

## Article

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

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**Abstract:** The structural and gas-sensitive properties of  $n\text{-N}$   $\text{SnO}_2/\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  heterostructures were investigated in detail for the first time. The  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  and  $\text{SnO}_2$  films were grown by the halide vapor phase epitaxy and the high-frequency magnetron sputtering, respectively. The gas sensor response and speed of operation of the structures under  $\text{H}_2$  exposure exceeded the corresponding values of single  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  and  $\text{SnO}_2$  films within the temperature range of 25–175 °C. Meanwhile, the investigated heterostructures demonstrated a low response to  $\text{CO}$ ,  $\text{NH}_3$ , and  $\text{CH}_4$  gases and a high response to  $\text{NO}_2$ , even at low concentrations of 100 ppm. The current responses of the  $\text{SnO}_2/\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  structure to  $10^4$  ppm of  $\text{H}_2$  and 100 ppm of  $\text{NO}_2$  were 30–47 arb. un. and 3.7 arb. un., correspondingly, at a temperature of 125 °C. The increase in the sensitivity of heterostructures at low temperatures is explained by a rise of the electron concentration and a change of a microrelief of the  $\text{SnO}_2$  film surface when depositing on  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$ . The  $\text{SnO}_2/\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  heterostructures, having high gas sensitivity over a wide operating temperature range, can find application in various fields.

**Keywords:**  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$ ;  $\text{SnO}_2$ ; HVPE; magnetron sputtering;  $n\text{-N}$  heterostructure; gas sensors



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## 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 ( $\text{SnO}_2$ ) and gallium oxide ( $\text{Ga}_2\text{O}_3$ ) 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<sub>2</sub> 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<sub>2</sub> surface occurs with the involvement of free electrons. However, pure SnO<sub>2</sub> does not have a high electron concentration. Localization of electrons in this semiconductor can be achieved by forming heterostructures. Ga<sub>2</sub>O<sub>3</sub> with an electron affinity  $\chi = 4.0$  eV can be paired with SnO<sub>2</sub>, which is characterized by  $\chi = 5.32$  eV [8], to form such a heterostructure. In turn, Ga<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> and Ga<sub>2</sub>O<sub>3</sub> films.

Gallium oxide has several polymorphs [9–12] namely  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\kappa(\epsilon)$ . Metastable  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub> 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.  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub> 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  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>: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<sub>2</sub> at room temperature (RT) [14]. In addition, the  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub> polymorph meets the conditions of heteroepitaxy on a commercially available (0001) Al<sub>2</sub>O<sub>3</sub> substrate better than monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [15]. Thus, doped  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>:Sn can be chosen to pair with SnO<sub>2</sub> to form a heterostructure.

SnO<sub>2</sub>/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub>/ $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub> heterostructures have previously been investigated for the development of power diodes [16,17] and solar-blind avalanche photodetectors with high sensitivity [8].  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures covered with ultrathin layers of SnO<sub>2</sub> demonstrated high sensitivity to ethanol at  $T = 400$  °C [18] and to H<sub>2</sub> in the range of  $T = 25$ –200 °C [19]. The gas-sensitive properties of SnO<sub>2</sub>/ $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructures have not been studied before.

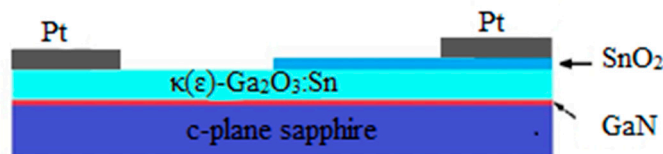
The purpose of this work is to gain insight into the gas-sensitive properties of SnO<sub>2</sub>/ $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructures.

## 2. Materials and Methods

The following films were deposited on (0001) single crystal Al<sub>2</sub>O<sub>3</sub> substrates:  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>:Sn and SnO<sub>2</sub> thin films as well as SnO<sub>2</sub>/ $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure. The process of the  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>:Sn films growth was multistage. In the first stage, a 3- $\mu$ m-thick semi-insulating (SI) GaN layer was deposited on the Al<sub>2</sub>O<sub>3</sub> substrate by gas phase deposition employing a homemade reactor. This layer served as a template for the  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>:Sn film growth. In the second stage, a 1- $\mu$ m-thick  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub> 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  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub> films was carried out during the growth by adding tin. The HVPE growth temperature of the  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>: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<sup>−3</sup>.

120-nm-thick pure SnO<sub>2</sub> thin films were deposited by means of magnetron sputtering of an Sn (5N) target in an oxygen–argon plasma on Al<sub>2</sub>O<sub>3</sub> and  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>:Sn. An Edwards A-500 (Edwards, USA) setup was employed. To prepare SnO<sub>2</sub>/ $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructures, SnO<sub>2</sub> thin films were deposited through a mask with square-shaped slots of 1 mm  $\times$  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<sub>2</sub>+Ar mixture was  $56.1 \pm 0.5$  vol. %. The as-deposited SnO<sub>2</sub> 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<sup>−3</sup>.

Pt contacts were deposited on the  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>:Sn and SnO<sub>2</sub> 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<sub>2</sub>/ $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure.

X-ray diffraction (XRD) analysis of the samples was performed at DRON-6 diffractometer (Bourestnik, Petersburg, Russia) equipped with a copper anode ( $\text{CuK}_{\alpha 1}$ ,  $\lambda = 1.5406 \text{ \AA}$ ). 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 <sub>$\alpha$</sub>  radiation ( $h\nu = 1486.6 \text{ eV}$ ). 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<sub>2</sub> in the wavelength range of  $\lambda = 300\text{--}600 \text{ nm}$ . The transmission spectrum of  $\kappa(\epsilon)$ -Ga<sub>2</sub>O<sub>3</sub>:Sn films was measured using a UV-VIS two-beam SPECORD (Analytik Jena, Jena, Germany) spectrophotometer in the range of  $\lambda = 230\text{--}360 \text{ nm}$ .

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 microrelief 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<sup>3</sup>, 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  $\pm 0.1 \text{ }^\circ\text{C}$ . The experiments were carried out under dark conditions. Streams of pure dry air or gas mixture of pure dry air + H<sub>2</sub> were pumped through the chamber to measure the gas sensing characteristics of the samples. The H<sub>2</sub> 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<sub>3</sub>, CH<sub>4</sub>, CO, NO<sub>2</sub>, and O<sub>2</sub>. A mixture of N<sub>2</sub> + O<sub>2</sub> was used to study the sensitivity of samples to O<sub>2</sub>. To study the effect of relative humidity ( $RH$ ) on the response of the samples to H<sub>2</sub>, 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<sub>2</sub> mixture streams from the other channels. Varying the ratio of flows through the channels, we set the desired level of  $RH$  in

the measuring chamber. An HHH 4000 Honeywell capacitive sensor with an absolute error of  $\pm 3.5\%$  was used to measure the *RH*. Just prior to these measurements, all the samples were subjected to heat treatment at  $T = 500\text{ }^{\circ}\text{C}$  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  $\text{SnO}_2/\text{Ga}_2\text{O}_3$  heterostructure deposited on an  $\text{Al}_2\text{O}_3$  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 0 12) reflections of the  $\text{Al}_2\text{O}_3$  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  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3$  phase. (The calculation was made on the basis of the Bragg equation for the case of  $\text{CuK}_{\alpha 1}$  anode ( $\lambda = 1.5406\text{ \AA}$ ). 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  $\text{SnO}_2$  could not be distinguished due to possible overlapping by neighboring reflections of other phases. Thus, the (101) reflection of  $\text{SnO}_2$  (AMCSD no. 99-100-8661) is close to the (0002) one of GaN, and the (111) reflection of  $\text{SnO}_2$  is close to the (004) one of  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3$ . The auxiliary vertical red lines of equal intensity depicted in Figure 2a are the tabular values of the  $\text{SnO}_2$  reflection positions. In addition, difficulties in  $\text{SnO}_2$  peaks identification may be caused by the low film thickness and the developed microrelief of the surface. Finally, the possible low crystallinity of the  $\text{SnO}_2$  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.

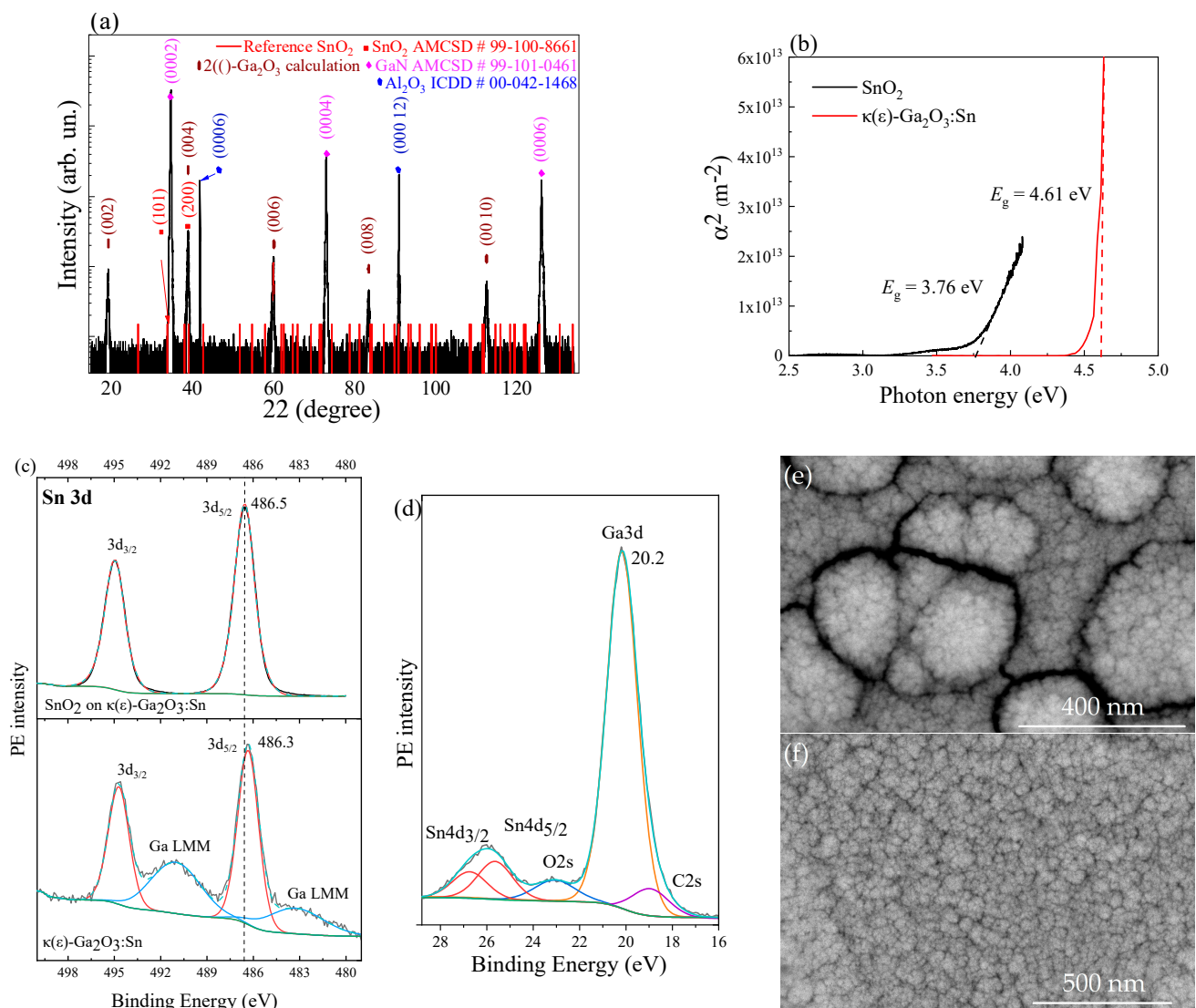
$\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  and  $\text{SnO}_2$  films are characterized by direct optical transitions according to the analysis of transmission spectra (see Figure 2b), where  $\alpha$  is the absorption coefficient.  $E_g$  values were graphically calculated and proved to be equal to  $4.61 \pm 0.01\text{ eV}$  and  $3.76 \pm 0.01\text{ eV}$  for the  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  and  $\text{SnO}_2$  films, respectively.

According to XPS analysis, the composition of the  $\text{SnO}_2$  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  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  film. 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  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  and  $\text{SnO}_2$  films, which confirms the high purity of the deposited films.

The analysis of the chemical state of Sn based on the  $\text{Sn}3d_{5/2}$  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– $\text{SnO}_2$  oxide. A lower value of the  $\text{SnO}_2$  energy position for the  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  film indicates the effect of  $\text{Ga}_2\text{O}_3$  on the charge state of  $\text{SnO}_2$ . Previously, we have observed a similar effect of the  $\text{Sn}3d_{5/2}$  PE line shift to low binding energies of the  $\text{SnO}_2$  film doped with rare-earth elements and platinum group metals [21,22]. Analysis of the Ga chemical state in the  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  film based on the  $\text{Ga}3d$  PE line showed that Ga corresponds to the higher  $\text{Ga}_2\text{O}_3$  oxide [23] (Figure 2d).

FESEM images of the  $\text{SnO}_2$  films surface deposited on  $\text{Al}_2\text{O}_3$  substrates and  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  film are displayed in Figure 2e,f, respectively. The microrelief of the  $\text{SnO}_2$  film on  $\text{Al}_2\text{O}_3$  (Figure 2e) contains small spherical grains with a diameter of  $\sim 35\text{ nm}$  and large agglomerates with a characteristic size of  $\sim 300\text{ nm}$ . Whereas the microrelief of the  $\text{SnO}_2$  film deposited on a  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  one (see Figure 2f) is represented by small grains with a diameter of  $\sim 35\text{ nm}$  only. The formation of large agglomerates for these structures was not observed.





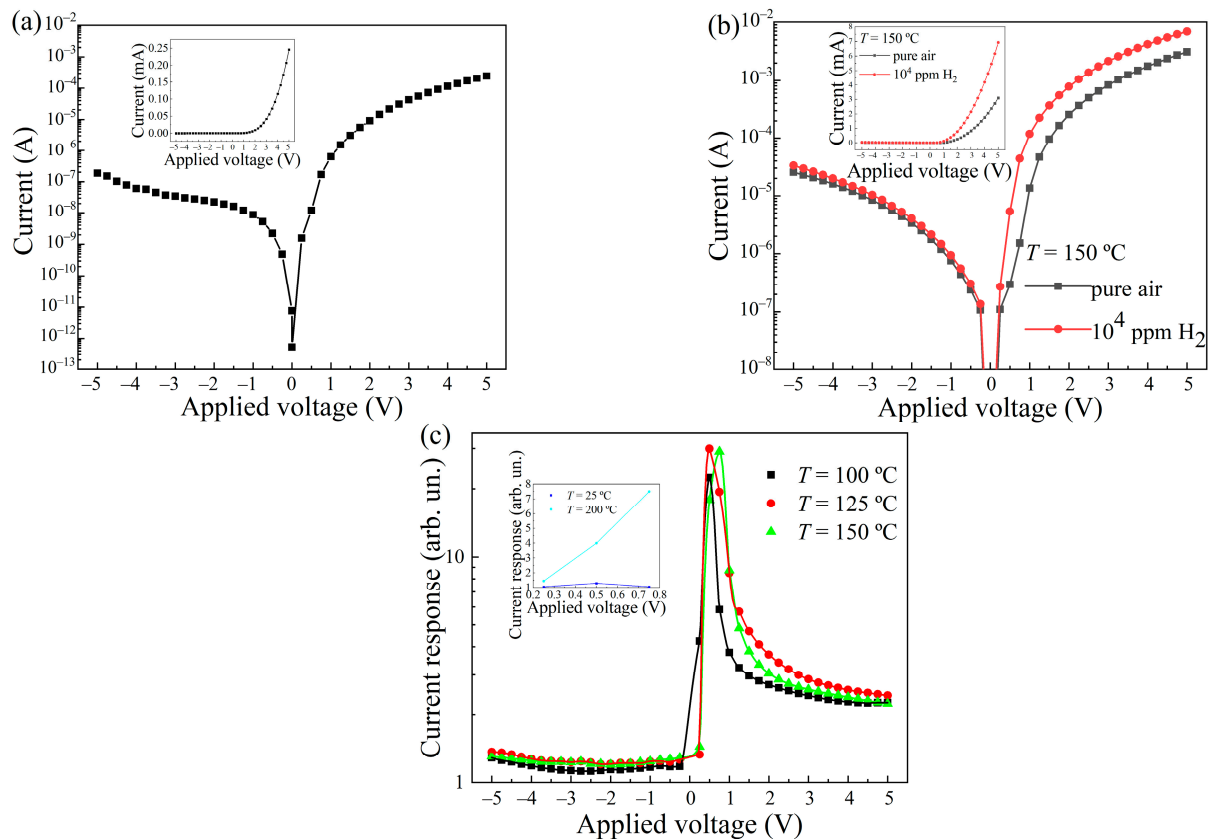
**Figure 2.** Structural characterization of the samples: (a) XRD pattern of the  $\text{SnO}_2/\text{Ga}_2\text{O}_3$  heterostructure grown on  $\text{GaN}/\text{Al}_2\text{O}_3$ ; (b)  $\alpha^2$  versus the photon energy for  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  and  $\text{SnO}_2$  films; (c)  $\text{Sn } 3d$  PE spectra of  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  and  $\text{SnO}_2$  films; (d)  $\text{Ga } 3d$ ,  $\text{Sn } 4d$  PE lines for  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$ ; FESEM images of the  $\text{SnO}_2$  film deposited on  $\text{Al}_2\text{O}_3$  (e) and  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  (f).

### 3.2. Gas-Sensitive Properties of the $\text{SnO}_2/\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$ heterostructure

The  $I$ - $V$  characteristics of the  $\text{SnO}_2$  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  $\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  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  $\text{Pt}/\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  interface [24]. The  $I$  value through the  $\text{Pt}/\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}/\text{Pt}$  structures exceeds 0.1 A at  $U > 12$  V which leads to the samples self-heating.

The  $\text{SnO}_2/\kappa(\epsilon)\text{-Ga}_2\text{O}_3\text{:Sn}$  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  $I(U = 4 \text{ V})/I(U = -4 \text{ V})$  ratio reaches the value of  $\sim 2 \times 10^3$  at  $T = 25^\circ\text{C}$ , then drops by half as  $T$  increases to  $150^\circ\text{C}$ . 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  $B_1 = 0.88 \pm 0.02 \text{ V}^{-1}$  at  $T = 25^\circ\text{C}$ . 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  $B_1 = 0.89 \pm 0.04$  V $^{-1}$  at  $T = 25$  °C. The forward-bias mode of the structure corresponds to the application of a positive potential to the SnO<sub>2</sub>/Pt interface.



**Figure 3.**  $I$ – $V$  characteristics of the SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure at  $T = 25$  °C in pure dry air in semi-logarithmic coordinates (a), at  $T = 150$  °C under exposure to  $10^4$  ppm of H<sub>2</sub> (b). The insertions show these  $I$ – $V$  characteristics in linear coordinates. Dependence of the response to  $10^4$  ppm H<sub>2</sub> on the applied voltage at different temperatures (c), the insertion shows the response to  $10^4$  ppm H<sub>2</sub> on the applied voltage at  $T = 25$  °C and  $200$  °C.

Exposure to H<sub>2</sub> leads to a reversible increase in the  $I$  through heterostructures at  $T = 25$ – $200$  °C. Figure 3b shows the change in the  $I$ – $V$  characteristics of the SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure when exposed to  $10^4$  ppm of H<sub>2</sub> at  $T = 150$  °C. The type of the functions, approximating the forward and reverse branches of the  $I$ – $V$  characteristics, does not change with increasing  $T$  to  $200$  °C and under exposure to  $10^4$  ppm of H<sub>2</sub>. 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<sub>2</sub>. Table 1 shows the  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$  values at  $T = 150$  °C and under exposure to  $10^4$  ppm of H<sub>2</sub>.

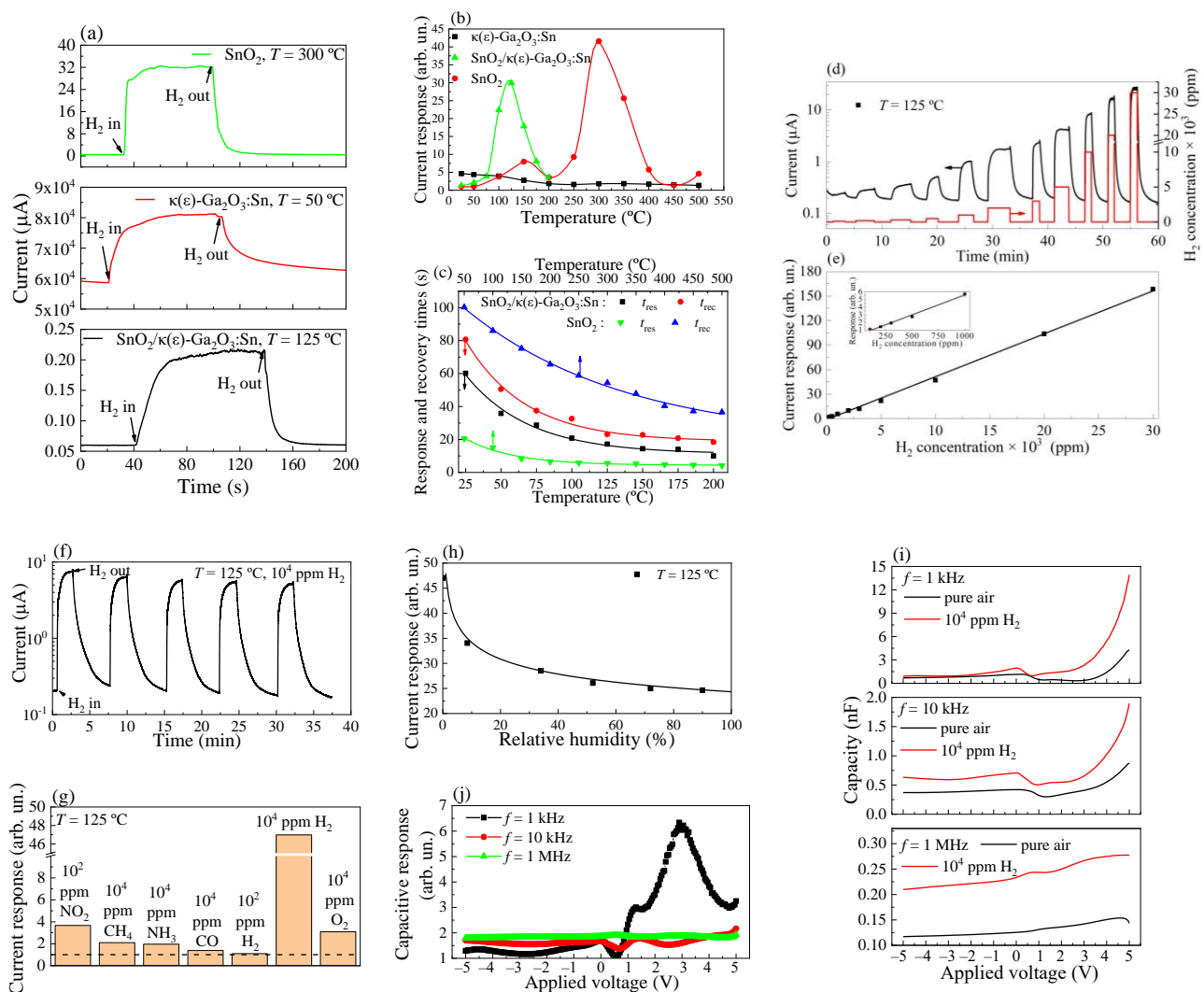
**Table 1.**  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$  at  $T = 150$  °C and under exposure to  $10^4$  ppm H<sub>2</sub>.

Conditions	$A_1$ (A)	$A_2$ (A)	$B_1$ (V $^{-1}$ )	$B_2$ (V $^{-1}$ )
Dry pure air	$(1.1 \pm 0.1) \times 10^{-4}$	$(1.1 \pm 0.1) \times 10^{-6}$	$0.65 \pm 0.03$	$0.65 \pm 0.02$
Dry pure air + $10^4$ ppm H <sub>2</sub>	$(2.6 \pm 0.3) \times 10^{-4}$	$(1.3 \pm 0.1) \times 10^{-6}$	$0.66 \pm 0.03$	$0.63 \pm 0.03$

To assess the effect of  $H_2$  on the  $I$  through the  $SnO_2/\kappa(\epsilon)-Ga_2O_3:Sn$  structures, the current response  $S_I$  was calculated based on the experimental  $I$ - $V$  characteristics by the following ratio:

$$S_I = I_H/I_{air}, \quad (1)$$

where  $I_H$  is the current of the charge carrier through the  $SnO_2/\kappa(\epsilon)-Ga_2O_3:Sn$  heterostructure in the gas mixture of pure dry air +  $H_2$ ;  $I_{air}$  is the current of the charge carrier through the  $SnO_2/\kappa(\epsilon)-Ga_2O_3:Sn$  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  $n-N$   $SnO_2/\kappa(\epsilon)-Ga_2O_3:Sn$  heterostructure and other samples: (a) time dependences of current upon exposure to  $10^4$  ppm of  $H_2$ ; (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  $T = 125$  °C and different frequencies; (j) effect of  $10^4$  ppm of  $H_2$  on C-V characteristics at  $T = 125$  °C and different frequencies; dependences in (d–h) were measured at  $T = 125$  °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  $\kappa(\epsilon)$ - $Ga_2O_3$ :Sn films show the highest response to  $H_2$  at  $T = 25$  °C. The  $S_1$  of  $\kappa(\epsilon)$ - $Ga_2O_3$ :Sn films exceeds those of  $SnO_2$  films in the temperature range of  $T = 25$ – $50$  °C; meanwhile, the  $S_1$  of  $\kappa(\epsilon)$ - $Ga_2O_3$ :Sn films decreases and  $S_1$  of  $SnO_2$  films increases drastically with further increase in  $T$ . Sensitivity of  $SnO_2$  and  $\kappa(\epsilon)$ - $Ga_2O_3$ :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 ( $T = 300$  °C) is characteristic of the  $SnO_2$  thin films. Low  $S_1$  for the  $\kappa(\epsilon)$ - $Ga_2O_3$ :Sn films are caused by a significant influence of the bulk conductivity  $G_b$ , which does not depend on the charge state of the surface. The dependence of the  $SnO_2/\kappa(\epsilon)$ - $Ga_2O_3$ :Sn heterostructures response to  $H_2$  on temperature is characterized by a maximum at  $T = 125$  °C. These samples demonstrate the highest  $S_1$  in the range of  $T = 75$ – $125$  °C.

The experimental results displayed in Figure 4c prove that the  $SnO_2/\kappa(\epsilon)$ - $Ga_2O_3$ :Sn heterostructures are characterized by the high speed of operation compared to the  $SnO_2$  thin films when exposed to  $H_2$ . The response  $t_{res}$  and recovery  $t_{rec}$  times were calculated to assess the speed of operation by the method described in ref. [9]. The calculated  $t_{res}$  and  $t_{rec}$  values can only be used to compare the speed of sensors operation at similar experimental conditions.  $t_{res}$  and  $t_{rec}$  decrease exponentially with  $T$ .  $t_{rec}$  and  $t_{res} + t_{rec}$  of the  $SnO_2/\kappa(\epsilon)$ - $Ga_2O_3$ :Sn structures are significantly lower than those of  $SnO_2$  thin films at  $T = 25$ – $200$  °C.  $SnO_2$  films are characterized by low  $t_{res}$ . The speed of operation for the  $\kappa(\epsilon)$ - $Ga_2O_3$ :Sn films was not evaluated due to their low responses at  $T > 50$  °C. These samples are of interest for developing room temperature  $H_2$  sensors. The  $t_{res}$  and  $t_{rec}$  of these films under exposure to  $10^4$  ppm of  $H_2$  at  $T = 25$  °C are 349.2 s and 379.6 s, respectively. Obviously,  $SnO_2/\kappa(\epsilon)$ - $Ga_2O_3$ :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  $SnO_2/\kappa(\epsilon)$ - $Ga_2O_3$ :Sn structure response on the  $H_2$  concentration  $n_{H_2}$  is linear (Figure 4d,e) in the  $n_{H_2}$  range of 100–30000 ppm. The  $I_{air}$  and  $I_H$  of the  $SnO_2/\kappa(\epsilon)$ - $Ga_2O_3$ :Sn heterostructure 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  $SnO_2/\kappa(\epsilon)$ - $Ga_2O_3$ :Sn heterostructures at  $T = 125$  °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  $SnO_2/\kappa(\epsilon)$ - $Ga_2O_3$ :Sn heterostructures were subjected to heat at  $T = 500$  °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  $I_{air}$ . The most significant changes in response were in the first 4 weeks of testing.

The responses of the  $SnO_2/\kappa(\epsilon)$ - $Ga_2O_3$ :Sn heterostructure to  $NO_2$ ,  $CH_4$ ,  $NH_3$ ,  $CO$ , and  $O_2$  gases at  $T = 125$  °C was measured to evaluate its selectivity (Figure 4g). Noteworthy, is that  $I$  through heterostructure increases reversibly when exposed to  $10^4$  ppm of  $CH_4$ ,



NH<sub>3</sub>h 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 SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure in the gas mixture of pure dry air + reducing gas (CH<sub>4</sub>, NH<sub>3</sub>, or CO). The responses to CH<sub>4</sub>, NH<sub>3</sub>, and CO are insignificant compared to the S<sub>1</sub> to H<sub>2</sub>, which equates to 29.92–46.98 arb. un. at  $T = 125\text{ }^{\circ}\text{C}$  and  $n_{\text{H}_2} = 10^4$  ppm.

It was found, that the  $I$  value of the SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn reversibly decreases when exposed to NO<sub>2</sub> and O<sub>2</sub>. The responses to NO<sub>2</sub> ( $S_{\text{NO}_2}$ ) and O<sub>2</sub> ( $S_{\text{O}_2}$ ) have been calculated by the following equations, correspondently:

$$S_{\text{NO}_2} = I_{\text{air}}/I_{\text{NO}_2}, \quad (2)$$

$$S_{\text{O}_2} = I_{\text{N}}/I_{\text{O}_2}, \quad (3)$$

where  $I_{\text{NO}_2}$  is the charge carrier current through the SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure in the gas mixture of pure dry air + NO<sub>2</sub>;  $I_{\text{N}}$  is the charge carrier current through the SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure in the nitrogen atmosphere;  $I_{\text{O}_2}$  is the charge carrier current through the SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure in the gas mixture of N<sub>2</sub> + O<sub>2</sub>. S<sub>1</sub> ratio when exposed to 100 ppm of H<sub>2</sub> at  $T = 125\text{ }^{\circ}\text{C}$  happened to be 26.7 times lower than those for 100 ppm of NO<sub>2</sub> (Figure 4g). The SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure also demonstrated relatively high response to O<sub>2</sub>. The response to O<sub>2</sub> appears to be higher than to CH<sub>4</sub>, NH<sub>3</sub>, or CO at same concentration values. Hence, we have shown that SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure is also attractive for developing highly sensitive NO<sub>2</sub> and O<sub>2</sub> sensors operating at low temperatures.

An increase in  $RH$  leads to a drop in the response of the SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure to H<sub>2</sub> (Figure 4h). The most significant decrease in S<sub>1</sub> occurs when  $RH$  increases from 0 to 34 %. In the range of  $RH = 34\text{--}90.0\%$ , the response varies slightly.

Furthermore, the effect of  $10^4$  ppm of H<sub>2</sub> on the C-V characteristics of the SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructures at  $T = 125\text{ }^{\circ}\text{C}$  and signal frequencies  $f = 1\text{ kHz}$ ,  $10\text{ kHz}$ , and  $1\text{ MHz}$  have been studied. The results are illustrated in Figure 4i,j. Evidently, exposure to H<sub>2</sub> leads to a reversible increase in the electrical capacity of the structures. The capacitive response  $S_C$  has been calculated by the following equation:

$$S_C = C_H/C_{\text{air}}, \quad (4)$$

where  $C_H$  is the electrical capacitance of SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure in the gas mixture of pure dry air + H<sub>2</sub>; 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 S<sub>1</sub> (Figure 3c). At  $f = 10\text{ kHz}$  and  $1\text{ MHz}$  the capacitive response varies weakly. The highest  $S_C$  value is observed in the range of  $U = 0.95\text{--}5.00\text{ V}$  at  $f = 1\text{ kHz}$  and has a maximum at  $U = 2.9\text{ V}$ .

### 3.3. The Mechanism of the Sensory Effect

Initially, the resistance of the Pt/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn interface is low and the Pt/SnO<sub>2</sub> contact is ohmic. The change in the potential barrier at Pt/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn and Pt/SnO<sub>2</sub> interfaces upon exposure to gases can be neglected. The observed high responses of the SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructure at  $T = 25\text{--}175\text{ }^{\circ}\text{C}$ ; are due to the formation of the  $n\text{-N}$  isotypic heterojunction, where SnO<sub>2</sub> is the base.

Diffusion of H atoms up to the SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn interface at  $T = 25\text{--}175\text{ }^{\circ}\text{C}$ ; is unlikely. Changes of  $I$  and  $C$  upon exposure to H<sub>2</sub> occur mainly due to the chemisorption of gas molecules on semiconductor's surface. In the air atmosphere within a temperature range of  $T = 25\text{--}175\text{ }^{\circ}\text{C}$ , 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:

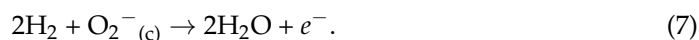


where  $S_a$  is a free adsorption center;  $e$  is the electron charge;  $O_2^-(c)$  is the chemisorbed oxygen ion. As a result of reaction (4), an electron-depleted region is formed in the near-surface part of the semiconductor. A negative charge on the surface causes the upward of energy bands bending 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  $\kappa(\epsilon)$ - $Ga_2O_3:Sn$  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  $SnO_2$ .

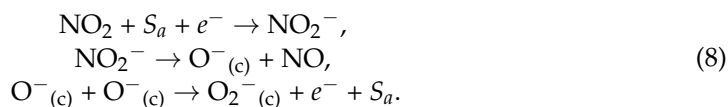
$G_t = G_b + G_s$  and the relationship between  $G_t$  and  $eV_s$  in our case is described by the following equation [28]:

$$G_t = G_b \times [1 - (L_D/D) \times [eV_s/(kT)]], \quad (6)$$

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:



As a result of reaction (7), a neutral  $H_2O$  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]:



$NO_2$  molecules chemisorb onto free adsorption centers and capture electrons from the  $SnO_2$  conduction band. Meanwhile,  $eV_s$  is proportional to  $(N_i + N_{NO_2})^2$  in the mixtures of air +  $NO_2$ , where  $N_{NO_2}$  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  $\kappa(\epsilon)$ - $Ga_2O_3:Sn$  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  $T = 75\text{--}175$  °C. The base region ( $SnO_2$ ) is filled with electrons from the  $\kappa(\epsilon)$ - $Ga_2O_3:Sn$  film with  $T$  rising,  $G_b$  of  $SnO_2$  increases and the response decreases.  $SnO_2$  films deposited on  $\kappa(\epsilon)$ - $Ga_2O_3:Sn$  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  $Ga_2O_3$  polymorphs when exposed to  $H_2$  and  $NO_2$  [9,14,18,19,30–42].  $n_g$  is a gas concentration.  $SnO_2/\kappa(\epsilon)$ - $Ga_2O_3:Sn$  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.  $Ga_2O_3$ -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].  $SnO_2/\kappa(\epsilon)$ - $Ga_2O_3:Sn$  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 NO<sub>2</sub> but generally do not differ in high speed of operation.

**Table 2.** Gas-sensitive characteristics of structures based on Ga<sub>2</sub>O<sub>3</sub> polymorphs.

Structure	$n_g$ (ppm)	$T$ (°C)	Response (arb. un.)	Ref.
H <sub>2</sub>				
$\alpha$ -Ga <sub>2</sub> O <sub>3</sub> :Sn	10 <sup>4</sup>	350	80	[9]
$\alpha$ -Ga <sub>2</sub> O <sub>3</sub> :Si	$3 \times 10^4$	400	69.3	[30]
$\beta$ -Ga <sub>2</sub> O <sub>3</sub>	500	RT	$7.9 \times 10^5$	[31]
$\beta$ -Ga <sub>2</sub> O <sub>3</sub>	2000	500	$\Delta I = 1.4$ (mA)	[32]
$\beta$ -Ga <sub>2</sub> O <sub>3</sub>	$3 \times 10^4$	600	4	[33]
$\beta$ -Ga <sub>2</sub> O <sub>3</sub>	200	300	6.3	[34]
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> :Cr <sub>2</sub> O <sub>3</sub>	2500	500	60	[35]
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> /Pd nanoclusters	10 <sup>4</sup>	625	$\sim 10^3$	[36]
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> (filter)	5000	700	$\sim 10^3$	[37]
$\alpha$ -Ga <sub>2</sub> O <sub>3</sub> / $\kappa(\epsilon)$ -Ga <sub>2</sub> O <sub>3</sub> :Sn	2500	125	1.25	[38]
$\kappa(\epsilon)$ -Ga <sub>2</sub> O <sub>3</sub>	10 <sup>4</sup>	500	9.44	[14]
$\kappa(\epsilon)$ -Ga <sub>2</sub> O <sub>3</sub> :Sn	10 <sup>4</sup>	RT	1.2	
Pt/ $\beta$ -Ga <sub>2</sub> O <sub>3</sub> /GaN	1000	RT	229.8	[39]
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> /SnO <sub>2</sub>	1000	400	8	[18]
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> /SnO <sub>2</sub>	1000	200	7075.5	[19]
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> /WO <sub>3</sub>	1000	200	4.1	[40]
SnO <sub>2</sub> / $\kappa(\epsilon)$ -Ga <sub>2</sub> O <sub>3</sub> :Sn	1000	125	5.7	This work
	10 <sup>4</sup>		47	
NO <sub>2</sub>				
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> /ZnO	10	300	73.5	[41]
$\beta$ -Ga <sub>2</sub> O <sub>3</sub>	200	800	5.1	[42]
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> /La <sub>0.8</sub> Sr <sub>0.2</sub> CoO <sub>3</sub>			25.7	
SnO <sub>2</sub> / $\kappa(\epsilon)$ -Ga <sub>2</sub> O <sub>3</sub> :Sn	100	125	3.7	This work

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

Structure	$n_g$ (ppm)	$T$ (°C)	Response (arb. un.)	Ref.
H <sub>2</sub>				
CeO <sub>2</sub> /In <sub>2</sub> O <sub>3</sub>	50	160	20.7	[43]
SnO <sub>2</sub> /ZnO	100	350	18.4	[44]
Pd/BN/ZnO	50	200	13	[45]
SnO <sub>2</sub> /NiO	500	500	114	[46]
rGO/ZnO-SnO <sub>2</sub>	100	380	9.4	[47]
RGO/ZnO	200	150	3.5	[48]
Al <sub>2</sub> O <sub>3</sub> /CuO	100	300	2.37	[49]
SnO <sub>2</sub> /κ(ε)-Ga <sub>2</sub> O <sub>3</sub> :Sn	1000	125	5.7	This work
	10 <sup>4</sup>		47	
NO <sub>2</sub>				
m-WO <sub>3</sub> /ZnO	1	150	167.8	[50]
WO <sub>3</sub> /SnO <sub>2</sub>	200	200	186	[51]
WO <sub>3</sub> /MWCNT composite	5	150	18	[52]
ZnO/SWCNT composite	50	150	5	[53]
Sb <sub>2</sub> O <sub>3</sub> /In <sub>2</sub> O <sub>3</sub> nanotubes	1	80	47	[54]
MoS <sub>2</sub> /In <sub>2</sub> O <sub>3</sub> nanotubes	50	RT	209	[55]
PdO/SnO <sub>2</sub> nanotubes	100	RT	20.3	[56]
TiO <sub>2</sub> /ZnO nanotubes	5	RT	2.05	[57]
In <sub>2</sub> O <sub>3</sub> /ZnO	50	200	78	[58]
NiO/In <sub>2</sub> O <sub>3</sub>	10	145	532	[59]
SnO <sub>2</sub> /κ(ε)-Ga <sub>2</sub> O <sub>3</sub> :Sn	100	125	3.7	This work

#### 4. Conclusions

The structural and gas-sensitive properties of the  $n$ -N SnO<sub>2</sub>/κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn heterostructures were investigated for the first time. The κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn and SnO<sub>2</sub> films were obtained by the halide vapor phase epitaxy and the high-frequency magnetron sputtering, respectively. The κ(ε)-Ga<sub>2</sub>O<sub>3</sub>:Sn crystalline film has a bandgap of  $4.61 \pm 0.01$  eV. The SnO<sub>2</sub>

nanocrystalline film has a bandgap of  $3.76 \pm 0.01$  eV and is characterized by a developed microrelief of the surface, represented by grains with a size of  $\sim 35$  nm. Exposure to  $H_2$  leads to an increase in electrical current and capacitance of  $SnO_2/\kappa(\epsilon)-Ga_2O_3:Sn$  structures. The current response of heterostructures to  $H_2$  significantly exceeds the capacitive one. Gas sensor response and speed of operation of the  $SnO_2/\kappa(\epsilon)-Ga_2O_3:Sn$  heterostructure under  $H_2$  exposure overperform those of the single  $\kappa(\epsilon)-Ga_2O_3:Sn$  and  $SnO_2$  films in the temperature range of 25–175°C. This heterostructure demonstrates a low response to  $CO$ ,  $NH_3$ , and  $CH_4$  and a high response to  $NO_2$  even at low concentrations. The current responses of  $SnO_2/\kappa(\epsilon)-Ga_2O_3:Sn$  heterostructure to  $10^4$  ppm of  $H_2$  and 100 ppm of  $NO_2$  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  $SnO_2$  surface, which is the base region of the heterostructure. The  $\kappa(\epsilon)-Ga_2O_3:Sn$  film is a source of electrons that are involved in reactions with gas molecules on the  $SnO_2$  film surface. The  $SnO_2$  film deposited on the  $\kappa(\epsilon)-Ga_2O_3:Sn$  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  $SnO_2/\kappa(\epsilon)-Ga_2O_3:Sn$  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.

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