the $\text{SnO}_2/\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ heterostructures at $T = 125$ °C and signal frequencies $f = 1$ kHz, 10 kHz, and 1 MHz have been studied. The results are illustrated in Figure 4i.j. Evidently, exposure to H₂ leads to a reversible increase in the electrical capacity of the structures. The capacitive response $S_C$ has been calculated by the following equation:

$$S_C = \frac{C_H}{C_{\text{air}}},$$

where $C_H$ is the electrical capacitance of $\text{SnO}_2/\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ heterostructure in the gas mixture of pure dry air + H₂; and $C_{\text{air}}$ is the electrical capacitance of structures in pure dry air. Visibly, the $S_C$ (see Figure 4i) is significantly lower than the S₁ (Figure 3c). At $f = 10$ kHz and 1 MHz the capacitive response varies weakly. The highest $S_C$ value is observed in the range of $U = 0.95$–5.00 V at $f = 1$ kHz and has a maximum at $U = 2.9$ V.

### 3.3. The Mechanism of the Sensory Effect

Initially, the resistance of the Pt/$\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ interface is low and the Pt/$\text{SnO}_2$ contact is ohmic. The change in the potential barrier at Pt/$\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ and Pt/$\text{SnO}_2$ interfaces upon exposure to gases can be neglected. The observed high responses of the $\text{SnO}_2/\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ heterostructure at $T = 25$–175 °C; are due to the formation of the n-N isotypic heterojunction, where $\text{SnO}_2$ is the base.

Diffusion of H atoms up to the $\text{SnO}_2/\kappa(\epsilon)$-$\text{Ga}_2\text{O}_3$-$\text{Sn}$ interface at $T = 25$–175 °C; is unlikely. Changes of I and C upon exposure to H₂ occur mainly due to the chemisorption of gas molecules on semiconductor’s surface. In the air atmosphere within a temperature range of $T = 25$–175 °C, the oxygen chemisorbs mainly in a molecular form on metal oxide semiconductors surface and captures electrons from their conduction band [25,27]. The reaction of reversible chemisorption of oxygen molecules can be represented as follows:

$$\text{O}_2 + S_o + e^- \leftrightarrow \text{O}_2^- (c),$$

(5)
when \( S_a \) is a free adsorption center; \( e \) is the electron charge; \( O_2^{−}(c) \) is the chemisorbed oxygen ion. As a result of reaction (4), an electron-depleted region is formed in the near-surface part of the semiconductor. A negative charge on the surface causes the upward of energy bands bending at \( eV_s \), where \( V_s \) is the surface potential and \( eV_s \sim N_i^2 \), where \( N_i \) is the surface density of chemisorbed oxygen ions. In our case, the Debye length \( L_D \) for SnO\(_2\) exceeds the grain size and the effect of grain boundaries on the transport of charge carriers in a semiconductor can be ignored. Oxygen chemisorption weakly changes the electrical conductivity of the \( \kappa(\epsilon)\)-Ga\(_2\)O\(_3\):Sn films due to the low contribution of the surface conductivity \( G_s \) to the total conductivity of \( G_t \). Thus, changes in the current during the chemisorption of gases are mainly due to changes in the concentration of charge carriers in the SnO\(_2\).

\[ G_t = G_o + G_a \] and the relationship between \( G_t \) and \( eV_s \) in our case is described by the following equation [28]:

\[ G_t = G_o \times [1 - (L_D / D) \times [eV_s / (kT)]] \],

where \( D \) is the SnO\(_2\) film thickness; \( k \) is the Boltzmann constant. An increase in the \( eV_s \) due to the oxygen molecule’s chemisorption on the SnO\(_2\) surface leads to a drop of \( G_t \). The increase in \( G_t \) when exposed to H\(_2\) is caused by the interaction of H\(_2\) molecules with previously chemisorbed \( O_2^{−}(c) \) on the SnO\(_2\) surface. This interaction can be represented as follows:

\[ 2H_2 + O_2^{−}(c) \rightarrow 2H_2O + e^{−}. \] (7)

As a result of reaction (7), a neutral H\(_2\)O molecule is formed and desorbed, an electron returns to the conduction band of SnO\(_2\), the \( eV_s \) decreases and the finally \( G_t \) increases. When exposed to NO\(_2\) the following reactions take place [29]:

\[ \begin{align*}
NO_2 + S_a + e^{−} & \rightarrow NO_2^{−}, \\
NO_2^{−} & \rightarrow O^{−}(c) + NO, \\
O^{−}(c) + O^{−}(c) & \rightarrow O_2^{−}(c) + e^{−} + S_a.
\end{align*} \] (8)

NO\(_2\) molecules chemisorb onto free adsorption centers and capture electrons from the SnO\(_2\) conduction band. Meanwhile, \( eV_s \) is proportional to \( (N_i + N_{NO2})^2 \) in the mixtures of air + NO\(_2\), where \( N_{NO2} \) is the surface density of chemisorbed NO\(_2^{−}\) ions [25,27]. An additional negative charge on the surface of the SnO\(_2\) film leads to a greater decrease in \( G_t \). Further, NO\(_2^{−}\) ions are dissociated to form chemisorbed O\(^{−}\)(c) ions and gaseous NO molecules. In the low temperature region, atomic O\(^{−}\)(c) ions associated to O\(_2^{−}\)(c) form and a free electron \( e^{−} \), which returns to the conduction band of the semiconductor.

The \( \kappa(\epsilon)\)-Ga\(_2\)O\(_3\):Sn film is a source of electrons that are involved in reactions (5) and (8) with the gas molecules on the SnO\(_2\) surface. This causes a high response of heterostructure at \( T = 75−175 \, ^{°}C \). The base region (SnO\(_2\)) is filled with electrons from the \( \kappa(\epsilon)\)-Ga\(_2\)O\(_3\):Sn film with \( T \) rising, \( G_b \) of SnO\(_2\) increases and the response decreases. SnO\(_2\) films deposited on \( \kappa(\epsilon)\)-Ga\(_2\)O\(_3\):Sn are characterized by the absence of large agglomerates (see Figure 2e,f). This leads to an increase in the specific surface area of SnO\(_2\) and the surface density of adsorption centers for gas molecules.

Table 2 shows a comparison of the responses and optimal operating temperatures of structures based on the Ga\(_2\)O\(_3\) polymorphs when exposed to H\(_2\) and NO\(_2\) [9,14,18,19,30–42]. \( n_b \) is a gas concentration. SnO\(_2\)/\( \kappa(\epsilon)\)-Ga\(_2\)O\(_3\):Sn heterostructure in comparison with other items listed in this table is characterized by relatively high sensitivity to H\(_2\) and NO\(_2\) at a relatively low operating temperature. Ga2O3-based structures with higher responses to gases are characterized by high operating temperatures [9,30,34–37,41,42], low speed of operation [18,19], or are diode-type sensors based on high-cost materials [31,32,39]. SnO\(_2\)/\( \kappa(\epsilon)\)-Ga\(_2\)O\(_3\):Sn heterostructures demonstrate relatively high responses to H\(_2\) and NO\(_2\) at lower temperatures in comparison with the heterostructures based on other metal.
oxides (see Table 3). Nano-structured heterostructures are characterized by higher responses to NO2 but generally do not differ in high speed of operation.

Table 2. Gas-sensitive characteristics of structures based on Ga2O3 polymorphs.

<table>
<thead>
<tr>
<th>Structure</th>
<th>( n_g ) (ppm)</th>
<th>( T ) (°C)</th>
<th>Response (arb. un.)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha )-Ga2O3:Sn</td>
<td>( 10^4 )</td>
<td>350</td>
<td>80</td>
<td>[9]</td>
</tr>
<tr>
<td>( \alpha )-Ga2O3:Si</td>
<td>( 3 \times 10^4 )</td>
<td>400</td>
<td>69.3</td>
<td>[30]</td>
</tr>
<tr>
<td>( \beta )-Ga2O3</td>
<td>500</td>
<td>RT</td>
<td>7.9 \times 10^5</td>
<td>[31]</td>
</tr>
<tr>
<td>( \beta )-Ga2O3</td>
<td>2000</td>
<td>RT</td>
<td>( \Delta I = 1.4 ) mA</td>
<td>[32]</td>
</tr>
<tr>
<td>( \beta )-Ga2O3</td>
<td>( 3 \times 10^4 )</td>
<td>600</td>
<td>4</td>
<td>[33]</td>
</tr>
<tr>
<td>( \beta )-Ga2O3</td>
<td>200</td>
<td>300</td>
<td>6.3</td>
<td>[34]</td>
</tr>
<tr>
<td>( \beta )-Ga2O3:Cr2O3</td>
<td>2500</td>
<td>500</td>
<td>60</td>
<td>[35]</td>
</tr>
<tr>
<td>( \beta )-Ga2O3/Pd nanoclusters</td>
<td>( 10^4 )</td>
<td>625</td>
<td>(-10^3)</td>
<td>[36]</td>
</tr>
<tr>
<td>( \beta )-Ga2O3/SiO2 (filter)</td>
<td>5000</td>
<td>700</td>
<td>(-10^3)</td>
<td>[37]</td>
</tr>
<tr>
<td>( \alpha )-Ga2O3/( \kappa (\varepsilon) )-Ga2O3:Sn</td>
<td>2500</td>
<td>125</td>
<td>1.25</td>
<td>[38]</td>
</tr>
<tr>
<td>( \kappa (\varepsilon) )-Ga2O3</td>
<td>( 10^4 )</td>
<td>500</td>
<td>9.44</td>
<td>[14]</td>
</tr>
<tr>
<td>( \kappa (\varepsilon) )-Ga2O3:Sn</td>
<td>( 10^4 )</td>
<td>RT</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Pt/( \beta )-Ga2O3/GaN</td>
<td>1000</td>
<td>RT</td>
<td>229.8</td>
<td>[39]</td>
</tr>
<tr>
<td>( \beta )-Ga2O3/SnO2</td>
<td>1000</td>
<td>400</td>
<td>8</td>
<td>[18]</td>
</tr>
<tr>
<td>( \beta )-Ga2O3/SnO2</td>
<td>1000</td>
<td>200</td>
<td>707.5</td>
<td>[19]</td>
</tr>
<tr>
<td>( \beta )-Ga2O3/WO3</td>
<td>1000</td>
<td>200</td>
<td>3</td>
<td>[40]</td>
</tr>
<tr>
<td>SnO2/( \kappa (\varepsilon) )-Ga2O3:Sn</td>
<td>1000</td>
<td>125</td>
<td>5.7</td>
<td>This work</td>
</tr>
</tbody>
</table>

| NO2                        |                 |              |                     |      |
| \( \beta \)-Ga2O3/ZnO      | 10              | 300          | 73.5                | [41] |
| \( \beta \)-Ga2O3           | 5               |              | 5.1                 | [42] |
| \( \beta \)-Ga2O3/La0.25Sn0.75CoO3 | 200             | 800          | 25.7                |      |
| SnO2/\( \kappa (\varepsilon) \)-Ga2O3:Sn | 1000 | 125 | 3.7 | This work |

Table 3. Gas-sensitive characteristics of heterostructures based on different metal oxide semiconductors.

<table>
<thead>
<tr>
<th>Structure</th>
<th>( n_g ) (ppm)</th>
<th>( T ) (°C)</th>
<th>Response (arb. un.)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO2/In2O3</td>
<td>50</td>
<td>160</td>
<td>20.7</td>
<td>[43]</td>
</tr>
<tr>
<td>SnO2/ZnO</td>
<td>100</td>
<td>350</td>
<td>18.4</td>
<td>[44]</td>
</tr>
<tr>
<td>Pd/BN/ZnO</td>
<td>50</td>
<td>200</td>
<td>13</td>
<td>[45]</td>
</tr>
<tr>
<td>SnO2/NiO</td>
<td>500</td>
<td>500</td>
<td>114</td>
<td>[46]</td>
</tr>
<tr>
<td>rGO/ZnO-SnO2</td>
<td>100</td>
<td>380</td>
<td>9.4</td>
<td>[47]</td>
</tr>
<tr>
<td>rGO/ZnO</td>
<td>200</td>
<td>150</td>
<td>3</td>
<td>[48]</td>
</tr>
<tr>
<td>Al2O3/CuO</td>
<td>100</td>
<td>300</td>
<td>2.37</td>
<td>[49]</td>
</tr>
<tr>
<td>SnO2/( \kappa (\varepsilon) )-Ga2O3:Sn</td>
<td>1000</td>
<td>125</td>
<td>5.7</td>
<td>This work</td>
</tr>
</tbody>
</table>

| NO2                        |                 |              |                     |      |
| m-WO3/ZN/ZnO               | 1               | 150          | 167.8               | [50] |
| WO3/SnO2                   | 200             | 200          | 186                 | [51] |
| WO3/MWCNT composite        | 5               | 150          | 18                  | [52] |
| ZnO/SWCNT composite        | 50              | 150          | 5                   | [53] |
| Sb2O3/In2O3 nanotubes      | 1               | 80           | 47                  | [54] |
| Mo2O3/In2O3 nanotubes      | 50              | RT           | 209                 | [55] |
| PdO/SnO2 nanotubes         | 100             | RT           | 20.3                | [56] |
| TiO2/ZnO nanotubes         | 5               | RT           | 2.05                | [57] |
| In2O3/ZnO                  | 50              | 200          | 78                  | [58] |
| NiO/In2O3                  | 10              | 145          | 532                 | [59] |
| SnO2/\( \kappa (\varepsilon) \)-Ga2O3:Sn | 1000 | 125 | 3.7 | This work |

4. Conclusions

The structural and gas-sensitive properties of the \( n-N \) SnO2/\( \kappa (\varepsilon) \)-Ga2O3:Sn heterostructures were investigated for the first time. The \( \kappa (\varepsilon) \)-Ga2O3:Sn and SnO2 films were obtained by the halide vapor phase epitaxy and the high-frequency magnetron sputtering, respectively. The \( \kappa (\varepsilon) \)-Ga2O3:Sn crystalline film has a bandgap of 4.61 ± 0.01 eV. The SnO2
nanocrystalline film has a bandgap of 3.76 ± 0.01 eV and is characterized by a developed microrelief of the surface, represented by grains with a size of ~35 nm. Exposure to H₂ leads to an increase in electrical current and capacitance of SnO₂/κ(ε)-Ga₂O₃:Sn structures. The current response of heterostructures to H₂ significantly exceeds the capacitive one. Gas sensor response and speed of operation of the SnO₂/κ(ε)-Ga₂O₃:Sn heterostructure under H₂ exposure overperform those of the single κ(ε)-Ga₂O₃:Sn and SnO₂ films in the temperature range of 25–175°C. This heterostructure demonstrates a low response to CO, NH₃, and CH₄ and a high response to NO₂ even at low concentrations. The current responses of SnO₂/κ(ε)-Ga₂O₃:Sn heterostructure to 10⁴ ppm of H₂ and 100 ppm of NO₂ at 125 °C were 30–47 A.U. and 3.7 A.U., correspondingly. The sensory effect is realized mainly due to the chemisorption of gas molecules on the SnO₂ surface, which is the base region of the heterostructure. The κ(ε)-Ga₂O₃:Sn film is a source of electrons that are involved in reactions with gas molecules on the SnO₂ film surface. The SnO₂ film deposited on the κ(ε)-Ga₂O₃:Sn film is characterized by a more developed surface microstructure. This leads to an increase in the surface density of adsorption centers for gas molecules. The advantages of the SnO₂/κ(ε)-Ga₂O₃:Sn heterostructure for gas sensors are shown, the main one being high sensitivity at relatively low operating temperatures. Doubtfully, this structure has every chance of being the base of the sensor.


Funding: This research was funded by the Russian Science Foundation, grant number 20-79-10043. Viktor Kopyev acknowledges the support of the grant under the Decree of the Government of the Russian Federation No. 220 of 9 April 2010 (Agreement No. 075-15-2022-1132 of 1 July 2022).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data that support the findings of this study are included within the article.

Acknowledgments: The FESEM investigations have been carried out using the equipment of Share Use Centre “Nanotech” of the ISPMS SB RAS. XPS studies were carried out using the equipment of the resource center “Physical Methods of Surface Investigation” (Saint Petersburg University Research Park). We are grateful to Bogdan Kushnarev from Research and Development Centre for Advanced Technologies in Microelectronics at National Research Tomsk State University for the deposition of tin oxide and platinum films.

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

References


13. Biswas, M.; Nishinaka, H. Thermodynamically metastable α-ε-(or κ-) and γ-Ga2O3: From material growth to device applications. APL Mater. 2022, 10, 060701. [CrossRef]


42. Zhang, B.; Lin, H.; Gao, H.; Lu, X.; Nam, C.; Gao, P. Perovskite-sensitized β-Ga2O3 nanorod arrays for highly selective and sensitive NO2 detection at high temperature. J. Mater. Chem. A 2020, 8, 10845–10854. [CrossRef]


59. Xie, J.; Liu, X.; Jing, S.; Pang, C.; Liu, Q.; Zhang, J. Chemical and electronic modulation via atomic layer deposition of NiO on porous In$_2$O$_3$ films to boost NO$_2$ detection. *ACS Appl. Mater. Interfaces* 2021, 13, 39621–39632. [CrossRef]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.