

OPTIMIZATION OF SnO₂ THIN FILMS FOR LOW TEMPERATURE NO₂ SENSORS APPLICATIONS.

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Abstract

In this work, a high-performance n-type semiconductor gas sensor based on undoped-SnO₂ thin films deposited by a conventional radio-frequency (RF) – magnetron sputtering process was successfully fabricated. The structure, morphology, and chemical composition of the sensing material were investigated using X-ray diffraction (XRD), Atomic Force Microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) respectively. The end results show that the thin film has a polycrystalline structure with the presence of oxygen vacancies. The resistive sensor architecture has been simulated using TCAD SILVACO software's in order to optimize the geometry for sensor response optimization.

In this study, undoped-SnO₂ resistive gas sensor exhibits compelling sensing performance for detecting 3 ppm of NO₂ mixed with dry air at low operating temperature, around 100°C. 3 ppm represents the maximum level of NO₂ concentration beyond which short-term exposure presents a risk to human health or environmental degradation. Lower concentrations were also investigated in our study and the lowest NO₂ concentration evaluated is about 0.25 ppm.

Keywords: Undoped-SnO₂ gas sensors, TCAD simulations, low operating temperature, NO₂ sensing.

1. INTRODUCTION

NO₂ is one of the largest automobile pollutants and presents harmful effects on the environment (acid rain) and health effects on humans [1]. In this context, several studies have been conducted in order to develop microsensors for air quality monitoring. As a result, an exponential increase in the gas sensors market is observed in recent years [2].

In the context of the Internet of Things (IoT) and the high demand for real-time measurements,

autonomous sensors present a real advantage. Lowering the operating temperature of the sensor is one of the solutions to reduce the power consumption for a better autonomy. The working temperature of a conventional sputtered metal oxide gas sensor varies between 200-300°C for NO₂ sensing applications [3,4]. The main objective of our work is to study undoped-SnO₂ in order to lower the operating temperature of NO₂ sensors.

2 Simulation and experimental setup

2.1 Simulating the sensor

The main purpose of the simulation is to study carefully the effect of geometrical parameters on the electric properties of the sensor. The objective is to obtain a well-defined geometry to achieve good sensing performance. The sensor (inter-digitated electrodes + SnO₂ film) is simulated using SILVACO TCAD tools. The simulation is carried out with 3D layout. Figure 1 displays the sensor scheme from two angles, top view and cross section. The materials used for the electrodes are titanium and platinum with a total thickness of 45 nm. The number, length, and width of electrodes fingers are indicated in figure 1. Different values of the gap (g) between electrodes were examined. The chosen g values are: 5, 10, and 20 μm .

The SnO₂ film is divided into two layers: the top layer, which represents the surface of the film, and the bottom layer, representing the bulk. These layers are represented in two different colors (in light and dark green, respectively) in figure 1b.

To understand the difference between these two SnO₂ layers, we give a brief summary of the mechanism of a resistive gas sensor [5]. When gas molecules are adsorbed on the surface of a SnO₂ film, an exchange of electrons takes place between the film surface and the gas molecules. However, the concentration of the free electrons varies during the gas detection.

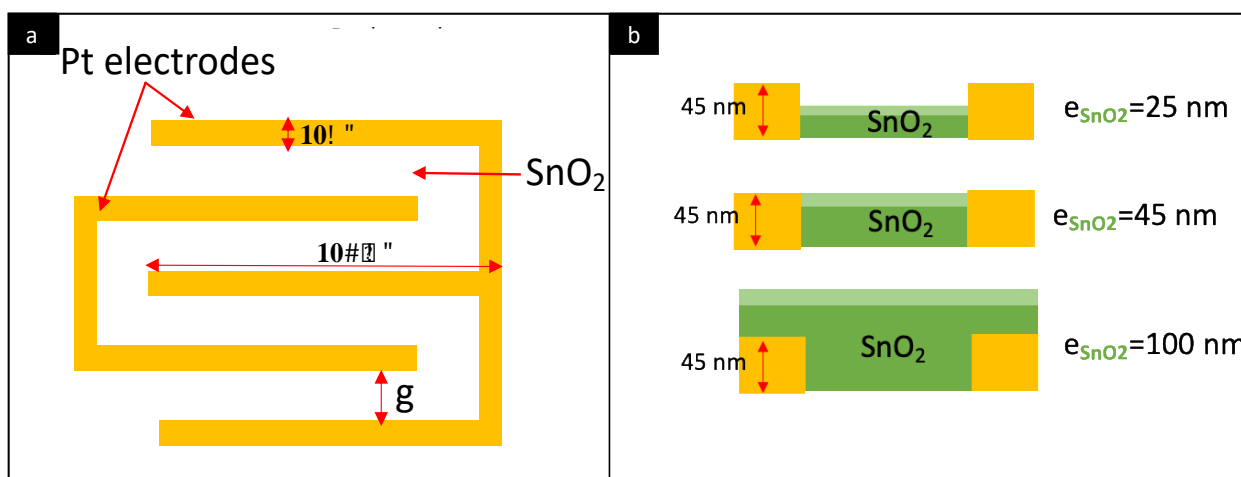


Figure 1:Top view of the simulated sensor b) cross section of the simulated sensor with variable SnO₂ thickness. The geometrical parameter given on the schemes.

Since SnO₂ is not included in the SILVACO material library, we have used silicon, and adjusted the material parameters, in a way to introduce the SnO₂ electric properties. Moreover, n-type doping is introduced in the material in order to consider the different electron densities in the top and bottom layers. The number of dopants, N_2 , of the top layer, varies under two conditions: $N_2 = N_1$ (N_1 is the number of dopants of the bottom layer) when the sensor is exposed to the air, whereas $N_2 < N_1$ when the latter is exposed to an oxidant gas such as NO₂.

The SnO₂ parameters used in simulation [6] for both top and bottom layers are the following:

The energy gap, $E_g = 3.6$ eV. The effective density of states in the conduction and the valence band are $N_c = 3.5 \times 10^{18}$ and $N_v = 1.3 \times 10^{19}$ respectively. The electron mobility, $\mu = 20$ m²·V⁻¹·s⁻¹. The number of dopants, $N_2 = N_1 = 1 \times 10^{18}$ when the sensor is exposed to air and $N_2 = 1.5 \times 10^{18}$ when it is exposed to an oxidant gas. The top layer thickness in the 3 examples above is about 10 nm, which represents the surface of the SnO₂ film accessible to the gas. The overall thickness of the entire sample (bottom and top layers) has a value $e = 25, 45,$ and 100 nm. The used models are the distribution of Fermi-Dirac and the recombination of Shockley Read Hall statistics [7]. These are built-in models in SILVACO software's. We hence obtain the I-V characteristics, hence the sensor resistance. The latter is exposed to an oxidant gas such as NO₂.

2.2 Material Deposition

Undoped-SnO₂ thin films are deposited at room temperature on SiO₂/Si substrates via sputtering of a 4" SnO₂ target in an Alliance Concept RF magnetron sputtering system (AC450). Therefore,

sputtering power, deposition pressure of the chamber, and annealing temperature were investigated and optimized. The optimal deposition parameters are: Sputtering power, $\omega = 300$ W; Deposition pressure, $P = 5 \times 10^{-3}$ Pa; Films thickness, $e = 25, 45,$ and 100 nm respectively. All the samples were then annealed for 10 min under nitrogen by rapid thermal annealing process at 450°C.

2.3 Material Characterization

The structures of the prepared samples are investigated using X-ray diffraction XRD (Smart Lab Rigaku, Cu K_{α1} radiation, $\lambda = 1.5406$ Å). The morphology of the surface is studied using Atomic Force Microscopy, AFM. The chemical composition of our samples (surface + bulk) is carried out via X-ray photoelectron spectroscopy (XPS), using a customized Thermo Fisher Theta 300 spectrometer, interfaced to a specific loading interface from Pfeiffer Vacuum. The bulk chemical composition is analyzed in situ in the XPS chamber by etching the sample using an Ar⁺ ion beam having an etching rate of approximately 1.85 nm/min.

2.4 Sensor fabrication

The sensor is manufactured by lithographic technique. The electrodes are deposited by evaporating Ti (5 nm) /Pt (40 nm) on SiO₂ (300 nm) /Si. Figure 2 shows the different geometries of the electrodes for gas sensing measurements. SnO₂ sensing films were then deposited on the interdigitated electrodes, forming the gas sensor device (Red zone in figure 2).

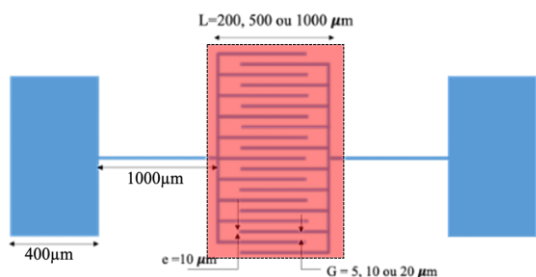


Figure 2: Device electrode geometry (blue), and SnO₂ zone (red).

2.5 Gas sensing measurements

A testing chamber with a total volume of around 1.6 L is used to study the detection conditions. The target gas (NO₂) is delivered to the chamber via a gas system. Mass flow regulators are used to dilute the analytes in order to study the effect of the gas concentration on the response of the sensor. This dilution system allows the generation of low concentrations, ranging between few tens of ppb to 3 ppm. Sensing measurements are carried out by monitoring the electrical resistance of the sensor in real-time using a Keithley 2450 source meter. The sensor is deposited on a heating substrate in order to control the temperature of the former.

3 Results and discussion

3.1 Simulation

Figure 3 shows the simulation result. The response r of the simulated sensor when exposed to the gas is given by:

$$r = \frac{R_2 - R_1}{R_2} \times 100 \quad (1)$$

such that,

R_1 : resistance of the sensor when exposed to an oxidant gas;

R_2 : resistance of the sensor when exposed to the air.

On one hand, the simulation results do not show any major effects when measuring the response as a function of the gap. More precisely, the response of the 25 nm thick SnO₂ only barely changes from 20% with a gap of 5 nm to roughly 19% with a gap of 10 nm. Clearly, the value of the response stays close to 19% for a gap of 20 nm. Similarly, the response of 100 nm thick SnO₂ remains around 5% as a function of the gap. However, the response of the 45 nm thick SnO₂ has produced different outcomes, by changing from 11% with a gap of 5 nm to 16% with a gap of 20 nm. The reason behind such behavior is still unknown since the two other sensors do not show the same behavior, nevertheless, it is important to

note that the gap effect was not evaluated experimentally.

On the other hand, the simulation results show that SnO₂ film thickness has an effect on the sensor response. For example, the response of 25 nm thick SnO₂ is 20%, which decreases significantly to 10% for a sensor thickness of 45 nm. Similarly, the response drops to 5% for a thickness of 100 nm. Following the above study, we conclude that an optimal sensor must have a sensing film thickness that rivals the electrode's thickness.

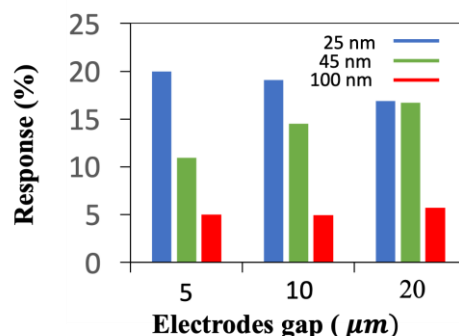


Figure 3: Response of the simulated sensors as a function of the gap and the SnO₂ thickness.

3.1 Material characteristics

The microstructure of the sensing surface affects the sensitivity of the sensor such as the SnO₂ grain size. Hence, the characteristics of the deposited SnO₂ films are examined, and the results are presented below.

Phase identification

The X-ray diffraction pattern of the 100 nm thick annealed SnO₂ film is presented in figure 4. This XRD pattern shows a cassiterite structure. The SnO₂ peaks (110), (200) (211) are being indexed as shown in the figure below. Such pattern signals the formation of SnO₂ crystallites which is crucial for sensing applications. Our SnO₂ films are polycrystalline.

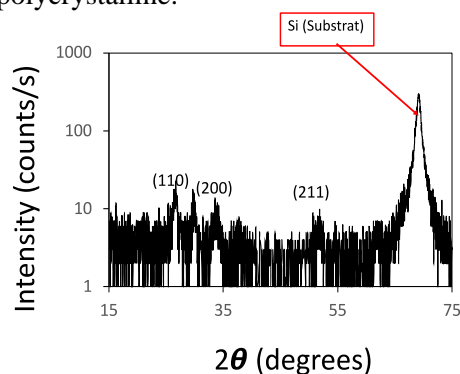


Figure 4: XRD diffraction pattern of the 100 nm undoped-SnO₂.

Morphology observation

Figure 5 presents AFM images of the surface morphology of the SnO₂ films having 25, 45, and 100 nm thickness respectively. These images are obtained using tapping-mode AFM. The size of each image is 2 μm × 2 μm. The below images show that the three films have a granular structure. These films differ in terms of their surface roughness along with the size of their grains. While increasing the film thickness, the grain size increases, leading to an increase in the roughness of the surface. The AFM images show the smallest grains size for the 25 nm thick SnO₂, when compared to the 45 nm and 100 nm thick SnO₂. More precisely, the average size of the

environment, while the second one is annealed in a N₂+O₂ environment. Furthermore, the third sample is annealed at 450°C in air inside a tubular oven for 30 min.

The XPS analyses were performed for etched samples under Ar. Figure 6 shows that our films are rich in oxygen at the surface with the ratio O/Sn = 2.2 while taking a value of 1.8 in the bulk.

Such high ratio at the surface is probably either due to the long-time sample storage in the air, and / or due to the oxygen atoms being linked to the carbon atoms contamination on the surface.

Moreover, this study has shown that the annealing conditions have no effect on the chemical composition of SnO₂.

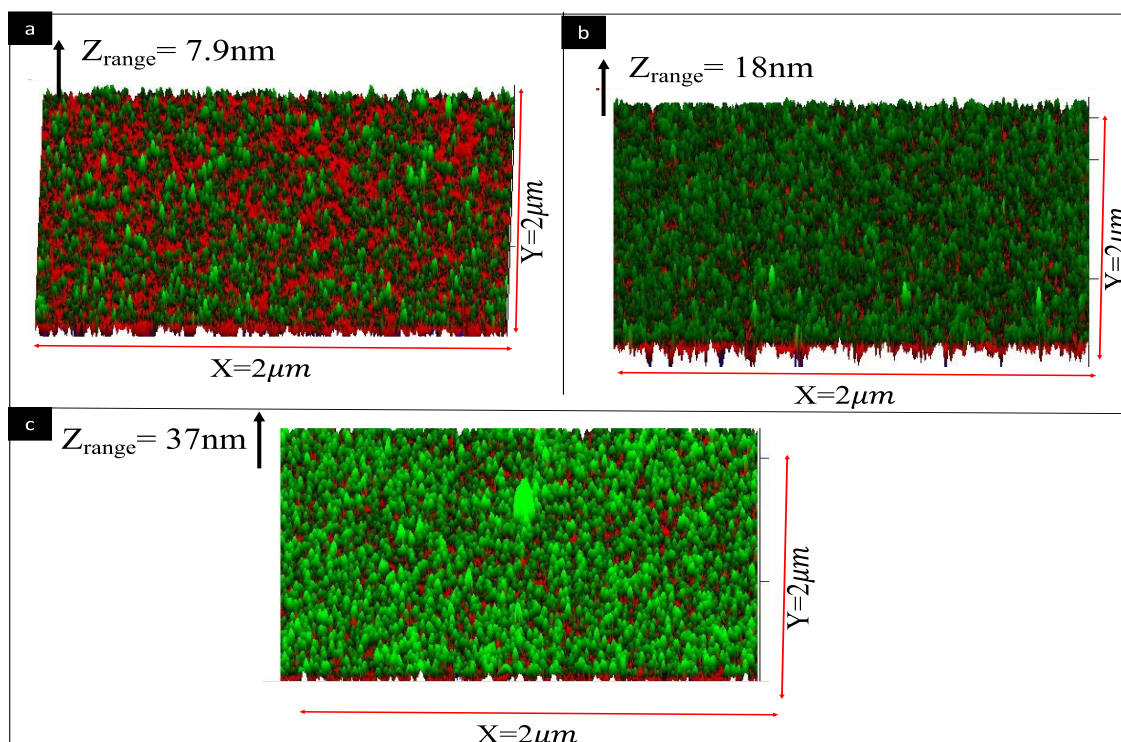


Figure 5: 3d AFM images of SnO₂ films of varying thickness: a) 25 nm, b) 45 nm and c) 100 nm.

former film (25 nm) is 10-15 nm, whereas the average size of the latter films (45 and 100 nm) happens to be 15-25 nm and 25-35 nm respectively. On the other hand, the surface roughness, which is determined by calculating the root mean square RMS, which takes a value of 0.823 nm for the case of 25 nm, while taking a value of 1.42 nm for the 45 nm and 3.09 nm for the 100 nm thick SnO₂.

Stoichiometry

In order to study the chemical composition of our SnO₂ films, in particular the ratio O/Sn, three SnO₂ samples, which have 100 nm thickness were deposited by sputtering. Two of these samples were annealed at 450°C using rapid thermal annealing (RTA) for 10 minutes: one is annealed in an N₂

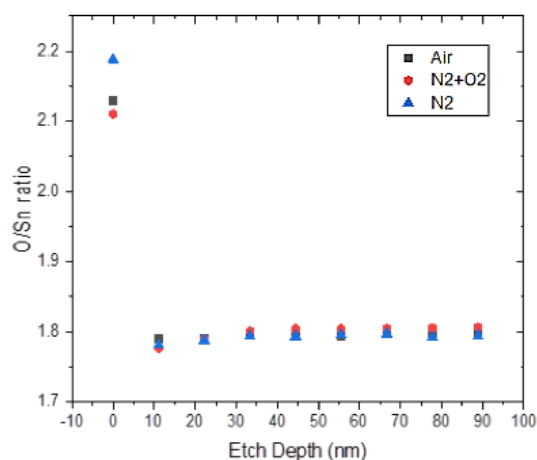


Figure 6: O/Sn ratio of 100 nm undoped SnO₂ samples as a function of etching depth. The sample is annealed in different environments (N₂, Air, N₂+O₂).

3.2 Sensing performance

In order to measure the response of our sensors, a bias of 0.05V has been applied on the electrodes. The electrical resistance is then recorded while the device is exposed to cycles of NO₂ and dry air. It is clearly demonstrated that relative humidity influences surface conductivity, as shown in [8]. Water molecules can enhance the sensor response toward gases. In their paper, [4]. Kiruba Mangalam Subramaniam and al. added 10% of humidity in order to detect NO₂.

The sensors in this study show low electrical resistance e . For example, the 45 nm thick-SnO₂ has a resistance of 12 k Ω in dry air at 50°C, 3.5 k Ω at 100°C, 2.6 k Ω at 150°C and 1.4 k Ω at 200°C. The latter measurements shows a better response as compared with the sensors with 25 nm and 100 nm-thick SnO₂. Figure 7 shows the real-time response, r , (as defined in equation 2) for the 45 nm-thick SnO₂ sensor for multiple cycles of 3 ppm NO₂ - dry air at different working temperatures.

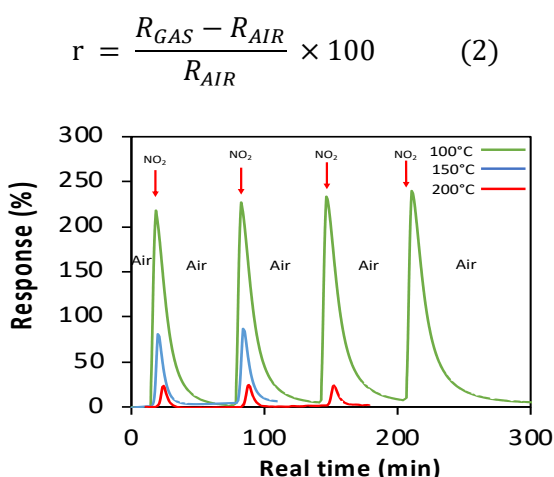


Figure 7: Response of 45 nm thick SnO₂ Sensor for 3 ppm NO₂ in real time, cycles of 4- 60 min of 3 ppm of NO₂ - Dry air, for different working temperatures.

The sensor shows the highest and the fastest gas sensing response, about 250 % towards 3 ppm of NO₂ at 100°C, in 3.4 min. At 150°C, the response is reduced to 120%, displaying a marginally slower response of 3.7 min. At 200°C, the response has dropped significantly to 25%, showing a slower response around 4.4 min. However, while increasing the temperature, the recovery time decreases, indicating that the NO₂ desorbs faster at higher temperatures. NO₂ molecules take 26.7 min to desorb at 100°C, 11.8 min at 150°C, and 7.8 min at 200°C. The response r , the response time and the recovery time are given in table 1.

Moreover, the response and recovery time are affected by the chamber dimensions. More tests will be held in a smaller chamber given that the present chamber is comparably big - it has a diameter and height of 16 and 8 cm, respectively.

Table 1: The response r , response time (t_{resp}) and the recovery time (t_{reco}).

	$r \pm 2$ (%)	$t_{resp} \pm 0.1$ (min)	$t_{reco} \pm 0.1$ (min)
100°C	234	3.4	26.7
150°C	125	3.7	11.8
200°C	25	4.4	7.8

Figure 8 displays the sensor response for different NO₂ concentrations, which exhibit a perfectly linear relationship within an accuracy of 1%. This linear behavior can be used to evaluate the sensitivity and the limit of detection (LOD) of the sensor. According to these results, the LOD of our sensor is a bit lower than 0.25 ppm.

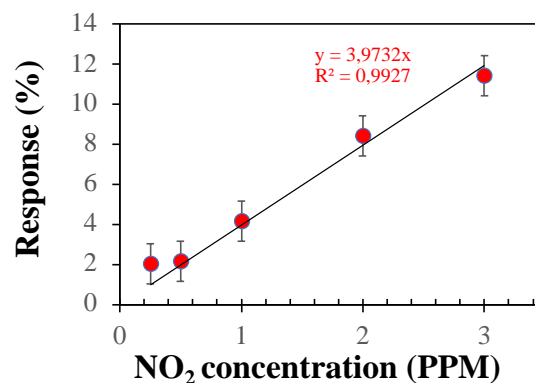


Figure 8: Relationship between the 45 nm thick SnO₂ sensor and NO₂ concentration.

At 50°C, the sensor shows a small and reproducible response of 1% (figure 9). However, the NO₂ molecules can't desorb for such a low temperature.

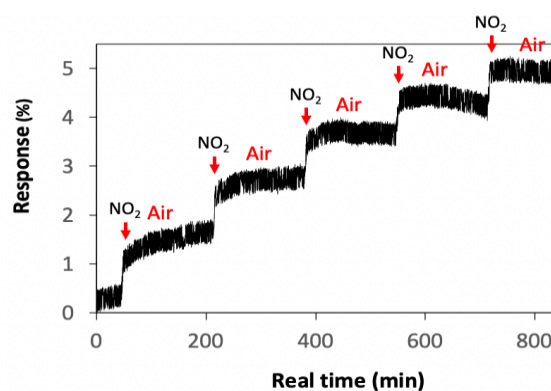


Figure 9: Response of 45 nm thick SnO₂ sensor for 3 ppm NO₂ in real time, cycles of 4- 120 min of 3 ppm NO₂ - Dry air at 50°C.

4 DISCUSSION

In this study, we have shown that lowering the operating temperature of NO₂ sensors using undoped-SnO₂ is possible. In this section, we intend to compare our results to others found in the literature.

D. L. Kamble synthesized NO₂ gas sensor of nanocrystalline SnO₂ using different spray solution concentrations [10]. The optimal operating temperature for detecting 40 ppm of NO₂ using this sensor is reported to be 150 °C.

G. D. Khuspe synthesized SnO₂ nanostructure via sol-gel spin coating technique [11]. His sensor demonstrated the highest response of 19% towards 100 ppm NO₂ at an operating temperature of 200 °C. When compared to the above studies, it is clear to deduce that our undoped-SnO₂ is shown to be more sensitive which operates at lower temperature of 100°C. Moreover, it reacts with NO₂ at 50°C.

The reason why our sensor reacts at lower temperatures could be attributed to multiple reasons. The most important ones in our case are the SnO₂ microstructure and the chemical composition. On the other hand, the sensor geometry has also a role in gas detection. This is clearly seen when the 100 nm thick SnO₂ did not show any response. Such behavior does not mean that the SnO₂ film didn't react with NO₂, but the geometry of the SnO₂ sensor was not accurately chosen.

5 SUMMARY

In this work, we have demonstrated low temperature (100°C) gas sensing properties with a detection of 3 ppm - NO₂ using undoped-SnO₂ sensor deposited using conventional RF-sputtering. Moreover, the SnO₂ sensing layer shows a response to NO₂ at 50°C. Nevertheless, NO₂ molecules cannot be desorbed at this temperature. Further investigations are required to improve the sensing operation at 50°C.

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